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Catalytic methods of cellulose transformation in pure water into valuable chemical substances

Nikolay Gromov

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By Nikolay GROMOV

CATALYTIC METHODS OF CELLULOSE TRANSFORMATION IN PURE WATER INTO VALUABLE CHEMICAL SUBSTANCES

Under the supervision of Dr. AYMONIER Cyril and Dr. TARAN Oxana

PhD defended October 12th, 2016

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NOMENCLATURE

Glu	glucose	
5-HMF	5-hydroxymethylfurfural	
LA, Lev	levulinic acid	
Man	mannose	
FA, Form	formic acid	
Olig	oligosachharide(s)	
Fru	fructose	
Furf	furfural	
Celb	cellobiose	
Cell	cellulose	
AA	acetic acid	
HPA	heteropoly anion, heteropolyacid	
LBET	Lobry de Bruyn–van Ekenstein transformation	
CI	crystallinity index	%
CSR	coherent-scattering region	nm
ICP-AES	inductively coupled plasma atom emission spectroscopy	
HPLC	High performance liquid chromatography	
XRD	X-ray diffraction	
XRF	X-ray fluorescence	
XPS	X-ray photoelectron spectroscopy	
TEM	Transition electron microscopy	
UV vis DRS	UV–vis diffuse reflectance spectrometry	
a	Element atomic weight	u
A ₀	Initial reacton rate	mol·L ⁻¹ ·s ⁻¹ , mol·s ⁻¹
C	Concentration	mol·L ⁻¹ ; g·L ⁻¹
<d _l >	Average length of cellulose particles	μm
<d _{pore} >	Average diameter of catalyst pores	nm
E _a	Activation energy	kJ·mol ⁻¹
E _{ACT}	Energy spent for cellulose mechanical pretreatment	kJ·kg ⁻¹
K _{dry}	Dryness coefficient	
m	Mass	g
M	Molar weight	g·mol ⁻¹
M	Molar concentration	mol·L ⁻¹

N_i	Element concentration on a catalyst surface	
P	Pressure	bar
S	Selectivity	%
S_{BET}	Specific surface area	$\text{m}^2 \cdot \text{g}^{-1}$
T	Temperature	$^{\circ}\text{C}$
TOF	Turnover frequency	s^{-1}
V	Volume	L
V_{pore}	Pore volume	$\text{cm}^3 \cdot \text{g}^{-1}$
$W_{\text{H}_2\text{O}}$	Cellulose humidity	%
X	Conversion	%
Y	Yield	%
Y_{Σ}	Combined yield	%
ω_i	Mass portion	
τ	Time	h, s

ABSTRACT IN FRENCH

Résumé en français de la thèse

**TRANSFORMATION CATALYTIQUE DE LA CELLULOSE EN MILIEU AQUEUX POUR
LA PRODUCTION DE MOLECULES PLATEFORMES**

Contexte de la thèse.

La cellulose, une des principales composantes de la biomasse, est une matière première pour la production de molécules chimiques à forte valeur ajoutée, en remplacement des ressources fossiles. La cellulose peut être renouvelée, ce qui est avantageux. De plus, la fixation du gaz carbonique pendant la production de la biomasse permet de remédier à l'effet de serre.

Dans le domaine de la transformation de la biomasse, un des challenges est le développement de procédés catalytiques «one-pot» permettant la production des produits désirés directement à partir de la cellulose, sans dégagement et raffinage de semi-produits. Ce type de procédé «one-pot» donne, par exemple, la possibilité de transformer la cellulose en 5-hydroxymethylfurfural (HMF) par des réactions d'hydrolyse-déshydratation. Le 5-HMF est une matière première pour la production de polymères, dissolvants, fongicides et biocombustibles. Il est aussi inscrit sur la liste des molécules dites plateforme. Le 5-HMF est aujourd'hui produit à partir des hydrates de carbone alimentaires (fructose, glucose, saccharose, amidon), ce qui pose un problème d'éthique entre leurs utilisations en alimentaire et en non-alimentaire. Un manque de ressources peu chères et des technologies compliquées multi-étapes pour la production du 5-HMF mènent à des prix élevés pour cette molécule.

Une autre molécule chimique intéressante est l'acide formique (AF) qui est un produit issu de l'hydrolyse et de l'oxydation de la cellulose. L'AF est utilisé comme un agent antibactérien, pour la préservation et comme solvant dans certaines réactions chimiques. Il peut aussi être utilisé comme agent réducteur ou source d'hydrogène dans des procédés chimiques comme, par exemple, dans la production de biocombustibles.

Le premier stade de la production du 5-HMF et de l'AF est l'hydrolyse de la cellulose en glucose. Le développement de ce procédé est lié à l'élaboration des catalyseurs solides d'hydrolyse. Un certain nombre de systèmes catalytiques a été proposé pour la transformation hydrolytique de la cellulose. Par exemple, des catalyseurs à base de carbone, des oxydes, des zéolithes, ... Par contre, pour l'hydrolyse-oxydation de la cellulose en AF, des catalyseurs bifonctionnels possédant à la fois des sites acides et oxydo-réducteurs sont développés.

Il est important de souligner que les données sur l'utilisation de catalyseurs dans les procédés de transformation de la cellulose, publiées à ce jour, sont souvent contradictoires. Les catalyseurs proposés sont peu actifs et/ou peu stables. En même temps, il y a peu de travaux sur la possibilité de transformation de la cellulose en 5-HMF ou AF par des procédés «one-pot».

Dans ce contexte, l'objet de ces travaux de thèse a porté sur la recherche et l'élaboration de catalyseurs multifonctionnels efficaces associés à des procédés catalytiques « one pot » tels que hydrolyse-déshydratation et hydrolyse-oxydation pour la transformation de la cellulose en molécules plateformes du type 5-HMF ou encore acide formique.

Les axes de recherche.

1) L'étude des réactions d'hydrolyse-oxydation de la cellulose en présence de catalyseurs du type hétéropolyacides (HPA), différenciés par l'acidité et la proportion en vanadium. Les paramètres du procédé ont été étudiés pour établir la corrélation activité catalytique - concentration en HPA, afin de permettre l'optimisation du procédé.

2) La synthèse et l'étude de catalyseurs acides solides pour l'hydrolyse-déshydratation de la cellulose en glucose et 5-HMF sur la base de Sibunit (matériau carboné modifié) et de $\text{NbO}_x/\text{ZrO}_2$.

3) L'étude de l'activité catalytique des catalyseurs carbonés et oxydes sur la réaction d'hydrolyse-déshydratation de la cellulose dans des réacteurs fermé et à flux continu. L'analyse de la stabilité des catalyseurs, l'optimisation des conditions du procédé et la sélection des catalyseurs ont été effectuées.

4) Des investigations sur les mécanismes et les cinétiques des réactions d'hydrolyse-déshydratation de la cellulose en présence des catalyseurs acides solides : a) l'identification des intermédiaires principaux et l'étude de leurs transformations, b) l'étude de la cinétique avec détermination des constantes de vitesse et c) la modélisation mathématique de la cinétique du procédé.

La nouveauté scientifique.

Les résultats obtenus pendant la réalisation de ces travaux de thèse possèdent un haut degré de nouveauté scientifique.

L'étude systématique du procédé de transformation de la cellulose à l'acide formique en présence des catalyseurs hétéropolyacides (HPA) vanadifères a été menée pour la première fois. L'influence de la composition des catalyseurs et des conditions du procédé sur le rendement en produit désiré a été étudiée. L'énergie d'activation a été déterminée. La relation linéaire entre la vitesse et l'acidité du milieu a été démontrée. Le rendement en acide formique est de 66%, ce qui surpasse tous les résultats, publiés à ce jour.

Un catalyseur tel que $\text{NbO}_x/\text{ZrO}_2$ a été appliqué pour la première fois pour l'hydrolyse-déshydratation de la cellulose microcristalline activée dans l'eau. Les rendements en glucose et en 5-HMF sont de 22% et 16% respectivement. L'influence de l'oxyde de niobium sur l'activité du catalyseur a été étudiée. Un rôle important des structures oligomériques NbO_x sur l'activité des catalyseurs a été observé.

Un catalyseur carboné basé sur la matière modifiée de la série Sibunit a été évalué pour la première fois comme catalyseur d'hydrolyse-déshydratation de la cellulose. Il a été établi qu'en

présence de Sibunité modifiée par sulfonation et (ou) oxydation le rendement en glucose atteint 74% (dans le réacteur à flux continu), tandis que celui en 5-HMF donne jusqu'à 21% (dans le réacteur fermé), ce qui sont des résultats considérablement plus hauts que ceux des systèmes catalytiques carbonés décrits dans la littérature scientifique. Pour la première fois des recherches systématiques avec l'établissement de corrélations entre l'activité pendant le procédé d'hydrolyse-déshydratation et le mode d'activation de la matière carbonée ont été réalisées.

Des études du mécanisme et de la cinétique du procédé d'hydrolyse-déshydratation de la cellulose en présence des catalyseurs acides solides ont été réalisées aussi pour la première fois.

RESUME DE LA THESE

Le premier chapitre de la thèse présente une revue de l'état de l'art. La première partie est consacrée au substrat – la cellulose, sa structure et ses caractéristiques, sa teneur en biomasse végétale. Les méthodes physique et chimique d'activation de la cellulose sont examinées. La deuxième partie propose un état de l'art sur la production de l'acide formique par les méthodes d'oxydation catalytique des oses et de l'hydrolyse-oxydation de la cellulose et de la biomasse en présence de Mo-V-P HPA. Les mécanismes d'oxydation des oses en acide formique (AF) sont décrits. La troisième partie est consacrée au traitement de la cellulose par les méthodes d'hydrolyse et d'hydrolyse-déshydratation. Les données sont exposées sur les transformations de la cellulose dans l'eau souscritique et sur des catalyseurs solides. Les mécanismes proposés pour les réactions d'hydrolyse et de déshydratation sont examinés de même que les modèles cinétiques essentiels, appliqués pour décrire des transformations de la cellulose.

Le deuxième chapitre présente les réactifs et les équipements utilisés dans ce travail de thèse, les méthodes d'analyse des substrats organiques et des produits des réactions (HPLC, Carbon Organique Total, spectroscopie UV-vis), les méthodes physico-chimiques d'étude des caractéristiques des catalyseurs solides (RMN, XPS, XRFA, titrage avec NaOH...) et les méthodes expérimentales. Notamment des méthodes sont décrites sur l'hydrolyse-oxydation de la cellulose en acide formique dans un réacteur fermé et sur l'hydrolyse-déshydratation du polysaccharide en glucose et 5-HMF dans des réacteurs fermés et à flux continu. Les catalyseurs ont été préparés à l'Institut de Catalyse G.K. Boreskov de l'Académie des Sciences. Les catalyseurs carbonés ont été préparés sur la base de la matière Sibunité (Institut des Problèmes du Retraitement des Hydrocarbures de l'Académie des Sciences, Omsk).

Le troisième chapitre présente les résultats des recherches sur le procédé d'hydrolyse-oxydation de la cellulose microcristalline activée en acide formique en présence des catalyseurs dissolubles Mo-V-P HPA contenant : HPA-2 -- $H_5PMo_{10}V_2O_{40}$, Co-HPA-2 – $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$, HPA-6 – $H_{11}P_3Mo_{16}V_6O_{40}$, HPA-10 – $H_{17}P_3Mo_{16}V_{10}O_{40}$.

Des expériences ont été réalisées dans l'atmosphère de la masse gazeuse $O_2/N_2 = 1/4$ (l'air artificiel).

L'analyse HPLC du mélange réactif a montré que l'acide formique est le produit essentiel du procédé. Outre cela on peut voir de faibles quantités en glucose et en acides organiques : malique, acétique, glycolique, lactique, lévulinique et aussi formaldéhyde (< 5%).

L'optimisation des caractéristiques du procédé (température, composition de la phase gazeuse, pression) a été réalisée en présence de la solution du catalyseur. Des expériences à différentes températures (130, 140, 150 et 180 °C) en atmosphère aérobie (pression 10 atm) ont montré que la température optimale est de 150 °C, température à laquelle le rendement en AF est plus important qu'aux autres températures (42% en 5 heures, Fig. 1). L'augmentation de la température du procédé mène à la destruction de l'acide formique. Il a été établi que, pendant le procédé, une atmosphère oxydante est nécessaire pour réoxyder des sites d'oxydation Mo-V-P HPA jusqu'à (V^{5+}), qui sont désoxydés pendant le procédé. En atmosphère inerte (Ar) dans la solution de catalyseur CoHPA-2 (6 h, 150 °C), le rendement en acide formique n'a constitué que 6%, et le rendement du glucose 8%.

Des recherches sur l'influence de la pression du gaz artificiel sur la cinétique étudiée du procédé ont été réalisées à 10, 20 et 50 atm et 150 °C. Il a été établi que la pression n'influence pas la formation en AF sur la partie initiale de la courbe cinétique. Néanmoins, la pression influence le rendement final en AF. La formation de l'acide formique cesse après 5 h à 10 atm, et après 7 h à 20 et 50 atm (Fig. 2). Ensuite la composition des produits ne change plus. Le rendement le plus haut en AF a été obtenu à 20 atm et a atteint 66%. La conversion complète de la cellulose après 7 h est

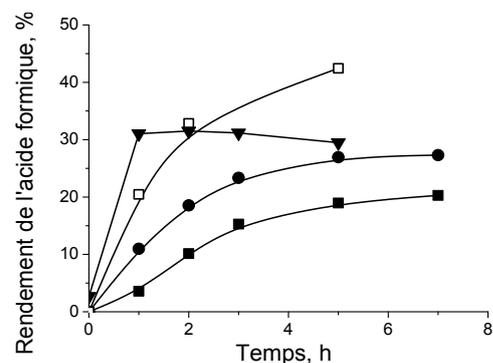


Fig. 1. Courbes cinétiques de la formation de AF à ■ – 130 °C, ● – 140 °C, □ – 150 °C, ▼ – 180 °C. Cellulose 10 g/l-1, catalyseur Co-HPA-2 10 mmole/l1, pression du gaz 10 atm.

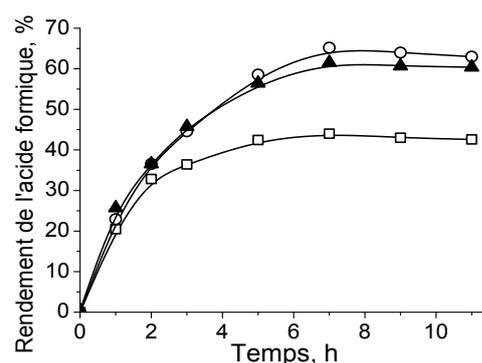


Fig. 2. Courbes cinétiques de la formation de AF à la pression du gaz artificiel ○ – 50 atm, ▲ – 20 atm, ■ – 10 atm, Cellulose 10 g-l-1, catalyseur Co-HPA-2 10 mmole-l-1, 150 °C.

confirmée par l'étude des solutions réactionnelles. Après la réalisation des rendements les plus hauts, des baisses des concentrations de AF étaient mineures, ce qui atteste sa stabilité suffisante à 150°C.

L'optimisation de la composition du catalyseur a été réalisée à 150°C et 20 atm. L'influence de l'acidité du HPA a été examinée à concentration constante en atomes de vanadium. Les rendements, la vitesse initiale du procédé et l'acidité des catalyseurs diminuent dans l'ordre suivant : HPA-2 > Co-HPA-2 > HPA-6 > HPA-10, c'est à dire, la vitesse maximale est assurée par les solutions les plus acides de HPA.

L'influence de la concentration en vanadium sur la cinétique du procédé a été examinée en présence du catalyseur Co-HPA-2 à pH = 1.5. La concentration en vanadium a varié de 1 à 20 mmol.L⁻¹. Lors de l'abaissement de la concentration en vanadium de 20 à 10 mmol.L⁻¹, les courbes cinétiques de formation de AF sont quasi-identiques (Fig. 3), ce qui prouve la limitation du procédé par l'hydrolyse (les expériences ont été réalisées au même pH). Lors de la diminution de la concentration en vanadium jusqu'à 2 et 1 mmol.L⁻¹, un abaissement de la vitesse initiale et des rendements en AF est observé. Le rendement final en produit désiré diminue de 58 à 23%. On peut conclure qu'à une concentration en vanadium inférieure à 10 mmol.L⁻¹, l'étape limitante du procédé change et la vitesse est déterminée par la vitesse de la réaction d'oxydation.

Le quatrième chapitre présente l'étude des résultats des recherches sur le procédé d'hydrolyse-

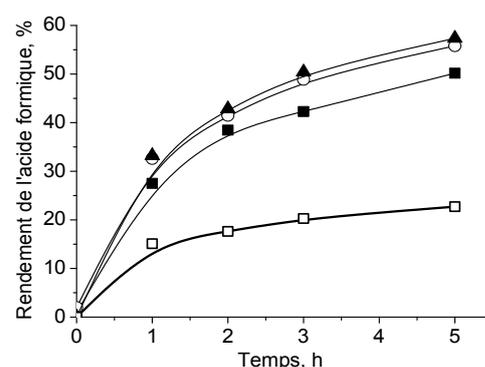


Fig. 3. Courbes cinétiques de la formation de AF dans la solution du catalyseur Co-HPA-2 à [V] différents: □ – 1 mmol.L⁻¹, ■ – 2 mmol.L⁻¹, ○ – 10 mmol.L⁻¹, ▲ – 20 mmol.L⁻¹. Cellulose 10 g.L⁻¹, pression d'air 20 atm, 150 °C, pH 1,5.

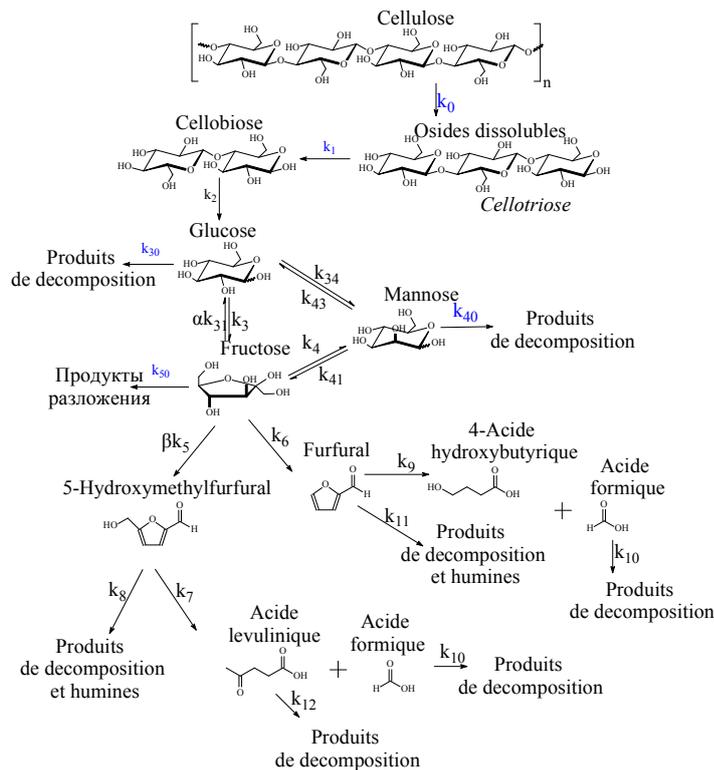
Tab. 1. Résultats des tests des catalyseurs NbOx/ZrO₂ en hydrolyse-déshydratation de la cellulose. Cellulose et catalyseur 10 g.L⁻¹, 45 ml, 180 °C, 10 atm. (Ar), 1500 r/min⁻¹, temps de réaction 5 heures.

Catalyseur	A ₀ , mole/l ⁻¹ ·c ⁻¹ ·10 ⁶	TOF, c ⁻¹ ·10 ⁷	pH du mélange réactif		Rendements des produits	
			avant	après	Glucose	5-HMF
					Y, %	Y, %
blanc	0.2	-	5.5	n.d.	7.0	0.0
ZrO ₂	2.3	2.8	4.5	2.7	12.7	13.3
0.5%Nb/ZrO ₂	1.1	1.4	4.0	3.0	12.9	12.9
1.1%Nb/ZrO ₂	4.0	4.8	3.6	2.8	21.3	16.3
2.8%Nb/ZrO ₂	4.3	5.2	3.6	2.7	22.0	16.1

déshydratation de la cellulose microcristalline activée en glucose et 5-HMF.

Dans la première partie du chapitre, on présente des résultats des recherches avec des catalyseurs oxydes $\text{NbO}_x/\text{ZrO}_2$, avec une concentration en Nb de 0,5, 1,1 et 2,8%. Les catalyseurs avant et après réaction ont été étudiés par des méthodes d'analyse (ICP-AES, XRFA, adsorption de N_2), qui ont montré leur stabilité exceptionnelle dans les conditions de réaction et les conditions hydrothermales jusqu'à de 300 °C.

Schéma 1



Les expériences ont été réalisées dans un réacteur fermé (autoclave) à la température de 180 °C sous atmosphère inerte (Ar) (Tab. 1). Les produits essentiels ont été le glucose et 5-HMF. La production de la faible quantité de fructose, d'acide formique, d'acide lévulinique a été relevée. (1-2,5%, Schéma 1). En l'absence des catalyseurs, le rendement en glucose est très bas (7.0% pour 5 heures de réaction) et la formation de 5-HMF n'a pas été observée. On a établi la suite d'activités : $0,5\% \text{Nb}/\text{ZrO}_2 < \text{ZrO}_2 < 1,1\% \text{Nb}/\text{ZrO}_2 \sim 2,8\% \text{Nb}/\text{ZrO}_2$. Les rendements maximaux en glucose et en 5-HMF en présence de l'oxyde pur de zirconium sans niobium sont 12.7 et

13.3%, respectivement. En ajoutant 0,5% de niobium sur le catalyseur, une diminution de l'activité de presque deux fois a été relevée (abaissement de la vitesse initiale A_0 et TOF), malgré l'augmentation de l'acidité du milieu par rapport l'expérience avec ZrO_2 . L'augmentation du teneur en niobium jusqu'à 1,1 et 2,8% mène à l'augmentation de deux fois des rendements en produits désirés (glucose et 5-HMF) par rapport a l'expérience avec ZrO_2 non modifié. Les changements d'activités des catalyseurs oxydes sont expliqués ainsi : l'oxyde de zirconium représente un catalyseur bifonctionnel, dont l'activité est déterminée par l'influence mutuelle des sites acides et basiques sur la surface. La diminution de l'activité catalytique de $0,5\% \text{Nb}/\text{ZrO}_2$ par rapport à ZrO_2 (malgré un pH du milieu plus faible) est expliquée par la présence de clusters isolés de NbO_4 qui isolent spatialement les sites acides et basiques sur l'oxyde de zirconium. D'après l'analyse UV-VIS DR, avec Nb 1,1-2,8%, des structures polymériques NbO_x (NbO_6) sont formées. Les sites acides augmentent l'activité catalytique.

La deuxième partie du quatrième chapitre est consacrée aux recherches sur l'activité des catalyseurs carbonés à base de Sibunité sur l'hydrolyse-déshydratation de la cellulose activée

mécaniquement dans des réacteurs fermé et à flux continu. Trois séries de catalyseurs ont été testés : Sibunite, sulfurée par l'acide sulfurique à 80, 150, 200 et 250 °C pendant 10 heures (échantillons C-S80, C-S150, C-S200 et C-S250), Sibunite, oxydée par de l'air humide à 450 °C (C-O) ou 23% et 32% d'une solution d'acide nitrique à 90 °C (C-N23 et C-N32) et Sibunite, préparée par sulfonation additive des carbones oxydés à 200 °C (C-O-S200, C-N32-S200 et C-N23-S200).

Tab. 2. Caractéristiques texturales des catalyseurs sur la base de Sibunite, déterminées par adsorption cryogénique de N₂, quantité des fonctions acides sur la surface mesurée par titrage en retour avec NaOH, parties pondérales des atomes de soufre (à titre de groupes sulfoniques) et d'oxygène sur la surface par XPS.

Catalyseur	S _{BET} , m ² ·g ⁻¹	V _{mésopore} , cm ³ ·g ⁻¹	C _{fonction acide} , mmole·g ⁻¹	Proportion d'élément i, %	
				S	O
C	379	0.213	0.042	0	5.02
C-S80	344	0.200	0.14	0.14	5.28
C-S150	360	0.222	0.32	0.25	6.81
C-S200	400	0.240	0.40	0.15	8.34
C-S250	221	0.069	0.62	0.11	8.63
C-O	348	0.33	0.28	0	6.38
C-N32	320	0.27	0.36	0	6.97
C-N23	306	0.22	0.33	-	-
C-O-S200	343	0.30	0.49	0.08	8.47
C-N32-S200	290	0.27	0.51	0.06	8.27
C-N23-S200	299	0.23	0.49	-	-

Il a été établi par adsorption de N₂ (Tab. 2), que la sulfonation à la température de 250 °C (à la différence du traitement à 200 °C et moins) mène à une diminution importante de la surface et du volume des mésopores à cause d'une destruction importante de la texture de la matière carbonée. L'oxydation et oxydation-sulfonation mènent aussi à la destruction partielle de la structure du carbone. La diminution de la surface et du volume des pores décroît selon : C > C-O > C-O-S200 > C-N32 > C-N23 > C-N23-S200 > C-N32-S200. Le contenu des fonctions acides (Tab. 2) dans les échantillons sulfurés augmente avec l'augmentation de la température de sulfonation. La concentration en fonctions acides augmente de 3 à 15 fois comparée à la Sibunite initiale (0,042 mmole.g⁻¹). Le nombre maximal de fonctions acides (0,62 mmole.g⁻¹) est contenu dans l'échantillon C-S250. Le nombre de fonctions acides après oxydation varie de 0,28 à 0,36 mmole.g⁻¹, et après la sulfonation augmente jusqu'à 0,49 – 0,51 mmole.g⁻¹. D'une façon générale, on peut conclure que le contenu total en fonctions acides dans

les échantillons oxydés est comparable à celui de l'échantillon sulfuré de Sibunite C-S150 et 1,5-2 fois plus grand que dans les échantillons oxydés-sulfurés.

Il a été établi par XPS que des catalyseurs acides sur la base de Sibunite sont très oxydés et contiennent de l'oxygène et des fonction acides soufrées. Aux températures de sulfonation supérieures à 150 °C, une oxydation de la surface de Sibunite a lieu, ce qui mène à la formation de fonctions acides. L'oxydation du carbone par l'air humide forme sur la surface moins de domaines oxygénés comparée au traitement avec l'acide nitrique. Lors la sulfonation des échantillons oxydés à 200 °C, la quantité de groupes sulfoniques est de 1,9 à 2,7 fois moins importante qu'avec l'échantillon C-S200. Ces résultats permettent de conclure qu'une plus large surface de Sibunite conduit à une quantité plus faible de groupes sulfoniques.

L'étude de la stabilité des catalyseurs soufrés à l'exemple de C-S200 et C-O-S200 par la spectrométrie de fluorescence X a relevé que les catalyseurs sont stables en milieu hydrothermal jusqu'à 200 °C et que dans des conditions plus sévères (jusqu'à 300 °C) l'élimination de soufre a lieu.

L'évaluation des catalyseurs carbonés en hydrolyse-déshydratation de la cellulose activée mécaniquement dans un réacteur fermé a été réalisée à 180 °C dans l'argon. Les produits essentiels du procédé ont été le 5-HMF et le glucose. Des espèces intermédiaires et sous-produits ont été relevés tels que cellobiose, fructose, mannose, furfural (Schéma 1). L'essai de référence dans l'eau pure a conduit à un rendement en glucose de 7%. La formation d'autres produits n'a pas été relevée, de 5-HMF non plus. En présence des catalyseurs carbonés, les rendements en glucose et en 5-HMF sont de 9-42% et 12-20%, respectivement. En présence du catalyseur C-S200, les rendements maximaux en glucose et en 5HMF ont été observés, 45,9 et 21,5% après 2 et 5 heures de réaction.

L'acidité totale mais pas le degré de sulfonation est le facteur déterminant de l'activité du catalyseur carboné. Dans la suite catalyseurs, C-S80 < C-S150 < C-S200 l'activité augmente avec l'augmentation de l'acidité. La morphologie influence considérablement l'activité. La vitesse diminue sensiblement pour des SBET inférieures à 300 m².g-1. Les catalyseurs C-S250, C-N32-S200 et C-N23-S200 contenant la plus grande quantité de fonctions acides mais avec une faible valeur de SBET ont montré une activité médiocre. L'oxydation de la surface par le mélange d'air humide permet d'appliquer sur la surface du carbone des fonctions acides ou des combinaisons de fonctions plus actives que la sulfonation ou l'oxydation par HNO₃. Les échantillons C-O et C-O-S200, possédant l'acidité totale proche à C-S150, sont plus actifs que ce catalyseur sulfuré. La sulfonation de la surface carbonée oxydée n'est pas efficace. Les catalyseurs oxydés-sulfurés ont une activité inférieure en comparaison des catalyseurs oxydés.

L'étude de l'activité des catalyseurs carbonés sur la réaction d'hydrolyse-déshydratation de la cellulose activée a aussi été réalisé dans un réacteur à flux continu. Les conditions optimales relevées

expérimentalement sont 200 °C, une pression de 250 atm, un arrêt de l'écoulement de 20 min, une vitesse d'écoulement de 0,5 mL.min⁻¹.

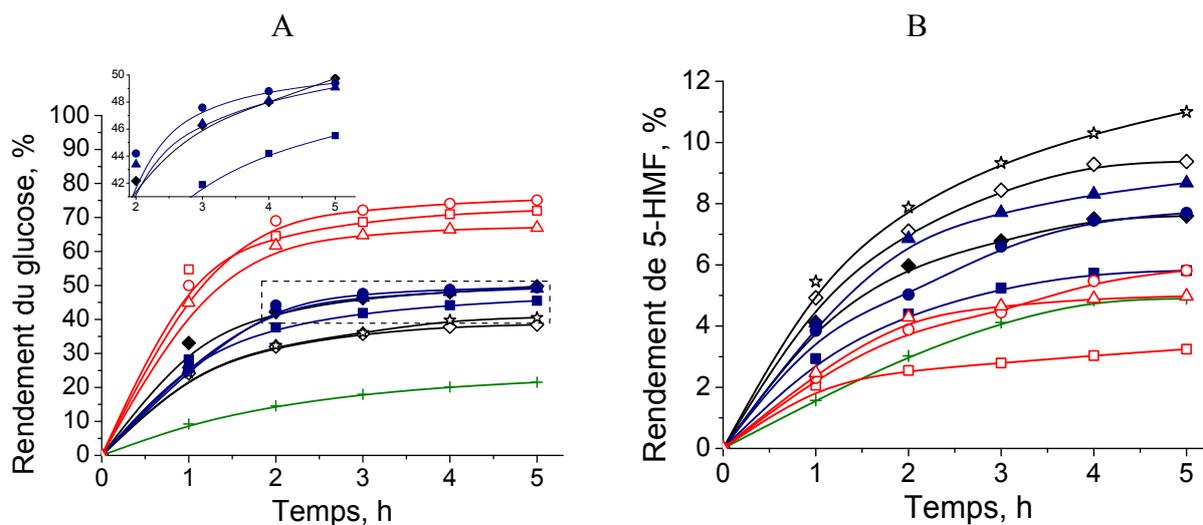


Fig. 4. Courbes cinétiques de formation du glucose (A) et du 5-HMF (B) par hydrolyse-déshydratation de la cellulose en présence de catalyseurs sur la base de Sibunite dans le réacteur à flux continu. Cellulose 0,25g, catalyseur 0,2 g, 200 °C, 250 atm., vitesse d'écoulement 0,5 mL.min⁻¹, temps d'expérience 5 heures. + – C, ◇ – C-S80, ☆ – C-S150, ◆ – C-S200, ■ – C-O, □ – C-O-S200, ● – C-N32, ○ – C-N32-S200, ▲ – C-N23, △ – C-N23-S20.

Les catalyseurs carbonés ont été divisés en trois groupes d'après leurs activités dans la réaction d'hydrolyse (formation du glucose) (Fig. 4 A). La Sibunite non modifiée se trouve dans le groupe avec la plus faible activité. Le deuxième groupe contient des catalyseurs sulfurés et oxydés. Pour les échantillons sulfurés, une augmentation des rendements C-S150 < C-S200 est observée. L'activité des catalyseurs oxydés est équivalente à celle des carbones sulfurés C-S150 et C-S200. L'activité du catalyseur C-O sur la formation du glucose s'est trouvée être supérieure, bien qu'il ait la moindre acidité. Ces résultats confirment les conclusions faites pour en réacteur fermé. Les catalyseurs oxydés-sulfurés forment le troisième groupe d'activités et se sont de 1,5 à 2 fois plus actifs que des catalyseurs oxydés ou sulfurés, ce qui correspond à une acidité totale plus importante. Le rendement en glucose le plus important dans le réacteur à flux continu a été obtenu en présence du catalyseur C-N32-S200 (74%). Dans le réacteur à flux continu, les rendements totaux en 5-HMF sont faibles (2-10%) ce qui témoigne d'une vitesse faible de déshydratation du glucose en 20 minutes. Les carbones sulfurés sont plus actifs dans la déshydratation et leur activité diminue selon : C-S150 > C-S80 > C-S200 (Fig. 4 B). C-S150 contenant le plus de groupes sulfoniques acides d'après l'analyse XPS est le plus actif. Les carbones oxydés-sulfurés sont moins actifs dans la réaction de déshydratation du glucose que dans celle des carbones oxydés.

Le catalyseur C-S200 a été utilisé dans les études cinétiques des transformations des intermédiaires basiques et des produits du procédé : cellobiose, glucose, mannose, fructose, 5-HMF, furfural dans les réacteurs fermé et à flux continu

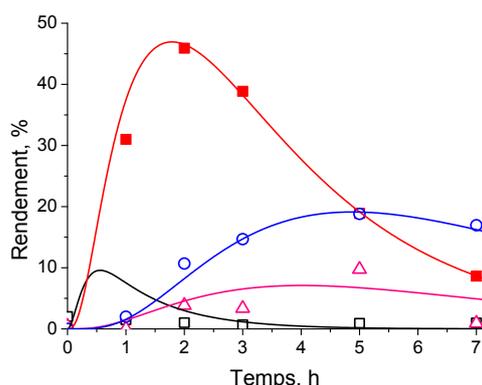


Fig. 5. Cinétiques des transformations des intermédiaires basiques d'hydrolyse-déshydratation de la cellulose (\square - cellobiose, \blacksquare - glucose, \circ - 5-HMF, \triangle - mannose,) en comparaison des courbes cinétiques modélisées (traits continus). Cellulose et catalyseur 10 g.L-1, 45 mL, 180 °C, 10 atm. (Ar), 1500 tr.min-1, temps de la réaction : 7 heures.

à flux continu (Schéma 1). Des constantes des vitesses des réactions d'hydrolyse-déshydratation de la cellulose ont été établies d'après les courbes cinétiques. Il a été établi que la dissolution de la cellulose et la transformation du glucose en fructose sont des étapes lentes (limitantes) tandis que l'hydrolyse et la transformation du glucose en fructose sont des réactions rapides. La transformation des oses en 5-HMF et furfural est irréversible.

Un modèle cinétique à 17 étapes a été élaboré sur la base du schéma du procédé (Schéma 1). Un système d'équations différentielles a été programmé pour la modélisation des courbes cinétiques et a été résolu à l'aide du logiciel Mathcad 15.0. Le modèle cinétique élaboré décrit

le procédé d'hydrolyse-déshydratation de la cellulose et aussi de transformation des intermédiaires du procédé non seulement avec une bonne qualité, mais aussi avec une haute précision (Fig. 5).

CONCLUSIONS

1. Des recherches systématiques, réalisées pour la première fois, sur le procédé catalytique d'hydrolyse-oxydation de la cellulose en présence des P-Mo-V hétéropolyacides comme catalyseurs en milieu aqueux ont abouti aux résultats suivants :

- La possibilité d'obtenir de l'acide formique à partir de la cellulose à des hauts rendements (jusqu'à 66%),
- L'optimisation des conditions de réaction : 150-160 °C, atmosphère oxydante (20% O₂ et 80% N₂). La pression n'influence pas la vitesse initiale du procédé,
- L'énergie d'activation de l'hydrolyse-oxydation de la cellulose estimée à 83 kJ.mole⁻¹,
- La vitesse maximale de la réaction est assurée par les solutions les plus acides de HPA ; des vitesses de réaction dépendent linéairement de la concentration en H⁺ et de façon moins évidente de la concentration en vanadium,

• Le mécanisme d'hydrolyse-oxydation des oses a été proposé, catalysé par HPA V-contenants et évoluant par la fixation de VO_2^+ aux groupes hydroxyles voisins des molécules de carbones, notamment du polysaccharide, succédée par la rupture de la liaison C-C.

2. Une haute activité catalytique des catalyseurs solides $\text{NbO}_x/\text{ZrO}_2$ dans le procédé d'hydrolyse-déshydratation de la cellulose en glucose et 5-HMF dans l'eau a été observée. Les travaux sur les catalyseurs ont donné les résultats suivants :

- Il a été relevé que les rendements maximaux en glucose et en 5-HMF (22 et 16%) sont obtenus en présence du catalyseur 2,8%Nb/ZrO₂,
- La stabilité exceptionnelle des catalyseurs dans les conditions hydrothermales jusqu'à 300 °C a été relevée,
- L'activité des catalyseurs a été évaluée selon : 0,5%Nb/ZrO₂ < ZrO₂ < 1,1%Nb/ZrO₂ ~ 2,8%Nb/ZrO₂.
- Il a été relevé que l'activité des catalyseurs augmente grâce à l'apparition de l'acidité Brønsted pendant la formation des structures polymériques NbO_x.

3. Des catalyseurs acides solides ont été élaborés sur la base de la Sibunite-4 pour l'hydrolyse-déshydratation de la cellulose en glucose et 5-HMF en milieu aqueux. Des recherches systématiques sur l'influence du mode d'activation du catalyseur carboné (sulfonation, oxydation, oxydation-sulfonation) sur la morphologie, la chimie de sa surface et sur ses fonctions catalytiques ont montré :

- Les produits essentiels de la réaction avec des catalyseurs acides solides sont le glucose et le 5-HMF. La possibilité d'obtenir de hauts rendements a été démontrée : jusqu'à 74% de glucose dans un réacteur à flux continu et jusqu'à 21% de 5-HMF dans un réacteur fermé,
- La sulfonation du catalyseur carboné forme des groupes oxygénés et sulfoniques sur la surface. Le nombre total de fonctions acides augmente avec l'augmentation de la température de sulfonation (de 80 à 250 °C). L'augmentation de la température au-delà de 200 °C mène à la destruction de la structure de la Sibunite et à l'abaissement de sa surface spécifique,
- Le nombre des groupes acides oxygénés par l'oxydation de la Sibunite (par l'air humide et HNO₃) et à la sulfonation à 150°C est comparable. La sulfonation des catalyseurs oxydés est peu efficace pour la fixation des groupements sulfurés, mais augmente la concentration des sites acides oxygénés qui possèdent l'activité catalytique et mène à la destruction de la structure du catalyseur carboné,
- L'activité des catalyseurs augmente avec l'augmentation de l'acidité totale et diminue avec la destruction de la structure Sibunite. Les systèmes catalytiques optimaux ont été trouvés : pour obtenir le glucose, c'est la Sibunite oxydée-sulfurée ; pour le 5-HMF, c'est la Sibunite sulfurée à 150-200°C, et la Sibunite, oxydée par l'air humide,

- La possibilité d'une extraction efficace du 5-HMF des hydrolysats par l'amylone ou par l'isopropylcarbinol a été montrée.

4. L'étude de la cinétique de la réaction d'hydrolyse-déshydratation de la cellulose en présence du catalyseur acide carboné solide dans des réacteurs fermé et à flux continu a été réalisée pour la première fois. Les résultats suivants ont été obtenus :

- La limitation du procédé par les étapes de dissolution de la cellulose et par la réorganisation du glucose en fructose a été établie,
- Le mécanisme catalytique hétérogène pour le procédé total a été établi,
- Le schéma général du procédé a été proposé comprenant les étapes de dissolution de la cellulose, d'hydrolyse des osides, d'isomérisation du glucose en fructose, de déshydratation du fructose en 5-HMF, la série des étapes de destruction des intermédiaires et des produits, de la polymérisation du 5-HMF,
- Le modèle cinétique du procédé à 17 étapes a été élaboré, permettant de décrire les données des expériences pour un réacteur fermé qualitativement et quantitativement avec une bonne précision.

INTRODUCTION

Cellulose, as the main component of plant biomass, is a promising alternative to fossil resources for the production of valuable chemicals and fuel components. This is a renewable, or even inexhaustible, plant material. It may be helpful in abating the greenhouse effect caused by CO₂ emission from petrochemical and chemical processes; the role of biomass is to absorb CO₂ during its growth [1-5].

Of particular interest is the search for catalytic one-stage technologies, the so-called “one-pot” processes, for synthesis of valuable chemicals directly from cellulose to eliminate technological stages of semiproduct isolation and purification. The one-stage process arrangement makes it possible to synthesize 5-hydroxymethylfurfural (5-HMF), which is among the so-called *platform molecules* as one of the most promising industrial resource, by hydrolysis-dehydration of the plant polysaccharide [1-4, 6-8]. Among potential application areas of 5HMF are: chemical industry including synthesis of polymer materials (furanedicarboxylic acid is produced from 5-HMF and can be used instead of terephthalic acid), resins (based on furfuryl alcohol, 2,5-dicarboxyaldehyde), solvents (furfuryl alcohol, 2,5-dimethyltetrahydrofurfurane), as well as biofuels (dimethylfurfurane is a high-calorific and high-octane fuel, γ -valerolactone is a semiproduct biofuel synthesis), fungicides (based on 2,3-diformylfurfurane) [7]. There are two methods used now to produce 5-HMF. First, alimentary carbohydrates (fructose, glucose, saccharose, starch, inulin) are converted in the presence of soluble acid catalysts (sulfuric acid, hydrogen chloride) [9] and two-phase water-organic mixture of solvents (dimethylsulfoxide, butanol, methylethylketone etc.) [9, 10] that results in the competition between alimentary and non-alimentary application of these products. The second way is a complex multistage organic synthesis based on fossil energy resources [7]. The lack of a wide base of inexpensive resources, as well as the use of complex and multistage technologies for synthesis of 5-HMF results in a high cost and unavailability of this compound for industrial processing [7].

Another promising chemical compound – formic acid (FA) – is a product of hydrolysis-oxidation of cellulose. FA is used as a conserving and antibacterial agent in pharmaceutical industry and for forage conservation, as a solvent in some chemical reactions. It can also be used either as a reductant or as a hydrogen source as reductant in various chemical processes including synthesis of biofuel [7, 11, 12].

The first stage in producing 5-HMF and FA is the hydrolysis of cellulose to glucose. It is currently accepted that the progress in production of such compounds as glucose and 5-HMF through hydrolysis is possible by developing solid catalysts for cellulose hydrolysis and technologies based thereon. Numerous R&D in the field are conducted in the world. A wide variety of catalytic systems are suggested for hydrolytic transformations of the renewable polysaccharide. These are, e.g., catalytic systems based on carbon, oxides, zeolites, ion exchange resins. In contrast, soluble bifunctional

vanadium-containing HPA with both acidic and redox properties seem promising for the hydrolysis-oxidation of cellulose to FA.

However, the literature data on the application of various catalytic systems for cellulose transformations often are contradictory, while the suggested catalysts are poorly active and/or unstable. Note that most of the researches focused only on the polysaccharide hydrolysis to glucose but not on the production of 5-HMF or FA through “one-pot” process.

The purpose of the present work was to search for and to develop effective multifunctional catalysts and catalytic one-stage processes (hydrolysis-dehydration, hydrolysis-oxidation) for transformation of cellulose to valuable chemicals (glucose, 5-HMF and formic acid).

The purpose was achieved by solving the following problems:

1) Studies of the process of cellulose hydrolysis-oxidation in the presence of soluble HPA catalysts, which differ in their acidity and vanadium content, by varying the process parameters in order to reveal the relation between the catalytic activity and HPA composition, to optimize the process conditions;

2) Synthesis and physicochemical characterization of solid acid catalysts based on modified carbon material Sibunit and $\text{NbO}_x/\text{ZrO}_2$ for cellulose hydrolysis-dehydration to glucose and 5-HMF;

3) Studies of the catalytic activity of carbon and oxide catalysts for cellulose hydrolysis-dehydration in static and flow reactors, examination of the catalyst stability, optimization of the process parameters and choice for the optimal catalyst composition;

4) Experimental investigations of the kinetics and mechanism of cellulose hydrolysis-dehydration in the presence of solid acid catalysts including: identification of main intermediates, studies of their transformations, studies of individual stages to determine rate constants and reaction pathway, mathematical modeling of the process kinetics.

The first chapter of the thesis reviews the literature in the field. It consists of four parts. Part 1 deals with the substrate (cellulose), its structure and properties, contents in the plant biomass. Physical and chemical methods for the cellulose activation are considered. Part 2 is devoted to synthesis of formic acid via catalytic oxidation of sugars and hydrolysis-oxidation of cellulose and biomass in the presence of Mo-V-P HPA. Mechanisms of sugar oxidation to formic acid are discussed. Part 3 is focused on cellulose processing using hydrolysis and hydrolysis-dehydration. There are data on cellulose transformations in sub/supercritical water, soluble and solid catalysts for the processes. The suggested mechanisms of hydrolysis and dehydration, as well main kinetic models used for description of the cellulose transformations are discussed. Part 4 is the conclusions made upon literature analysis.

The second chapter describes reagents and equipment, analytic techniques (HPLC, TOC, UV-vis spectroscopy) used for analysis of reaction substrates and products, methods of catalyst characterization (NMR, TEM, XPS, XRD, XRF, UV-vis DRS, N₂ adsorption, titration with NaOH). The description of experimental techniques of cellulose hydrolysis-oxidation into formic acid in the batch reactor and cellulose hydrolysis-dehydration to glucose and 5-HMF in the batch and flow systems are also presented in the chapter

A high level of scientific novelty characterizes the results obtained.

Systematic investigations of the preparation of formic acid in the presence of vanadium-containing HPA catalysts was first conducted; the influence of the catalyst composition and process parameters on the yield of the target product was studied, the activation energy determined, a linear dependence of the rate on acidity of the medium revealed. The obtained FA yield (66 %) was superior to all the results reported in literature.

The NbO_x/ZrO₂ type catalyst was used for the first time for hydrolysis-dehydration of activated microcrystalline cellulose in pure water. High yields of glucose and 5-HMF (22 and 16 %, respectively) were observed. The influence of niobium oxide impurity on the catalytic activity was studied to identify the key role of oligomeric NbO_x structure in the catalyst activity.

A carbon catalyst based on modified Sibunit material was used for the first time for cellulose hydrolysis-dehydration. The yields of glucose (up to 74 % in a flow reactor) and 5-HMF (up to 21 % in a static reactor) were obtained in the presence of Sibunit modified by sulfonation and/or oxidation; these are much superior to the results on carbon catalytic systems reported in literature. The relation between the activity to hydrolysis-dehydration and the method of the carbon activation was thoroughly studied for the first time.

The following investigations were also carried out for the first time: studies of the kinetics and mechanism of cellulose hydrolysis-dehydration in the presence of solid acid catalysts including identification of intermediates, studies of the kinetics of individual stages to determine the rate constants, determination of the process pathways through 17 stages and mathematical modeling of the process kinetics.

The results obtained are a part of the world activities aimed at the development of complex energy- and resource-effective approaches to waste-free processing of plant biomass including its main component – cellulose – as a promising alternative to the fossil resources.

Potentialities of the process of cellulose hydrolysis-oxidation were demonstrated in the production of easy-to-store reductant (formic acid) to be used for the reductive processing of plant biomass components to biofuels.

The developed heterogeneous catalytic systems (modified Sibunit and $\text{NbO}_x/\text{ZrO}_2$) allow glucose and 5-HMF (a promising compound that may cost up to 10 000 \$/t [7]) to be synthesized from cellulose in pure water at the yields as high as 74 and 22 %, respectively.

The obtained kinetic data on the cellulose hydrolysis-dehydration in the presence of solid catalysts allow the process to be optimized and may be used to the process scaling-up.

CHAPTER 1.
LITERATURE REVIEW

1.1 Cellulose. Structure and properties. Pretreatment of cellulose for chemical transformations

Cellulose is a polysaccharide which consists of monomer units (anhydro- β -D-glucopyranose or glucose residues) being connected to each other by 1,4-glycosidic bonds. Cellulose is the main component of lignocellulosic biomass. General chemical formula of cellulose can be written as $(C_6H_{10}O_5)_n$ or $(C_6H_7O_2(OH)_3)_n$. The origin of the term "cellulose" refers to the first half of the 19th century (see. designation in [13]). The cellulose content in cells varies from one plant species to another one. It may also depend upon climatic conditions of the natural growth zone and the season (drought, excessive rainfall, etc.). The average cellulose content in plant biomass is 40-60 wt.%. The rest components of the plant biomass are lignin (15-35 wt.%), hemicelluloses (10-30 wt.%) and extractive and inorganic substances (about 1 wt.%) [8, 14]. Thus lignocellulosic biomass makes about 99 wt.% of green material [6]. The main purpose of natural cellulose is structural one. This polymer provides a shape of plant cells, and also determines the rigidity of plant tissues. The highest content of cellulose is in the wood, the lowest one is in the leaves of annual plants [15, 16]. The degree of polymerization of natural cellulose depends on the plant species. Each glucose unit in cellulose chains contains three alcohol groups, one primary and two secondary, with different reactivities.

The large number of hydroxyl groups in close-packed cellulose polymer chains results in a significant number of hydrogen bonds subdivided into intramolecular and intermolecular ones (Figure 6). Intramolecular interactions occur between adjacent glucose residues within one sequence what makes such chain stiffer. Besides hydroxyl groups oxygen atoms of the pyranose cycle and glycoside bond can take part in forming hydrogen bonds. Thus intramolecular hydrogen bond is formed between the OH group of the third carbon atom of one link and the adjacent pyranose oxygen level (bond $O_{(3)}H \cdots O_{(5)}$).

Intermolecular interactions occur between the various links in the different chains. Such cooperation forms a close-packed structure. The interactions $O_{(6)} // \cdots O_{(3)}$ (connection between CH_2OH group of the one chain and the OH-group at the third carbon atom in the other chain) belong to intermolecular bonds. The existence of the $O_{(6)} \cdots O_{(5)}$ (connection between the CH_2OH - group of one chain and pyranose oxygen in the other), as well as the $O_{(6)} \cdots O_{(4)}$ bond (connection between CH_2OH - group and glycosidic oxygen adjacent chain) is also admitted [17].

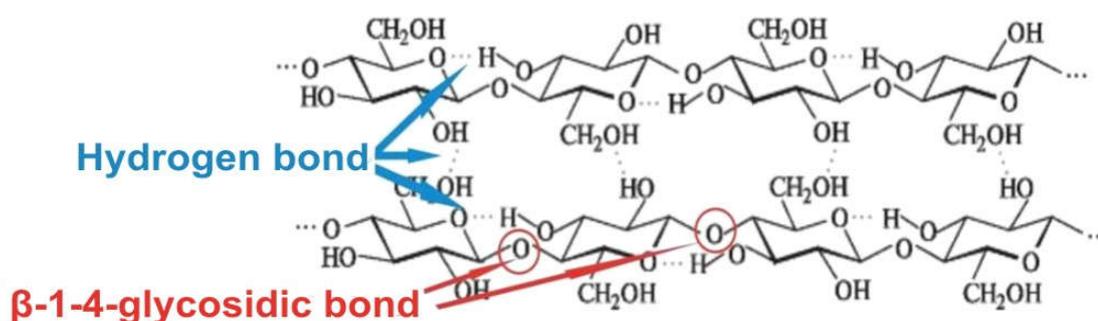


Figure 6. Scheme of intra- and intermolecular hydrogen bonds in cellulose structure [17].

Hydrogen bonds determine the physical and chemical properties of cellulose including ability of cellulose molecules to form supramolecular structures made of molecular beams possessing different crystallinity degrees. The primary structures of the cellulose supramolecular structure are microfibrils. According to XRD, microfibrils consist of alternate crystalline and non-crystalline (amorphous) regions, in which the order of arrangement of molecules is maintained by hydrogen interactions [17]. In amorphous parts long-range order is absent, and only a general longitudinal direction of the chains is conserved. Sizes highly ordered domains (crystallites) vary significantly depending on the type of cellulose. Their length may be 10-200 nm, and transverse sizes 2-5 nm.

Thus, due to forming a lot of hydrogen bonds both within and between chains, cellulose has a very stiff, partially crystalline structure. This very robust structure of cellulose being in pure state or as part of lignocellulosic materials makes further processing into valuable compounds difficult. Over that, it is necessary to conduct a preliminary stage of cellulose transformation - its activation. Activation significantly changes the physico-chemical properties of raw materials and increases its' reactivity in the destroying the supramolecular cellulose structure and reducing the crystallinity degree [18, 19] (Figure 7).

All the activation methods could be divided into three groups according to the nature of the impact. Chemical [20-24], physical [22-25] and biological [22, 24] methods of raw material pre-treatment could be mentioned. However, biological methods are less efficient than physical and chemical ones and could spend a lot of time. Furthermore, sugars allocated from biomass are partly consumed by the microorganisms during their growth [26]. Therefore, this method of activation was left out of account.

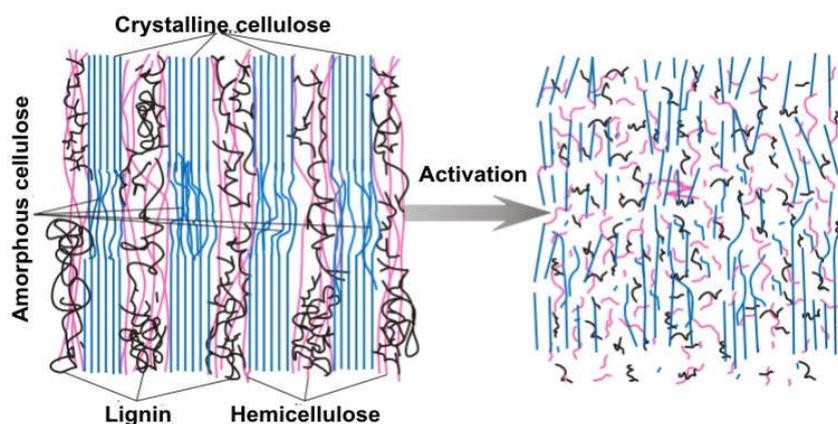


Figure 7. Structural changes of cellulose (blue) during the activation.

When activating cellulose by chemical agents the destruction of cellulose crystals takes place due to partial hydrolysis [22]. Chemical methods for processing biomass are of great interest for the modern industry due to their relative simplicity and relatively low energy consumption. Nowadays, the most widespread chemical treatment methods in the industry are, firstly, alkaline methods including kraft pulping method which are technologically and economically most beneficial; secondly, various modifications by sulphite acid pulping. These groups of methods are used to produce fibers (hemicellulose, cellulose) from biomass, and technologies using those activation methods make 60% and about 5% of the world industrial production of cellulosic materials, respectively [27]. Sulfuric acid solutions do not have broad industrial application for the initial processing of raw materials, however, they are used as catalysts for transformation of sugars to furfural [27].

Over the last 20 years, a number of chemical agents has been studied in the processes of activation and pretreatment of cellulose, for example, bases (solutions of NaOH, KOH, Ca(OH)₂, ammonia), mineral and organic acids (H₂SO₄, H₃PO₄, HCl, HNO₃, acetic acid) and H₂O₂, ammonium salts, Lewis acids and organic acid anhydrides [20-24].

Although chemical activation methods have been fairly well developed, chemical agents used during processing have several drawbacks, for example for acids and alkalis - formation of by-products, corrosive impact to equipments, and a lot of waste waters; for ionic liquids - environmental toxicity, high cost compared to water which is a cheap and readily available solvent [24, 28]. Some chemical activation methods spend a lot of time (several days) [29]. Therefore, physical methods are intensively developed on a par with the chemical activation methods.

The mechanical impacts (grinding) [21, 30-32], microwave radiation [33], heating [14], including steam explosion method [34], γ -radiation [35], microwave radiation [36] and ultrasonic treatment [37, 38] could be mentioned as physical methods. Among the proposed methods, the mechanical activation seems to be one of the most sufficiently effective and environmentally friendly

method for increasing cellulose reactivity because of reducing the particle size [39, 40], increasing the total surface area [41], destructing the crystal structure through the rupture of intermolecular hydrogen and glycosidic bonds in cellulose chains [21, 30]. These structural changes lead to increasing the solubility, reactivity and accessibility of cellulose for various reagents [40, 41]. Mechanical activation could be effective even at short impact times (up to several minutes) [42].

1.2 Cellulose hydrolysis-oxidation

One of the promising areas of cellulose complex processing is a polysaccharide hydrolytic oxidation process [43] which allows ones to obtain a number of valuable chemical compounds such as glucolic acid [44, 45], furandicarboxylic acid [46] and formic acid [11, 43]. These compounds are promising in the manufacture of polymers [47] and in the textile and chemical industries [48].

Formic acid represents a special interest, it can be used as a reducing agent or a hydrogen source [49] in the preparation of fuels and it can be synthesized from the same biomass raw [11, 50]. The methods of molecular hydrogen replacement into formic acid in the number of biomass transformations into bio fuel stages have been developed [12]. The method is to decompose formic acid directly in a reaction mixture into CO_2 and H_2 that can react as reduction agent [12]. Using formic acid as reduction agent has a number of advantages over conventional reducing agent namely molecular hydrogen whose disadvantages is increased security measures at its storage and transport and although difficulties and/or high cost of its producing from biomass. Moreover it was shown the possibility to use formic acid in fuel cells for electricity producing [51], as environmentally friendly de-icing agent [52].

Valuable oxidation products can be obtained in two ways: 1) two step process including cellulose hydrolysis to glucose and its oxidative transformation; 2) one-pot process wherein the target products are obtained from the substrate, without isolation of the intermediate compounds. The second method is more promising to improve the process economic efficiency, as well as its environmental safety by reducing the amount of waste. Using bifunctional catalysts containing in one particle acid-base and redox active centers, one step processes can increase the selectivity due to an acceleration of intermediates mass transfer between catalytic sites [5].

1.2.1 Oxidative synthesis of formic acid

Glucose could be effectively oxidized to formic acid by hydrogen peroxide at a temperature of 250°C and a reaction time of about 1 minute [53]. Yield of the target product in this case is less than 25 wt.%, what could be explained by the rapid decomposition of hydrogen peroxide under hydrothermal conditions [54]. Adding to the reaction solution a hydroxide (NaOH and KOH are most effective) results in a sharp decreasing the hydrogen peroxide decomposition rate making the formation of formic acid with high yields possible (up to 75 wt.% at 95% selectivity) [52, 53].

Cellulose peroxide oxidation to formic acid may be carried out in sub- and supercritical conditions too. However, this process has low both yield and selectivity of target product formation [55]. An example of biomass thermal cracking with formic acid production also exists. In this method FA is converted into hydrogen and carbon dioxide over Ru catalyst [56].

The process of FA production from cellulose consists of two consecutive steps: 1) acid catalyzed hydrolysis of cellulose to glucose and 2) subsequent oxidation of glucose to formic acid. Hence, for cellulose to be efficiently converted into formic acid via a one-pot process, a bifunctional catalyst system is necessary to be created. Solutions of Mo-V-P HPA possessing both acid and oxidizing properties are perspective bifunctional catalysts [57] of some processes including the FA formation from cellulose under mild conditions [11, 58, 59]. As noted above, HPAs are big group of polyoxocompounds formed by metals of V and VI groups of the periodic table of elements [60]. The prospect as catalysts for different reactions of solutions of Mo-V-P HPA with Keggin as well as non-Keggin structures (HPA-x and HPA-x', respectively) and with the composition $H_aP_zMo_yV_xO_b$ ($z > 1$, $x' > 4$) can be explained by both high Bronsted acidity, typical for all types of HPA, and well oxidation properties. By introducing a certain number of vanadium atoms into the structure of HPA, as well as the partial substitution of H^+ ions by the metal cations it is possible to obtain HPA solution properties being specific to a particular type of reaction. HPAs are also known as catalysts for "green chemistry", as in their presence low-waste processes can be carried out [61].

By now, several works devoted to the synthesis of FA from polysaccharides using bifunctional Mo-V-P HPA as a catalyst have been published. First studies on cellulose hydrolysis-oxidation in the presence of Mo-V-P HPA are described in references [62, 63]. Significant conversion of the polysaccharide was observed but the authors did not report any formation of formic acid. Oxidative processing of the polysaccharide in the presence of HPA was found to be most effective at pH 1-2 and temperatures of 90-120°C [62]. In the papers [58, 59], comparative hydrolysis of cellulose, hemicellulose, xylan, lignin and real biological objects (pine sawdust, birch and poplar and cyanobacteria biomass) was described in the presence of HPA $H_5PV_2Mo_{10}O_{40}$ under a temperature of 90°C (in order to avoid product decomposition). In [59] formic acid was found to be the only one reaction product dissolved in the aqueous media, and CO_2 was the only one by-product. Glucose was easily oxidized. Thus, about 50% yield of FA was achieved at 80°C under 30 atm oxygen pressure. Under the optimal oxidation conditions, a number of polysaccharides was tested in the hydrolysis-oxidation reaction. Cellulose was the most difficult-hydrolysing substrate, and the maximum output of HCOOH using cellulose as a substrate was the lowest one (7% after 24 hours of reaction). FA yields were higher in the transformation of water-soluble oligo- and disaccharides. Thus, a degree of conversion of 98% and a yield of FA 47% were shown for cellobiose after 26 hours reaction. 14% FA yield was revealed in the experiment with the plant biomass (poplar sawdust). This result was better

compared to cellulose transformation experiment what can be explained by the presence of hemicelluloses in the plant sample that makes biomass more soluble in water and, correspondingly, more available for catalytic transformations. To improve the efficiency of cellulose conversion, it is necessary to use a stronger acid than $H_5PV_2Mo_{10}O_{40}$. The same group of authors showed that the addition of toluenesulfonic acid to the reaction mixture allows to increase up to 19% the yield of the target product from cellulose [59]. In the paper [11] various vanadium-containing compounds, such as the commercial HPA $H_5PV_2Mo_{10}O_{40}$, V_2O_5 , $VOHPO_4$, $VOSO_4$ were tested in the reaction of glucose oxidation to identify the most effective oxidation catalyst. Mo-V-P HPA was found to be the most effective catalyst for this process. Negative impact of high oxygen concentration and high temperature on the yield of FA was shown. In general, the authors of Ref [11] could fix the highest yield of formic acid at 35% at 100°C under air pressure of 50 atm. XRD of V and Mo atoms in the HPA catalyst structure revealed that it is the oxidized state of vanadium V^{+5} that is the oxidative center in the catalyst structure [11]. At the same time no one paper has been devoted for investigating the influence of HPA composition on the FA yield.

1.2.2 Paths of carbohydrate oxidation reaction

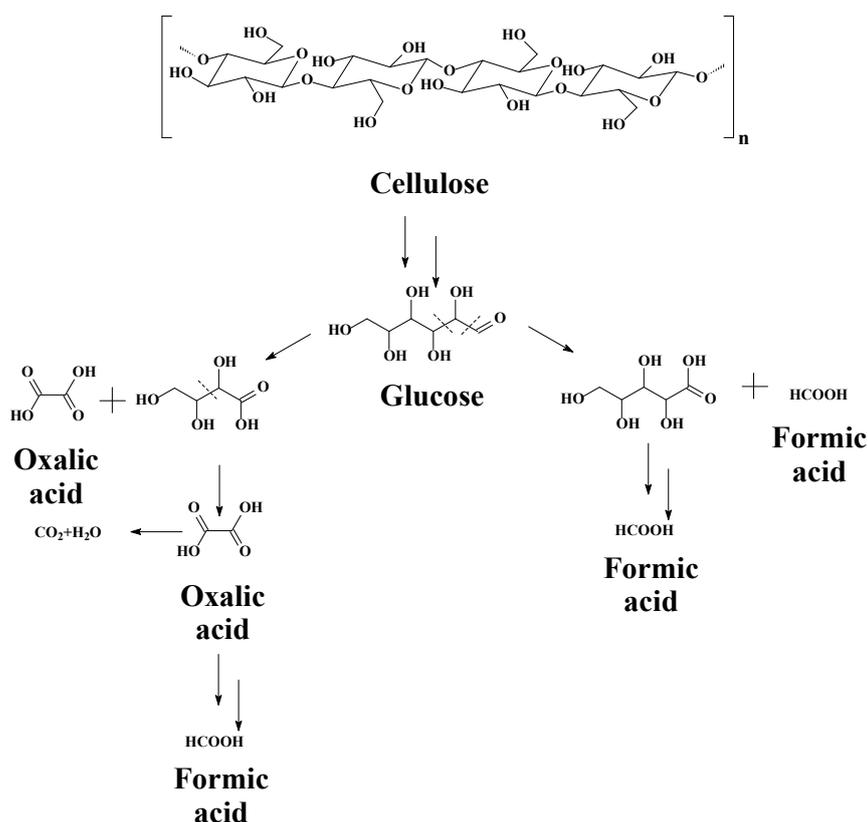
Formic acid is formed from cellulose via the oxidation of glucose released by the hydrolysis of the polysaccharide, so it is necessary to consider the possible routes of glucose oxidation.

The oxidation of glucose into FA is a process which requires sufficiently strong oxidizing agents. One mole of the substrate can give up to six moles of product:



Possible reaction pathways of glucose oxidation depend on the oxidant being used and oxidation conditions. One of the most common methods is the oxidation by H_2O_2 in the presence of bases of alkali metals, preferably [52]. According to [52, 64], the cleavage of sugar carbon skeleton passes via radical mechanism involving the formation of the hydroxyl radical and a number of intermediate products which are also oxidized into FA (Scheme 2).

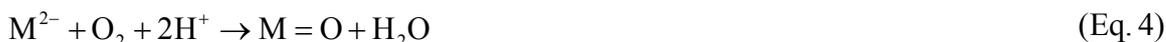
Most probably, the oxidation begins with the elimination of aldehyde group releasing one FA and one arabinoic acid molecule [65]. The elimination reaction with formation of oxalic and C_4 aldonic acid. The last molecule undergoes decarboxylation reaction with formation of two oxalic acid molecules. Oxalic acid can either be oxidized to CO_2 and water or converted into formic acid [64]. During the oxidation of the saccharides to FA dehydration reaction into 5-HMF, levulinic acid or lactic acid should be avoided, as acetic acid would be the main oxidation product in these cases [52].



Scheme 2. Possible mechanism of FA production from cellulose [52, 64]

Another way of oxidating sugars to FA described in several papers [11, 58, 59] is a catalytic air oxidation in the presence of heteropolyacids. HPA contains a heteropolyanion $[\text{A}_x\text{B}_y\text{O}_z]^{n-}$, where O - oxygen, A - heteroatom (phosphorus, silicon, boron, etc.), B - metal (molybdenum, vanadium, tungsten, rarer niobium and tantalum are most commonly used). Heteropolyanions may contain several metals. HPA having close structures are united into several structural groups, for example HPAs with Keggin structure $\text{AB}_{12}\text{O}_{40}$, Dawson structure $\text{A}_2\text{B}_8\text{O}_{48}$, Silverton $\text{AB}_{12}\text{O}_{42}$. HPAs with Keggin structure are the most used in catalysis [1, 60].

Vanadium-containing HPAs seem to be promising catalysts for the oxidation of various organic compounds [66, 67]. The first studies on using HPA as a catalyst for such transformations were carried out at the Boreskov Institute of Catalysis SB RAS in 1970-80 [68, 69]. The oxidative action of HPA bases on the transfer of electrons from the organic compound to HPA with the simultaneous reduction of vanadium atoms from V^{+5} into V^{+4} followed by the regeneration of the catalyst with oxygen [67, 70] (Eqs. 2-4). The oxidized form of the catalyst may again join the reaction with organic substrate [67, 70]. This mechanism named electron-oxygen transfer (ET-OT mechanism) is known for a long time [71]. Matveev and Kozhevnikov first showed that HPA containing more than one atom V in the heteropolyanion structure are multi-electron oxidants [69].

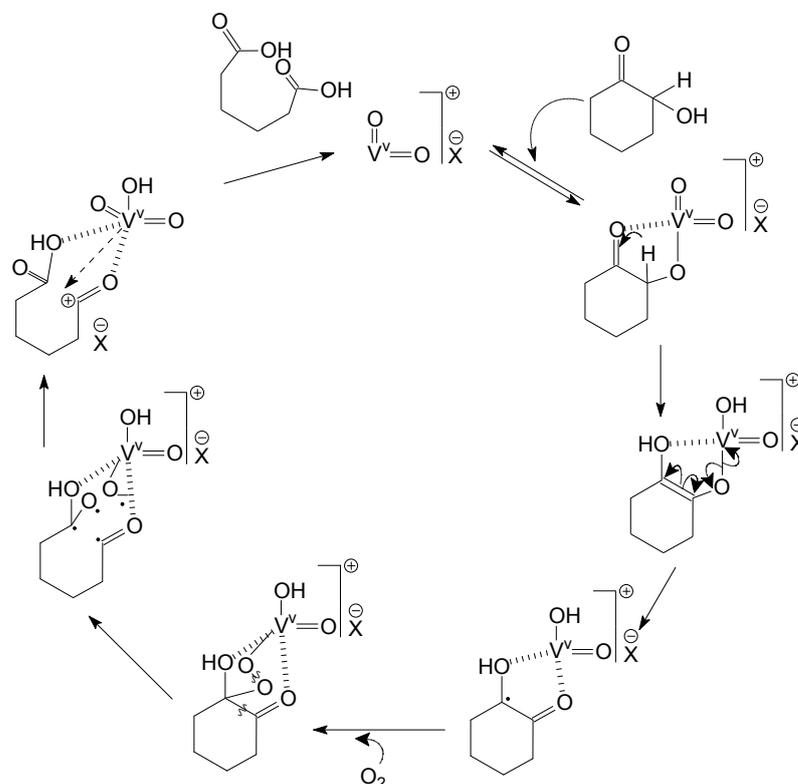


HPA $H_5PV_2Mo_{10}O_{40}$ is often considered to be a promising oxidation catalyst [67]. For the first time in oxidation reactions, this HPA solution was used by Matveev and Kozhevnikov in the oxidation of sulfur-containing compounds [72]. The catalytic role of the vanadium centers was proved by ^{51}V NMR analysis conducted under oxygen or oxygen-free atmosphere [63, 73]. The oxidation of organic substrates via ET-OT mechanism (Eqs. 2-4) is to be accompanied by cleavage of C-H bond, but the oxidation of organic alcohols on Mo-V-P HPA does not result in C-H bond cleavage, causing, however, the decarbonylation process of the carbon skeleton with a formaldehyde molecule cleavage. [73]. Similar results are observed for the diols and some derivatives of cyclohexane: cyclohexanol, cyclohexanone and 2-hydroxycyclohexanone. In this case the oxidation of carbon atoms associated with oxygen takes place to form a dicarboxylic acid product [66, 67, 71]. The authors of the work [58] proposed a two-electron transfer mechanism in the process of sugar hydrolysis-oxidation. HPA catalyst $H_5PV_2Mo_{10}O_{40}$ comprising two vanadium atoms in the oxidized state (V^{+5}) provides the transfer of two electrons from a molecule being oxidized and transforms into the reduced form (V^{+4}). New form of the catalyst is then re-oxidized by molecular oxygen. Carried out for over last 20 years under the supervision of Jean-Marie Breugeot, studies of the catalytic activity in the oxidation of organic substances, various metal complexes of Fe(III), Ce(IV), Ru(II), Ru(III), as well as various monomeric vanadium particles (VO_2 , $[VO(acac)_2]$, $[n-Bu_4N]VO_3$) showed that it is vanadium-containing HPAs that possess the highest redox potential for such reactions and provide the highest yields of organic matter oxidation products [66, 74]. High activity of HPA containing in their structure two or more atoms of vanadium is explained by means of the cleavage of C-C bond is a two-electron transfer process, so that at least two catalytic centers are required for the transfer of two electrons [62, 66, 67].

At low concentrations of HPA, heteropolyanion structure is subjected to dissociation with release of VO_2^+ particles [62], which have more redox potential compared to the V(V) in the HPA structure making VO_2^+ even more active than HPA in the oxidation reactions of organic compounds [75, 76]. Reduction of vanadium atoms accelerates dissociation of a heteropolyanion [75, 77]. Thus, when oxidizing organic substances and breaking up C-C bonds, this is VO_2^+ that is the active catalytic particle. Taking into account all these statements, in the paper [66] a mechanism of 2-hydroxycyclohexanone oxidation accompanied by C-C cleavage was proposed (Scheme 3). In this

scheme the authors demonstrated the possibility of simultaneous coordination of the organic molecule and oxygen to the active site, rather than a two-stage sequential mechanism WRA (Eqs. 2-4).

Talking about the catalytic role of HPA it should be noted that the heteropolyacid is a superacid due to the high mobility of proton, what makes it promising catalyst for the hydrolysis [78, 79]. Therefore, Mo-V-P HPAs seem to be promising bifunctional catalysts for hydrolysis-oxidation processes including the conversion of polysaccharide substrates.



Scheme 3. Mechanism of 2-hydroxycyclohexanone oxidation accompanied by C-C cleavage [66]

1.3 Cellulose hydrolysis-dehydration

Currently, a number of approaches are provided to the implementation of cellulose hydrolysis-dehydration processes via using various catalytic systems which can be divided into three main groups according to the type of catalysts used:

- a) hydrolysis processes conducted at high temperatures and pressures in near- or supercritical conditions;
- b) processes catalyzed by solutions of mineral acids or bases, ionic liquids, enzymes;
- c) transformations over various solid acidic catalysts such as insoluble salts, activated carbons, the oxides of transition metals.

The methods mentioned under b) and c) are characterized by relatively low process temperature compared with the a) group (so called subcritical or just hydrothermal conditions).

Water or non-aqueous solvents may be used as solvents [81, 82]. The most detailed studied is the polysaccharide hydrolysis in the aqueous media due to simplicity of the experiments in water and

its availability in comparison with organic solvents and ionic liquids. Using non-aqueous media for the hydrolysis is highly prohibited from environmental problems and the high cost of organic solvents and ionic liquids.

1.3.1 Cellulose transformation under near- and supercritical conditions

Cellulose processing in pure water

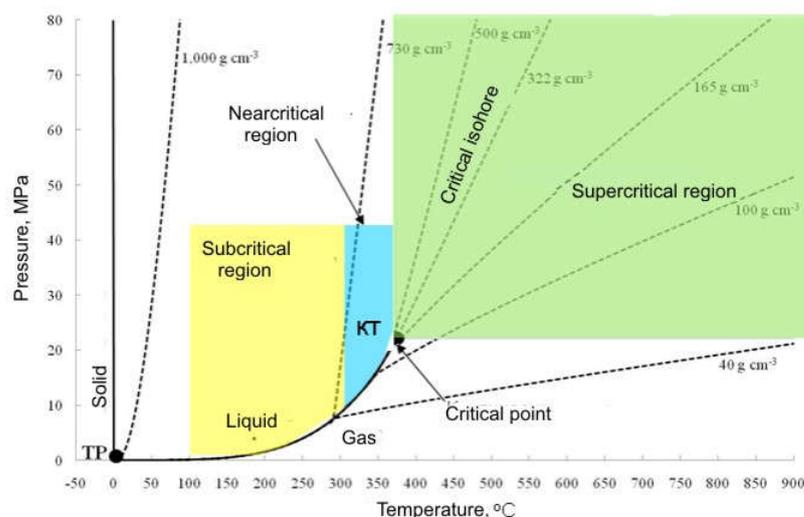


Figure 8. PT diagram of pure water

As stated above (see the part 1.1), cellulose is a polysaccharide with a robust structure which prevents the chemical transformation. This requires using an activation step as well as the use of rather harsh conditions like high temperatures and pressures. It is known that cellulose hydrolysis may proceed in pure water without any catalyst at temperatures of 150 °C or higher (amorphous cellulose) and 180 °C or higher (crystalline cellulose) [80, 81]. The fast cellulose treatment in the heated water is the simple way for the polysaccharide dissolution [82]. The catalytic activity of water under harsh conditions is caused by the changes of solvent properties. Depending on the physical parameters the water behaviours are divided into 4 groups (Figure 8).

Conditions of water existence in the temperature range 100-150 °C (lower limit) and 300-350 °C (upper limit) are named subcritical, the region near the water critical point (374 °C and 22.1 MPa) is called nearcritical [83]. There is no drastic difference in the properties of water in either sub- or nearcritical conditions, so often, they are combined into one area, called subcritical. After passing above the critical point of water we are entering the supercritical domain. At sub- and supercritical conditions water has different physical characteristics (density, dielectric constant, ionic product). With increasing temperature, the density of liquid water drops down and vapor density increases [84].

In areas near the critical point (near- and subcritical conditions) the properties of liquid and gas (vapor) phases becomes similar and more sensitive to temperature and pressure changes [85]. Water dielectric constant decreases from 78.5 at 25 ° C and 0.1 MPa to about 14 at 350 ° C and 25 MPa [86]. This dielectric constant value is close to ones of some polar organic solvents at room temperature (f. e. acetone and ethanol). It resulted in increasing of the solubility of some organic compounds in supercritical water [87]. Water ionic strength also rises with temperature growing [88]. In subcritical conditions, K_w are several orders of magnitude higher compared with normal conditions, due to increased concentration of H^+ and OH^- [89]. Noted property changes allow water to act as an effective catalyst in sub- and near-critical conditions (250-350 °C), for example in the alkylation, dehydration, hydrolysis, oxidation, decomposition, and gasification etc. [32, 90, 91].

Researches aimed cellulose transformation are often carried out in the temperature range from 200 to 400 °C. The pressure for all experiments is usually constant that makes influence of pressure outside the experiment framework. Cellulose complete conversion is achieved in pure water at temperatures above 320-380 °C [92-94] and the exact temperature is apparently determined by the degree of the initial substrate crystallinity. A study of reaction time influence on microcrystalline cellulose depolymerization shows that under optimal conditions (380 °C and 22 MPa in a batch reactor) sharp rising of cellulose conversion from 20% to 95% is observed when increasing reaction time from 13 to 17 seconds [94]. Sasaki et al. [93] have shown that reaction time equal to 10 seconds is necessary to achieve full conversion of cellulose at 320 °C. But at temperature of 400 °C full conversion of cellulose is achieved after 0.05 seconds. While increasing time or temperature of an experiment rapid dropping of dehydration and hydrolysis product contents is observed and thus decomposition products are accumulated [92, 94]. Thus, for carrying out cellulose depolymerization it is necessary to select the optimal reaction time at an optimum temperature. These conditions should be chosen individually for each type of cellulose since, depending on the degree of crystallinity of the sample, they can vary greatly. For example, in [94], the hydrolytic conversion of microcrystalline cellulose was studied in a batch reactor under the pressure of 22 MPa and the temperature in the range 374 - 386 ° C. The authors propose the temperature of 380° C and the pressure of 22 MPa as optimal for the process because under these conditions a maximum yield of glucose and oligomers equal to 39 and 24%, respectively, have been obtained with the cellulose conversion degree of 80%. Sasaki et al. studied the hydrolysis of microcrystalline cellulose in a flow reactor at 290 - 400 °C and under a constant pressure of 25 MPa; they registered the formation of erythrose, dihydroxyacetone, fructose, glucose, glyceraldehyde, piruvaldgid and soluble oligosaccharides. The optimum temperature was 320 °C [92].

The results described in [93] are devoted to microcrystalline cellulose depolymerization at 320-400 °C, 25 MPa, and reaction times of 0.1-10 seconds. The authors have achieved complete

conversion of cellulose only at 400 °C with a total yield of all products equal to 76%. The reaction rate significantly increased at temperatures above 350 °C, what emphasises the influence of the water property changes on the glucose depolymerization process under supercritical conditions.

Rogalinski et al. studied the conversion of glucose polymers (starch and cellulose) as well as samples of biomass (rice silage and rice straw) in batch and flow reactors under relatively mild subcritical conditions. The temperature was varied in the range of 210-310 °C [95, 96]. The liquefaction of the polysaccharides reached 25% and the yields of glucose and monosaccharide degradation products were 5 and 10%, respectively [96]. In the flow experiments, the maximum glucose yield was 3% at low temperature and 10 MPa. The authors concluded that glucose was relatively stable at the temperatures below 240 °C [96].

Studies of holocellulose depolymerization into monosaccharides were carried out in supercritical conditions (flow reactor, pressure of 22 MPa, temperatures of 325-425 °C, reaction time of 60 s) [97]. In the experiments at 325 and 350 °C (i.e. sub- and nearcritical conditions) the conversion degree was less than 50%. However, under supercritical condition at temperatures above 380 °C, the conversion of the substrate exceeded 80% although low total yield of monosaccharides of about 7% were observed. Acidic hydrolysis under mild conditions of the aqueous solutions obtained in critical conditions increased the total yield of monosaccharides by the factor of 2, approximately, due to the hydrolysis of dissolved oligosaccharides, apparently.

Studying cellulose conversion in critical media proves the generally used scheme of cellulose depolymerization (see Scheme 4 in Section 1.3.4) [92]. Cleavage of hydrogen and glycosidic bonds in cellulose structure is the first step to form soluble oligomers of glucose. Then the destruction of the first step product occurs with the formation of furan compounds, low molecular carboxylic acids and gaseous products [98, 99]. It should be noted that reaction rates rapidly grow with the temperature increase. After passing through the critical point, the reaction rates of cellulose depolymerization and glucose destruction grow sharply [92]. Hence a time of forming water soluble target products becomes critically short and lower than few seconds. Longer processing times result in the formation of deep decomposition products: coke and gases. At the temperatures of 300-400 °C the transformation of glucose reaches ~50% in 1-2 seconds. The fructose transformation reaches 100% faster than 1 second at the same conditions [100-102]. Experiments with fructose and glucose provide different main products because sugar degradation rates in near- and supercritical conditions are significantly higher than the rate of isomerization of glucose to fructose [103-105]. Thus for glucose the main products are the carbon skeleton destruction products: glyceraldehyde, piruvaldegid, glycolaldehyde, etc. [103, 106]. The fructose dehydration may form 5-HMF as the main product under the catalysis by water [104, 106]. Thus, in the near- and supercritical conditions, even at extremely low reaction times, it is not possible to produce 5-HMF with high yields from substrates as cellulose. To produce the furan

derivative from the polysaccharide it is necessary to use milder conditions to reduce the rates of sugar decomposition reactions and to use catalysts for the isomerization of glucose to fructose.

Combining catalytic and subcritical cellulose conversion methods

In [107] the process of cellulose transformation to 5-HMF was studied in presence of catalysts (calcium, sodium and lithium hydrophosphates LiH_2PO_4 , NaH_2PO_4 , CaHPO_4) at 250-330 °C and 5-35 atm. Studying the influence of the reaction conditions on the process showed the highest yield of the main product was found at 270 °C and, at higher temperatures, yield of 5-HMF becomes lower. At a constant temperature (270 °C) main product yields growth was observed while pressure increased from 5 to 35 bar. Output of 5-HMF in the experiment without catalyst raised in 2 times from 5 to 10%. This observation was explained by higher density of the superheated pressurized steam and increasing the number of water molecules adsorbed on the cellulose surface accelerating depolymerization. Mentioned in the article data about influence of pressure are unique as authors usually leave effect of pressure outside of consideration. A comparative study of activities of dihydrogen phosphates versus medium salts and phosphoric acid has shown that the greatest activity was with NaH_2PO_4 for which a maximum yield of 5-HMF was equal to 35% [107].

Water insoluble salts of CaP_2O_6 and $\text{Sr}(\text{PO}_3)_2$ also catalyzed cellulose transformation to 5-HMF at hydrothermal conditions [108]. Compared to the blank experiment where the total yield of glucose and 5-HMF was equal to 12 %, using the catalyst increased the total yield up to 18 and 35 % over CaP_2O_6 and $\text{Sr}(\text{PO}_3)_2$ salts, respectively, thereby indicating a low hydrolytic activity of the calcium salt. At the same time, in the process of glucose and fructose dehydration to 5-HMF the activities of both salts were similar and 5-HMF yields reached 20-21% and 34-39% from glucose and fructose, respectively.

Sinağ et al. [109] carried out a study of cellulose hydrolysis and model biomass sample transformation in a batch reactor (at 225, 300 and 375 °C) in the presence of K_2CO_3 , HZSM-5 and Ni/SiO_2 catalysts. HPLC analysis revealed that the 5-HMF was the main reaction product. Moreover, there was formation of acetic acid, formic acid, formaldehyde, furfural and metilfurfurol. The maximum yield of 5-HMF was 18.3 % at 225 °C without using of catalyst. With rising of temperature to 375 °C increasing yields of glucose degradation products were observed. The presence of the catalyst result in reducing 5-HMF yield and increasing the yields of acetic, formic and levulinic acid.

Minova et al. studied glucose rapid depolymerization with the temperature range 240-280 °C and nitrogen pressure 30 MPa [99]. Full conversion of cellulose was at 280 °C. At temperatures lower than 240 °C (200 and 220 °C) glucose and soluble oligosaccharides were the main reaction products. The maximum glucose yield was at 260 °C when yields of glucose transformation products were negligible. The authors also conducted studying influence of the reaction time on the depolymerization

rate and the minimum initiation temperature of the process. Thus, an addition of sodium carbonate into reaction mixture led to reducing temperature when cellulose hydrolysis started to 180 °C, but the reaction rate still was low at temperatures lower than 260 °C and in the range of 260 - 300 °C, it significantly increased. In presence of industrial nickel catalyst depolymerization process was initiated at temperatures of 260-320 °C but at temperatures lower than 260 °C hydrolysis of cellulose did not occur. Above 260 °C the formation of water-soluble products was observed, including cellobiose and 5-HMF, as well as gases.

Thus supercritical conditions provide rapid cellulose hydrolysis and at the same time catalyze glucose decomposition whereas subcritical conditions allow to avoid rapid destruction of monosaccharides. In [94, 110] it was supposed to combine super- and subcritical conditions to increase the total yield of glucose. Authors proposed a two step processing method that consists in consecutive application of supercritical conditions for the cellulose dissolution and subcritical ones for soluble oligosaccharides hydrolysis. They was succeeded in achievement of 40 % glucose yield and in registration of glyceraldehyde, erythrose, dihydroxyacetone and 5-GMP with a maximum total yield of 28.3%. Apparently, this is the best result achieved in sub- and supercritical water.

According to the literature data on cellulose transformations in sub-, near- and supercritical conditions, high process rates of sugar transformations at extremely high temperatures and formation of gaseous products under these conditions make near- and supercritical processing a very promising way for biomass gasification. Near- and subcritical conditions (150-350 °C) are more suitable for the liquefaction of biomass, the high temperature limit is rather for biooil and biocoil producing while low temperature limit is for manufacturing valuable compounds (Figure 9). Combining of hydrothermal and catalytic approaches allows one to improve some important process parameters such as substrate conversion, yields and selectivity of main product, as well as to decrease the energetic consumption due to milder conditions.

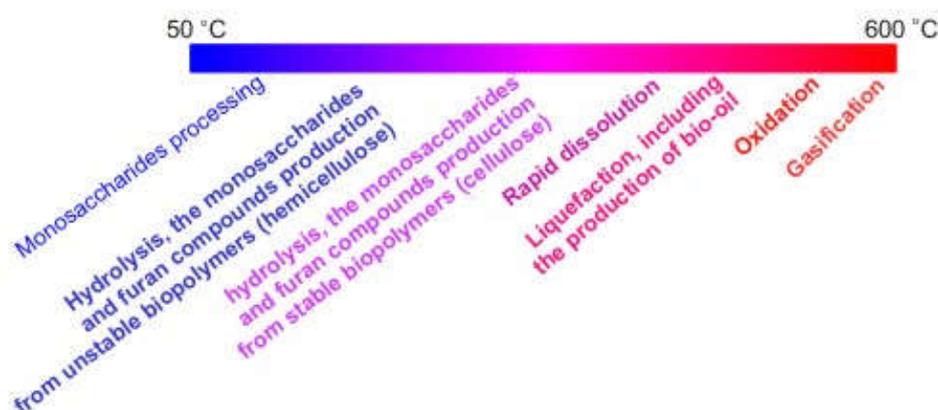


Figure 9. Optimal temperature range for processing carbohydrates

1.3.2 Cellulose hydrolysis in the presence of soluble catalysts**Hydrolysis in acid or base solutions**

Articles about cellulose hydrolysis were firstly published at the beginning of the XIX century. Bracont described acid hydrolysis of raw plant materials which contained cellulose (see indication in ref. [13] and [111]). Industrial methods of polysaccharide hydrolysis were originated at the beginning of the XX century [111, 112]. In pioneer works, polysaccharide hydrolysis was carried out in the presence of bases and acids [112, 113]. Due to a long period (about 100 years) of polysaccharide hydrolytic transformation, studying its features and mechanism is well known but the interest to this process stays very strong yet [114].

Strong acids and bases are commonly used as catalysts for cellulose hydrolysis in water solutions [115]. Commonly used are sulfuric acid [116] and its derivatives [111] and sodium hydroxide [115]. Hydrochloric acid [117, 118], nitric acid [119], phosphoric acid [116, 119] and organic acids [111, 120] have also catalytic activity in this process. Among examined mineral acids H_2SO_4 is the most active cellulose hydrolysis catalyst [121].

Historically cellulose hydrolysis in concentrate sulfuric acid was the first developed method (see indication in ref.[111]). In the first half of XX century, in Germany first, and later in the USA and Japan, the technologies of cellulose and biomass hydrolysis by 70-75% sulfuric acid have been developed [111]. The lack of necessity to activate cellulose was an advantage of such method. Moreover, a number of activation methods was developed by using H_2SO_4 [122, 123]. However, a strong corrosive impact of concentrated acid prevents the widespread use of these techniques [24].

More promising method is cellulose depolymerization by diluted solutions of acids. The first such industrial cellulose hydrolysis processes were developed before the first World War. Their development was continued in the United States of America and Germany (Sholler's and Madison's processes) (see in [111]).

The degree of cellulose hydrolysis by soluble catalysts is influenced by two main factors: 1) concentration of a catalyst in solution and 2) the temperature.

In diluted (~ 0.1-2%) sulfuric acid solutions glucose could be formed with yields up to 40-50% at temperatures of 200-230 °C [81, 124-127]. Varying one of the process parameter (using more diluted acid or decreasing temperature) decreases glucose yield significantly [81, 124, 125]. Moreover during cellulose hydrolysis a number of glucose destruction products are formed and their yields are influenced by pH. Thus, the formation of 5-HMF and levulinic acid is typical of acid hydrolysis [128].

Total yield of glucose in cellulose hydrolysis can be equal to 80% if the reaction is carried out in 5 mM sulfuric acid in a flow reactor [129]. High yields are provided by removing glucose in a solution flow from the active zone of the reactor. The optimal temperature to obtain glucose in flow

reactor is in the range of 200-220 °C and the yields are decreased with increasing temperature due to glucose destruction [111].

When studying cellulose transformation, diluted sulfuric acid solutions are often used but there are some examples when other mineral acids are applied. Thus, diluted (2.5-10%) solutions of phosphoric acid hydrolyze cellulose of potato peels to produce glucose with yield of 80 % at temperatures of 135-200 °C [116]. To hydrolyze sugarcane straw at 100-128 °C 2-6% solutions of HCl were used and such scheme allowed to produce xylose from hemicellulose with high yields but glucose yield was only 3.8 % [117].

Mineral acid solutions catalyze not only cellulose hydrolysis reactions but glucose dehydration too. Thus they could be used to obtain valuable compounds such as 5-HMF and levulinic acid [7, 130]. However such feature of mineral acids is undesirable if target product is glucose. Therefore, search of more mildly acidic catalysts such as organic acids, to reduce the rate of dehydration of cellulose, was conducted. Such acids as acetic, formic, malic, oxalic acids were tested in [111]. Among them the most interesting is oleic acid because it provides glucose yields compatible with sulfuric acid [26]. Glucose yield is ~ 6% with conversion of 20% in 50 mM solutions of mentioned acids during 3 hours at temperature of 175 °C. Yields are similar due to low dehydration catalytic activity of oleic acid [26].

Under equal reaction conditions including pH media, sulfuric acid demonstrates higher activity compared to formic acid in the hydrolysis of microcrystalline cellulose [114]. FA shows high stability in the reaction media at 180-220 °C what means that low catalytic activity of FA is not caused by its decomposition under hydrothermal conditions. The authors note that according to the literature data anions containing sulfur influence on physical properties of cellulose therefore sulphate anions also act in cellulose depolymerization [114].

Indeed, salt effect influence on yields of cellulose depolymerization products. Thus, vom Stain et al. [131] investigated depolymerization of microcrystalline cellulose at 105-125 °C in a solution of 0.1M oxalic acid. The experiments were made with and without NaCl. In the presence of the salt the yields were higher by the factor of two.

Sulfuric acid and its aryl and alkyl derivatives demonstrate close activity. Maximal yields of reducing sugars revealed by spectrophotometry could reach 35% [120].

A soluble catalyst made of water solutions of formic and chloric acids (78% and 4 v/v%, respectively) let to produce glucose with the maximal yield equal to 32% from cotton fibers under soft conditions at 65 °C and the reaction time 5 h [132].

Soluble catalysts could be also used for one-pot transformations of cellulose. Thus, water-soluble poly(arylene oxindole) catalyst makes possible the production of LA from starch with the yield up to 30% [133].

Hydrolysis in heteropolyacid solutions

Heteropolyacids possessing acid strength which is higher compared to mineral acids have been studied as hydrolysis catalysts for a long time [78, 134].

Comparative study of microcrystalline cellulose in the presence of HCl and HPA shows higher efficiency for HPA [118]. In solutions with similar proton activity, cellulose conversion and glucose yield in the presence of HPA approximately in two times higher than in the case of HCl catalysis. The maximal glucose yield equal to 60% has been achieved in the presence of HPA at 170 °C while the total yield of side products (LA and 5-HMF) in the same experiment is lower than 5%.

HPAs substantially differ from each other in structure and composition, therefore they could also have different catalytic activities. Testing of tungsten HPA with different compositions (P, Si, B, Al, Ga, Co-containing) in comparison with hydrochloric and sulfuric acids showed that the most effective catalyst is a boron-containing one. In the presence of $H_5BW_{12}O_{40}$, the yield of glucose was more than 75% [135]. A comparative study of the catalytic activity of the four HPA ($H_3PW_{12}O_{40}$, $H_4SiW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ and $H_4SiMo_{12}O_{40}$) revealed P-W- containing acid to be the most active one [136]. Studying catalytic activity of HPA soluble salts with the structure of $XH_YPW_{12}O_{40}$ (where X = Ag^+ , Ca^{2+} , Co^{2+} , Y^{3+} , Sn^{4+} , Sc^{3+} , Ru^{3+} , Fe^{3+} , Hf^{4+} , Ga^{3+} , Al^{3+} and Y cation containing HPA) has shown that the highest degree of cellulose conversion and the highest total yield of reducing sugars have been obtained in the presence of $Sn_{0.75}PW_{12}O_{40}$. Moreover $H_3PW_{12}O_{40}$ and $Sn_{0.75}PW_{12}O_{40}$ catalysts are more active than sulfuric acid and provide 23% yields of reducing sugars in comparison with 10% for H_2SO_4 [136].

HPA can be used in hydrolysis of not only cellulose but also hemicelluloses and other polysaccharides. Thus, in presence of soluble HPA $H_5BW_{12}O_{40}$ the hydrolysis of xylan occurs with high yield of xylose equal to 73% during 3 hours at 60 °C, the starch hydrolysis with glucose yields 85% during 6 hours at the same temperature and cellobiose provides glucose yield of 82% during 6 hours [135].

1.3.3 Hydrolysis by solid acid catalysts

As already mentioned above, the application of industrial processes with soluble acid catalysts is limited by high costs of equipment due to corrosion and separation of the catalyst from the dissolved substrate. These disadvantages could be overcome via the creation of high performance solid acidic catalysts for polysaccharide hydrolysis to valuable substances. Recently a lot of articles have been published aimed on this problem solution. A few types of promising catalysts could be pointed. 1) Carbon materials containing acid sites. 2) Nanodispersed metals of the platinum group (Pt, Pd, Ru, etc.) and Au deposited on a carbon or oxide support. Such catalysts are typically used in the combined hydrolysis-oxidation or hydrolysis-reduction processes, however, they are also observed to have

catalytic activity in the hydrolysis of polysaccharides. 3) Ion-exchange resins and polymers (Amberlyst, Nafion) having Bronsted acid sites ($-\text{SO}_3\text{H}$). 4) Non-soluble HPA, for example, CsHPA or AgHPA, being acid catalysts with a strong Brønsted acidity. 5) Zeolites (H β , HZSM-5, etc.) being aluminosilicate framework structure which have Bronsted or Lewis type acid centers. 6) Insoluble oxides (ZrO_2 , TiO_2 , SiO_2 , etc.) containing Lewis and Bronsted acidic sites.

The comparison of catalytic properties of different acid catalysts tested by different authors in reaction of cellulose hydrolysis is shown in the Attachment 1.

Cellulose hydrolysis over insoluble HPA salts

Catalytic systems based on P-W HPA are usually studied as it has been previously shown that HPAs of such composition have demonstrated the best activity in cellulose hydrolysis among HPAs with various compositions and structures [136]. For the first time, hydrolysis-dehydration of cellulose over cesium HPA salts were described in 2010 by Tian et al. [118]. In a number of salts with the composition $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$ (where x was in the range of 1-3) the most promising was HPA with composition of $\text{CsH}_2\text{PW}_{12}\text{O}_{40}$. Using this catalyst, the authors achieved 27% of glucose yield after 6 hours at 160 °C. The rate of hydrolysis-dehydration and cellulose conversion was inversely proportional to cesium quantity in HPA because with the increase of Cs the catalyst acidity decreases. However when Cs ratio is $x=2.0-2.5$ it is observed a rapidly growth of selectivity on glucose with a maximum at 85% (when $x=2.2$). At greater or lesser Cs quantity the selectivity is about 50% [118]. Analogous abrupt increase for CsHPA with $x = 2.0-2.5$ was observed for glucose yields, although it does not affect on the overall dynamics of the yield dependence from the catalyst acidity.

A group of authors in [137] investigated a similar catalyst $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ having a composition close to the optimal one. The glucose yield achieved was 21% at 170 °C after 6 hours and glucose selectivity equal 89.9%. The catalyst developed was 2 times more active in comparison with analogous one in Tian's work [118]. Thus in Cheng's et al. paper [137] a substrate conversion of 20% has been achieved against 10% of Tian's work [118]. The glucose selectivity and reaction conditions were similar in both papers (selectivity 89.9 and 80%, respectively, 160 °C, 6 hours). Such effect could be explained by differences in catalyst acidity of the samples with the same composition. The compared study of cellulose hydrolysis in presence of the catalysts (CsHPA, Zeolites, sulfonated coals) was represented in [138]. It was established that HPA cesium salt ($\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$) at 190 °C and a molecular hydrogen pressure of 50 atm allowed a 30% conversion of the substrate; although this value was comparable with the results for other acidic catalysts.

Cellulose hydrolysis over catalysts based on carbon or resin

Comparative study of different solid acid catalysts shows that carbon materials with acid sites could be referred to the most promising cellulose depolymerization catalysts [32, 90, 139, 140].

Different carbons (e.g. activated carbons, pyrolytic carbons derived from monosaccharides (glucose, sucrose), lignin, cellulose or phenol-containing organic waste) could be used for creating acid catalysts [90, 139, 141-143]. Acid carbon catalysts are able to hydrolyze cellobiose and glucose [144, 145]. In [144] the authors obtained 35% of glucose yield from cellobiose in a batch reactor at 100 °C after 6 hours. In [145] cellulose transformation was studied in a flow fixed bed reactor. The stable catalyst operation was observed during four hours at 200 °C; cellulose conversion was about 50%.

Carbon catalysts have shown a high activity in cellulose hydrolysis. For example, Onda et al. compared a wide range of solid acid catalysts (oxides, zeolites, sulfonated carbon, Amberlyst resin). The catalytic activity of the sulfonated carbon was several times greater than the activity of the other acid catalysts. The yield of glucose over the carbon reached 40% [90, 140]. In the paper [32] the authors reached the glucose yield of 62% in mildly conditions at 150 °C and 24 hours of reaction between mechanically activated microcrystalline cellulose. Studies of solid carbon acid catalysts in several reaction cycles demonstrate high stability of the catalyst systems [142, 146-148]. Yang et al. in [146] showed that catalyst $\text{Fe}_3\text{O}_4@\text{C-SO}_3\text{H}$ exhibits a slight decrease in catalytic activity over 5 reaction cycles.

It should be noted that a non-modified carbon support does not show any significant catalytic activity in polysaccharide depolymerization reactions [31, 32, 144]. The most widespread method to increase the acidity of the carbon materials is a treatment by sulfuric acid; it allows to fix sulfo groups onto the carbon surface [32, 90, 139, 140, 149-153]. Moreover, a treatment with solutions of HNO_3 [32, 145], H_2O_2 [31, 145], oxidation by air [145], wet air [154], NaOCl [154] is also possible as well as a combination of different activation methods. Thus, the authors of [32, 145] used the nitric acid for the surface oxidation and formation of acid groups on it. The carbon catalysts sequentially treated with nitric and sulfuric acids were also tested. In [31] activated carbon was modified by sulfuric acid and H_2O_2 , as well as both methods simultaneously. The authors have revealed that oxidation by H_2O_2 increases acid sites content (phenol, lacto and carboxyl sites) in 6 times. However, increasing the catalyst activity was negligible, a glucose yield was only 2 % with a low selectivity of 8% (150 °C, 24 hours). The additional sulfonation of the carbon by H_2SO_4 increased the glucose yield in 5 times with growth of selectivity to 26%. Similar results were obtained by using the catalysts sulfonated at 100 and 200 °C.

The conditions (temperature, contact time and agent concentration) of carbon treatment by sulfuric acid and/or by oxidants make a significant influence on catalysts properties. For example, increasing sulfonation temperature rise up a content of sulfo groups on a surface and, as a result, a catalyst activity. However, at higher temperatures the destruction of activated carbons takes place due to deep oxidation processes [32]. Insufficient mechanical strength and stability of activated carbons are an impediment to their practical use in processes of cellulose hydrothermal hydrolysis. At the same

time, treated by sulfuric acid or any oxidants carbon material is sufficiently stable under prolonged hydrothermal treatment [145]. Sulfonated carbon materials may exhibit a sufficiently high stability towards leaching of the active ingredient – sulfo groups – from the surface. Van Pelt et al. in [145] held a comparative study of the stability of the activated carbons treated by various oxidants to leaching of acid groups from surface after hydrothermal processing. Carbon materials treated with sulfuric acid, showed greater stability than the samples oxidized by other oxidants - nitric acid, hydrochloric acid and hydrogen peroxide. In [140] the amount of sulfur was determined in the reaction media after the reaction. It was less than 0.03 L mmol^{-1} , that corresponded to a slight leaching of $-\text{SO}_3\text{H}$ to reaction mixture (less than 0.7% of the initial sulfur content in the catalyst). However at longer times of treatment a degree of sulfur leaching could be significantly higher. In [145] the stability of a sulfonated activated carbon was studied under hydrothermal conditions at $200 \text{ }^\circ\text{C}$ during 24 hours. XRF analysis for sulfur content and the titration by alkali of the catalysts before and after hydrothermal treatment have shown decreasing of sulfur content (and reducing of sulfo groups, consequently) in the catalysts in 38% and total acidic groups in 47%. Analogous studies conducted for carbon samples treated by nitric acid, hydrogen peroxide and oxygen also exhibited a decrease of total acid groups containing.

The presence of $-\text{SO}_3\text{H}$ groups on surface let us to conclude two possible types of hydrolysis mechanisms. The first one is mediated catalysis by H^+ ions generated in solution via $-\text{SO}_3\text{H}$ dissociation. According to this mechanism, the surface of carbon does not affect the processes occurring, and it plays only the role of acid support which facilitates separation of the catalytic sites from the reaction medium after the end of the process. The second mechanism supposes involving of a catalyst surface into a process or a reaction occurring onto catalyst surface. Conducted in recent years studies aimed at identifying the impact of the surface on the catalytic conversion of cellulose, indicate a heterogeneous mechanism at least at the stage of hydrolysis of water-soluble oligosaccharides [31, 139, 143, 147, 155, 156].

The first assumption about heterogeneous mechanism of hydrolysis was made by Suganuma et al. [139]. Carbon materials treated by strong acids contain at their surface functional groups with a different strength. It makes necessary determining the role of these groups during the depolymerization of polysaccharides. Onda et al. [90, 140] were also among the first groups who made an assumption about the influence of the catalyst morphology on the degree of conversion of cellulose. They suppose that catalysts with high surface area and sufficiently large pore size (meso- and macropores) are needed for an efficient cellulose transformation.

The authors of [139, 152] conducted a study to investigate the role of acid groups with different natures: $-\text{SO}_3\text{H}$, $-\text{COOH}$, $-\text{OH}$ during the hydrolysis of cellulose. $-\text{OH}$ group was found to play a significant role in the adsorption of soluble oligosaccharides via hydrogen bonding like $-\text{OH} \cdot \text{O}-$

between hydroxyl group on a carbon surface and oxygen β -1,4-glycosidic bond in a saccharide. It is apparently that hydrolysis is carried out on the catalyst surface at Bronsted acid sites type $-\text{SO}_3\text{H}$ and $-\text{COOH}$. The authors suggested a mechanism of cellulose hydrolysis in the presence of carbon catalysts which involve depolymerization of cellulose to soluble oligosaccharides via mediated mechanism, adsorption of these sugars on the carbon catalyst surface and hydrolysis to glucose oligomers in the surface layer of the catalyst. On the other hand, there is opinion that oligo- and monosaccharides adsorption on carbon surface can be provided by Van-der-Waals interactions which occur on hydrophobic surface regions, and hydrophilic groups such as hydroxyl, are not involved in the adsorption process [31, 157]. In favor of the heterogeneous mechanism of cellulose hydrolysis reaction occurrence may indicate the difference of the process activation energy for the soluble H_2SO_4 and solid carbon catalysts having the same nature of the catalytically active proton, occurs when $-\text{S}-\text{O}-\text{H}$ bond dissociates. The activation energy E_a observed for cellulose conversion in the presence of $\text{C}-\text{SO}_3\text{H}$ is 110 kJ mol^{-1} [139], and in the presence of sulfuric acid - $170-180 \text{ kJ mol}^{-1}$ [158]. Suganuma et al. made an assumption that a smaller activation energy was explained by higher concentration of acids in a surface layer of the catalyst due to smaller amount of water around the hydrophobic carbon surface. This uniform distribution of acidity near the carbon surface and in the solution may indirectly indicate that the cleavage reaction of 1,4- β -glycosidic linkage occurs only on the surface of solid carbonaceous catalyst [139].

Shen et al. have demonstrated a positive influence of chloride ions on the cellulose depolymerization [143, 155]. They conducted a comparative study of pyrolytic carbon activity in the absence and the presence of salts NaCl , KCl , KNO_3 at 160°C and 6 h reaction time. In the absence of additives the yield of reducing sugars were 39%. An addition of NaCl and KCl increased sugar yield up to 55% and an addition of potassium nitrate slightly increased sugars yields. A weak influence of alkali metal cations could be explained by an exchange of H^+ ions by Na^+ (K^+) in SO_3^- groups what increases the reaction medium acidity and product yields. This effect was presented very well in the hydrolysis of cellobiose on Nafion[®]-50 as a catalyst, when in the presence of 10 g L^{-1} NaCl glucose yields were increased by the factor of 2.5 from 15% to 45% [159]. On the other hand, it is known that well solubility of cellulose in ionic liquids is explained by disappearing the hydrogen bonds $-\text{O}\cdots\text{H}-\text{O}-$ in the cellulose structure by interaction of the $-\text{O}-\text{H}$ groups with halide anions (Cl^- or Br^-) which are strong electron acceptors. Ions Cl^- have the greatest effect [160]. Thus, the development of a carbon catalyst bearing both strong acid and Cl^- groups may be promising for the processing of cellulose. Shen et al. have obtained the carbon materials by co-pyrolysis of both PVC and starch or starch alone. The amount of acid groups in the catalysts was the same - 0.8 mmol g^{-1} . However, the first sample containing $\text{C}-\text{Cl}-$ structures was in 2 times more active in comparison with the sample obtained from starch only. The yields of reducing sugars were 95 and 40%, respectively [155]. Influence of chloride

ions on the destruction of the hydrogen bonds $-O \cdots H-O-$ has been proved by experiments on cellobiose hydrolysis, which has no hydrogen bonding, wherein both catalyst showed similar activity. It is interesting that chlorides fixed to the surface (according to FT-IR spectrometry) have influenced on hydrolysis, indicating its implementation on or near the surface of carbon material.

To facilitate the removal of a carbon catalyst from the reaction mixture containing saccharides and their dehydration products as well as unreacted solid particles of cellulose, catalysts are developed, which contain a magnetic Fe_3O_4 core covered by sulfonated carbonaceous material. In the articles of Yang et al. [146] such catalyst was able to catalyze the hydrolysis of cellulose with a glucose yield of about 50%. Pure Fe_3O_4 is catalytically inactive. Guo et al. [161] proposed to use a composite material carbon/ Fe_3O_4 instead of the core-shell system but they didn't perform testing in aqueous solutions. The research made in the ionic liquid (1-butyl-3-methylimidazolium chloride [BMIM] Cl) showed that the activity of such system significantly exceeded one of the other solid catalysts such as sulfonated carbon and polymer: Amberlist[®]-15 and Nafion[®] NR-50. However, the composite showed low stability. Falling of the catalyst activity when tested in three reaction cycles was about 30% and it was explained by the destruction of the poorly bounded composite material.

Carbon catalysts may be used in a combination with other catalytic systems. Thus, using a carbon catalyst in a combination with hydrochloric or sulfuric acid produces glucose with yields up to 35% [162]. With adding carbon catalyst in cellulose mechanical activation step the yields of desired products increase significantly. Thus, the system in the presence of carbon-sulfuric acid and carbon-hydrochloric acid glucose yield was 69 and 88% while the conversion of the substrate was 95 and 98%, respectively.

Highly dispersed metal particles supported on carbon supports may also be catalysts of polysaccharide hydrolysis. Such catalytic activity of nano-dispersed metals has been discovered in the group headed by Professor Atsushi Fukuoka from the Institute of Catalysis at Hokkaido (Hokkaido University, Japan) [156]. In [163] a comparative study of the activity of highly dispersed metal particles of Ru, Pt, Pd deposited on carbon support was carried out. The study was conducted in an inert atmosphere at 230 °C. The greatest activity was shown by Ru-containing catalysts. The yield of glucose by using a metal-containing catalyst exceeds glucose yield in the presence of pure carbon (34 and 20%, respectively). The authors also found that the yields of the hydrolysis products (glucose and soluble oligosaccharides) increase with the growth of Ru content. For the catalysts containing 0, 2, 5 and 10% ruthenium glucose yields reach 16, 20, 25 and 31%, respectively. The high stability of the Ru/C was shown in 5 reaction cycles [164, 165]. Importantly, in the absence of any catalyst glucose yield was only 4%, what proved catalytic action of Ru/C and not of hot water [80]. Fukuoka's group suggested an explanation for the catalytic activity observed with nano-dispersed metals. Metal nanoparticles generate on the surface the in-situ formation of H^+ and/or OH^- via dissociation of either

hydrogen (in experiments on hydrolysis-hydrogenation of cellulose) or water [156, 166]. The protons and hydroxide ions formed on metal particles are stabilized on the surface of carbon support. Further the adsorption of water-soluble oligomers on carbon support and/or metal particles of catalyst takes place. Then the hydrolysis of 1,4- β - glycosidic bond by protons and hydroxide ions occurs to form glucose according to mechanisms known for acidic or basic hydrolysis of saccharides (see

Scheme 6 in **Section 1.3.4**). In an inert medium glucose is desorbed from the catalyst surface, and in a hydrogen medium it is reduced on metal active sites [156].

The high activity in the hydrolysis of cellulose has been demonstrated by polystyrene resins. Thus, using of a polystyrene resin containing -Cl and -SO₃H groups on the surface makes it possible to obtain glucose from cellulose with the yield of 95% after 10 hours of the reaction under very mild conditions at 120 °C [167]. Testing the catalyst in several reaction cycles showed reproducibility of its catalytic activity. Polymeric ion exchange resin Amberlist[®]-15 representing a phenylsulfo acid based on polyvinyl(styrene) is a catalyst for a large number of organic synthesis processes including hydrolysis [168]. However, an information about Amberlist activity in the cellulose hydrolysis reaction is mutually contradictory. Thus, the authors of [140] observed a significant activity of this catalyst, but in [169] the activity was negligible. Lower glucose yield in the second case may be explained by the lower hydrolysis temperature (130 vs. 150 °C, respectively) and 2 times less contact time.

Hydrolysis of cellulose over zeolite catalysts and transition metal oxides

Oxide catalysts (oxides of aluminum, silicon, niobium, and others) and zeolites with different composition and structure may also be of interest to produce valuable products from cellulose due to the high acid properties.

Zeolites are widely used as catalysts in oil cracking process and they could also be used in a number of organic synthesis processes [141]. The number of Bronsted acid sites in zeolites is determined by Si/Al ratio, the smaller the ratio, the higher acidity. By varying the ratio at the preparation stage of the zeolite catalysts it may be synthesized with a predetermined acidity [141]. However, in the hydrolysis of cellulose to glucose reaction zeolites did not show very high activity. Onda et al. [90] have studied a number of acid catalysts. They have come to the conclusion that the reason of low activity is diffusion difficulties caused by small pore size. It makes impossible to penetrate molecules of the water-soluble oligomers formed from the cellulose within catalyst grains to active centers. However, in [141] it is suggested another explanation for the low activity of zeolites in water. Under the proposed mechanism, the hydrolysis of polysaccharides on the zeolite takes place by heterogeneous way, suggesting that the dissolved oligomers enter the pores of the catalyst, where the surface layer of water interact with adsorbed oligomers. Thus zeolite catalyst does not promote the

dissolution of the cellulose to oligosaccharides. Using ionic liquids being capable of dissolving cellulose in place of water makes zeolite catalysts much more effective [141, 170].

Note, the author of the study who used zeolites as catalysts for the depolymerization of cellulose in water, focused on the study of formation of glucose. However, the authors [171] explored the possibility of a direct one-pot conversion of cellulose into a valuable product 5-HMF. Bimodal zeolite H-Z-5 with a ratio Si / Al equal to 30.15 obtained by treating the structure of the zeolite H-ZSM-5 (the ratio of Si / Al = 37.00) with sodium hydroxide yielded the desired product in a yield of 49% of microcrystalline cellulose at 190 ° C. Besides, there was the formation of a sufficiently large amount of levulinic acid which is a product of 5-HMF hydration. The resulting bimodal zeolite catalyst turned out to be stable for four reaction cycles. Presented in this work the catalyst H-Z-5 preparation of 5-HMF from cellulose is the most promising of the suggested zeolite catalysts.

Along with zeolites hydrolysis-dehydration can be used and silicate MCM-41 type structure representing mesoporous materials with a large specific surface area and mesopores. However, MCM-41 has a very low acidity, so [172] it was modified by introducing titanium and sulfonated with sulfuric acid. In the static reactor, the authors were able to receive the 5-HMF from cellulose yields 2.0-7.5% at a temperature of 190-230 ° C.

Oxides of some metals are promising catalysts of hydrolysis-dehydration due to high mechanical and thermal stability [111]. Most often tested catalysts based on oxides of silicon (IV), zirconium (IV), niobium (V), titanium (IV) and tungsten (VI).

Niobium oxide is a promising catalyst for a number of processes of the hydrolysis [173] and dehydration [141] due to the high content of acid sites on the surface. Catalysts based on niobium oxide (Nb_2O_5), tantalum (Ta_2O_5) and zirconia (ZrO_2) have been very effective in the process of hydrolysis of soluble polysaccharides, as well as dehydration of fructose and glucose into 5-HMF [174-177].

However, the number of studies aimed at the study of the catalytic activity of oxide systems in the hydrolysis-dehydration of cellulose, is insignificant [178]. As in the case of catalysts with carbon, most of the work is devoted to the hydrolysis of cellulose to glucose. The possibility of obtaining 5-HMF either not mentioned or indicated 5-HMF as a byproduct of the reaction with low yield.

Nb-containing catalysts were studied in the hydrolysis-dehydration cellulose [179]. However, Nb-W mixed oxide showed low activity in the test process, the overall yield of cellobiose and glucose - 8.5%. Hydromolibdat of niobium NbHMoO_6 also showed little activity in the depolymerization of cellulose [169]. High catalytic activity in the hydrolysis of cellulose-dehydration oxides show such as the ZrO_2 , TiO_2 , Al_2O_3 [90, 148, 180, 181]. Oxides ZrO_2 and Al_2O_3 demonstrate activity close to idle experiment in pure water [90]. Low activity was attributed by the authors either to insufficient pore size of catalysts either to insufficient force acidic groups or to their low concentration. As in the case

of zeolites oxide catalyst activity and reaction yields of the target products during the hydrolysis rise in ionic liquids [141].

The activity of SiO_2 in the process of hydrolysis-dehydration of cellulose gives conflicting data. Thus a comparative study of the activity of oxides SiO_2 , ZrO_2 , TiO_2 , Al_2O_3 , and zeolite structure H-ZSM-5 (Si / Al ratio = 28 and 35) in the reaction of depolymerization of cellulose in water showed that the silica has an activity several times surpassing all other activity catalysts. The presence of SiO_2 glucose yield was 50% at 73% substrate conversion and the total yield of byproducts, including furan derivatives, 14.6% in the presence of other catalysts; yields of glucose and by-products do not exceed 9%, and the conversion was not higher than 17%. The authors explain the high activity of the catalyst as compared with other catalysts significantly higher content of acid groups on the surface acid sites of greater strength and a sufficiently large pore size. On the other hand, the study [148] showed that pure silica does not show activity in the hydrolysis-dehydration of cellulose, which in this case can be explained by the extremely low acidity of catalyst.

In work [176] was investigated activity of mixed oxide $\text{TiO}_2\text{-ZrO}_2$ and separate oxides ZrO_2 and TiO_2 in the hydrolysis-dehydration of cellulose plant biomass samples and 5-HMF. The highest yields of 5-HMF from cellulose were obtained in the presence of catalysts $\text{TiO}_2\text{-ZrO}_2$ and TiO_2 (14 and 13%, respectively). However, monoxide TiO_2 was more active compared to mixed $\text{TiO}_2\text{-ZrO}_2$, as the 13% yield of 5-HMF content was achieved with the acid groups on the catalyst surface is less than 5 times compared to the $\text{TiO}_2\text{-ZrO}_2$. Similar ratios for the activities of $\text{TiO}_2\text{-ZrO}_2$ and TiO_2 catalysts were obtained by hydrolysis-dehydration corn cobs. The highest yields of 5-HMF (cellulose conversion product) and furfural (hydrolysis-dehydration xylan) were 8.6 and 10.3%.

The low content of acidic groups on the surface of oxide catalysts compared to, for example, with the sulfonated coals (according to [32, 181-183] for oxide systems $0.1\text{-}1 \text{ mmol} \cdot \text{g}^{-1}$, and for the sulfonated coals $1.5\text{-}3.5 \text{ mmol} \cdot \text{g}^{-1}$) makes it necessary to promotion of acid catalysts. By analogy with the sulfonated coals can be assumed that the treatment with sulfuric acid of transition metal oxides can also enhance the catalytic activity of the materials in comparison with untreated oxides. Most often investigated sulfated system $\text{SO}_4^{2-}/\text{Al}_2\text{O}_3$, $\text{SO}_4^{2-}/\text{TiO}_2$, $\text{SO}_4^{2-}/\text{ZrO}_2$, $\text{SO}_4^{2-}/\text{SnO}_2$ and $\text{SO}_4^{2-}/\text{V}_2\text{O}_5$ [111].

The work of Onda et al. in the presence of sulphated zirconium oxide (IV) was able to receive the glucose yield 14.2%, which is 3.5 times less than in the presence of sulfonated carbon. At the same time the total yield of reducing sugars for $\text{ZrO}_2\text{-SO}_3\text{H}$ are only slightly lower than in the experience with coal, which indicates the low selectivity of the developed sulfated oxide catalyst. Yield 24% of glucose may be achieved by using as catalyst sulfated silica(IV), coated on the ferromagnetic particles Fe_3O_4 [184].

Study of cellulose conversion to 5-HMF in the presence of TiO_2 , ZrO_2 and samples of sulfated ZrO_2 , zirconium oxide obtained by treatment with sulfuric acid at 70°C [181], showed that the preparation conditions (the chemical nature of the precursor, the processing temperature) significantly affect the properties of the resulting catalysts. Thus, the use of nitrate as a precursors of zirconium and titanium instead of corresponding chlorides, and calcining the precursor at lower temperatures allows to obtain oxides with a large surface area and consequently with a high content of acid groups on the surface, thereby enhancing their activity in reactions depolymerized polysaccharide materials. Promotion of ZrO_2 by sulfuric acid allows to increase the catalyst activity. The greatest activity was observed in the presence of ZrO_2 , containing 1.8 wt.% of sulfur. However, the activity of this catalyst is slightly inferior to the activity of the untreated titanium oxide, in the presence of which the authors were able to achieve a 12% yield of 5-HMF from cellulose at 250°C . Promotion by sulfuric acid ZrO_2 - SiO_2 mixed oxide catalysts with different ratios of oxide forms obtained by simultaneous hydrolysis of the precursor that increased activity to hydrolyze cellobiose by 4-5 times, allowing glucose to be obtained with a yield of up to 50% [185]. Sulfation of SiO_2 in the work [148] significantly increased the activity of the catalyst, thus yielding glucose from cellulose with a 50% yield.

As the additive promoter may be not only mineral sulfuric acid but also organic sulfonic acid [182]. Supported on SiO_2 7.5 and 15% arensulfonic and 15% propilsulfonic acid catalyzed hydrolysis of cellobiose to glucose, providing deep conversion (over 80%) for half an hour of the reaction [182]. Carboxylic acid supported on an oxide carrier not show activity comparable with sulfonic acids [182].

To facilitate the removal of the oxide catalyst from the reaction mixture containing solid particles of unreacted cellulose, catalysts based on magnetic particles Fe_3O_4 were developed. The first time such catalyst systems representing core coated with a magnetic shell sulfated oxide, $\text{Fe}_3\text{O}_4 @ \text{SiO}_2\text{-SO}_3\text{H}$, were used to hydrolyze cellulose. Lai et al. [148] and showed high catalytic activity in the hydrolysis of cellulose and cellobiose at 150°C . glucose yields were 96 and 50% of di- and polysaccharide, respectively. Effective use of such catalysts dropped twice when using microcrystalline cellulose (glucose yield 28%). At long times for processing cellulose for 12 hours block product of cellulose hydrolysis-dehydration became levulinic acid, which yield was 42% [148]. Takagaki et al. [186] developed easily separated from the unreacted cellulose the oxide catalyst structure of - a core-shell - $\text{CoFe}_2\text{O}_4 @ \text{SiO}_2\text{-SO}_3\text{H}$. This catalyst system was active in the hydrolysis of the disaccharides maltose and cellobiose, making it possible to obtain glucose yields to 80-90%. However, the activity of the catalyst in the hydrolysis of cellulose polysaccharide was very low and comparable with the activity of the catalyst Amberlyst 15 [169, 186].

A significant drawback of sulfated catalysts washability of active ingredient is proven. So, testing the catalysts SiO_2 and ZrO_2 in a few cycles of the reaction showed a slight decrease in their activity [180, 181], while the activity of the sulfated ZrO_2 samples gradually decreases from cycle to

cycle [181]. Sulfonic groups washed from the catalyst, not only during the reaction, but even at hydrothermal tests. For example, in [185] hydrothermal test on sulfated ZrO_2-SiO_2 at 160 ° C leads to almost complete (90%) of acid leaching of the active groups 30 minutes. Within one hour sulfo washed away completely.

Analogously in studies on nanosized metals supported on carbon supports, the activity in the hydrolysis of the polysaccharide and of Ru and Pt nanoparticles, deposited on oxide supports of various nature and zeolites (HZSM-5, HUSY, HY, H β , SiO_2 , ZrO_2 , Al_2O_3) were investigated in [187]. Developed catalysts showed sufficiently high activity in the hydrolysis-reduction of cellulose, giving yields of up to 30% of polyols. However, there is very low activity in the hydrolysis of carriers this has led the authors to conclude that the high yields of polyols can not be achieved only in hydrolytic activity of carriers, and metal deposition also contributes [187]. The mechanism of the hydrolysis of polysaccharides on metal catalysts proposed by Fukuoka et al. in [156], is discussed in **Section 1.3.3**.

Catalysis by micellar and nanocatalysts

Considering hydrolysis-dehydration of cellulose in water in the presence of solid catalysts should be noted that this process has severe diffusion limitations caused by the fact that both the substrate and the catalyst are solid [156]. However, the availability of active catalyst sites can be increased by using finely divided catalyst stabilized by the surfactant micelle structures [137]. An attempt to create on the basis of the HPA catalyst was made by Cheng et al.[137]; they have elaborated micellar catalyst HPA $H_3PW_{12}O_{40}$, stabilizing surfactant being hexadecyltrimethylammonium bromide $[C_{16}H_{33}N(CH_3)_3]Br$. The resulting micellar catalyst $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ was tested in the cellulose hydrolysis reaction at 170 ° C. Maximum glucose yield was 39.3% (89.1% selectivity of formation) after 8 hours of reaction, which is 1.5 times higher than in the presence of a solid catalyst $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, but 39% less than in the solution $H_3PW_{12}O_{40}$. TOF values for the catalysts changed in the following order: $H_3PW_{12}O_{40} > [C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40} > Cs_{2.5}H_{0.5}PW_{12}O_{40}$; and relate as a: $3.6 > 1.3 > 1$. Catalyst $[C_{16}H_{33}N(CH_3)_3]H_2PW_{12}O_{40}$ was tested in 5 reaction cycles, and showed sufficient high stability [137].

It is known that hydrolysis-dehydration reactions may not only catalyze the Bronsted acid centers, but also the Lewis type acid centers, which can significantly increase the selectivity and yields of sugars and formation of 5-HMF from cellulose by suppressing the degradation products of reactions [1, 4]. However, the activity of Lewis acid sites (electron acceptors) is observed only in the dry (anhydrous) media such as ionic liquids [188], as it happens in the water hydration of such centers advent type Bronsted acidity. However, ionic liquids are expensive, so holding them hydrolysis-dehydration quite expensive [1, 188]. Zhao et al. in the work [189] experienced heterogeneous (but not solid) micellar system $Cr[(DS)H_2PW_{12}O_{40}]_3$ where DS named sodium dodecyl sulfate is a surfactant.

In this type of catalyst a Lewis acid centers Cr^{3+} stabilized within particles of an organic surfactant, externally associated with P-W HPA. The catalyst test at 150°C for 2 hours allowed to obtain 5-HMF in 53% yield in the «one-pot» hydrolysis-dehydration of cellulose in water, which is 1.6 times higher than the yield of 5-HMF in the presence of $\text{Cr}(\text{H}_2\text{PW}_{12}\text{O}_{40})_3$ without surfactant, and 5-10 times higher than in the presence of CrCl_3 and $\text{Cr}([\text{DS}])_3$. A solution of HPA $\text{H}_3\text{PW}_{12}\text{O}_{40}$ is inactive with respect to the formation of 5-HMF [188].

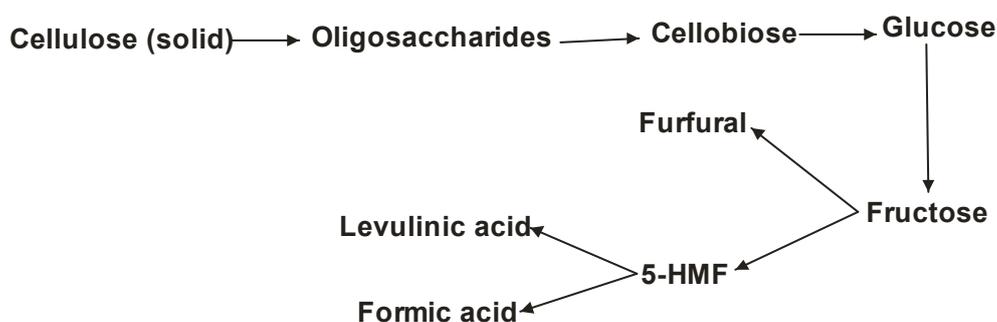
Along with micellar catalytic systems nanosized colloidal catalysts can also be used for polysaccharide hydrolysis-dehydrating materials. Unlike systems with massive solid catalysts wherein oligomeric sugars are adsorbed on the catalyst surface in the case of nanoscale catalysts catalytic center adsorbed on the surface of the solid cellulose catalysing the cleavage of glycosidic linkages. Analogously solid catalysts, nanoscale particles can be modified with fixing active catalytic sites on their surface: metal complexes, enzymes or organic acid structures [141]. An example of such catalysts is given in [190], wherein investigated the possibility of the depolymerization of cellulose in the presence of nanoparticulate hydrotalcite activated by $\text{Ca}(\text{OH})_2$. In the presence of such a catalyst was obtained with a yield of glucose is 46.6% selectivity of its formation at 85.3%.

Thus, micellar, and nanosized catalysts are a new direction of research in the field of processing a raw polysaccharide securities chemicals. Although number of papers demonstrated the stability of such catalyst systems, one can expect that the nanostructure agglomeration and adsorption of the reactor walls or on the particles of unreacted cellulose can be a serious obstacle to the development and use of this method.

1.3.4 Overview of cellulose hydrolysis-dehydration mechanisms

The conversion of cellulose in the hydrolysis-dehydration process is a complex multistage process. It passes through the formation of a large number of intermediates and comprises a large number of stages [128]. In the study of such a complex chemical system it becomes a very important to identify the process mechanism concept, the determination of reaction routes, identification of intermediates, detection limited steps, and in the case of solid catalysts and catalytic mechanism of action (homogeneous or heterogeneous).

Schematic diagram of the conversion of cellulose to glucose and 5-HMF during the hydrolysis-dehydration process includes the number of steps [191, 192]. Firstly, the hydrolysis of cellulose occurs with the formation of oligosaccharides; secondly, there is the hydrolysis of the oligosaccharides to glucose; thirdly, the isomerization of glucose into fructose is happening; fourth, the dehydration of fructose to form 5-HMF or furfural is proposed. Finally, in the presence of the same acid catalysts can be 5-HMF hydration to form levulinic and formic acids (Scheme 4).



Scheme 4. Schematic diagram of the conversion of cellulose to glucose and 5-HMF

It should be noted that the vast majority of works devoted to the development of new catalysts and processes to convert cellulose in valuable chemicals do not study the kinetics (reaction order and rate constant) and do not offer any mechanisms or processes schemes. The authors having conducted kinetic studies usually describe the reaction routes of the conversion of a substrate and desired products. It should be emphasized that the complexity of the process of hydrolysis-dehydration causes authors to make serious simplification of process scheme during the kinetic description and definition of kinetic parameters.

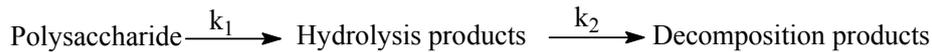
To describe the kinetics of obtaining glucose and/or 5-HMF from cellulose four simple kinetic model are mainly used (Figure 10). They allow to carry out a simple simulation and mathematical description of the process, and to calculate the kinetic parameters of the depolymerization of cellulose (activation energy, kinetic constants steps) [193]. The simplest kinetic scheme often used in the literature to describe the observed transitions includes a two-stages: conversion of cellulose to the desired product in the first step and the decomposition of the target product is smaller organic compounds in the second stage (Scheme 5, Model 1) [116, 117, 126, 129, 193-195]. This model, known as Saeman's model [127, 196] was proposed in 1945 [112]. As applied to cellulose, the kinetic equations are as follows:

$$\frac{d\text{Cell}(t)}{dt} = -k_1 \cdot \text{Cell}(t) \quad (\text{Eq. 5})$$

$$\frac{d\text{Glu}(t)}{dt} = k_1 \cdot \text{Cell}(t) - k_2 \cdot \text{Glu}(t) \quad (\text{Eq. 6})$$

where Cell(t) and Glu(t) are the current concentrations of substances [112].

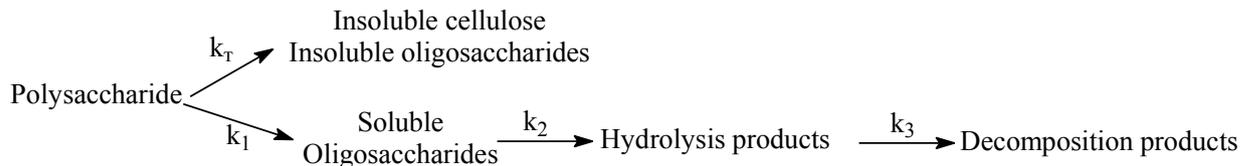
Model 1 (Saeman's Model)



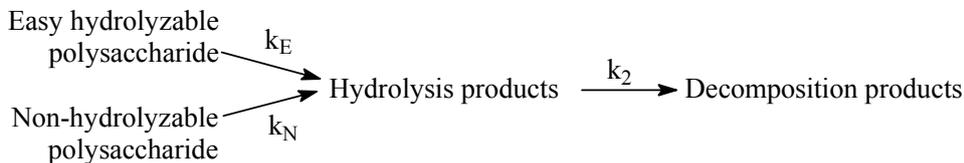
Model 2A



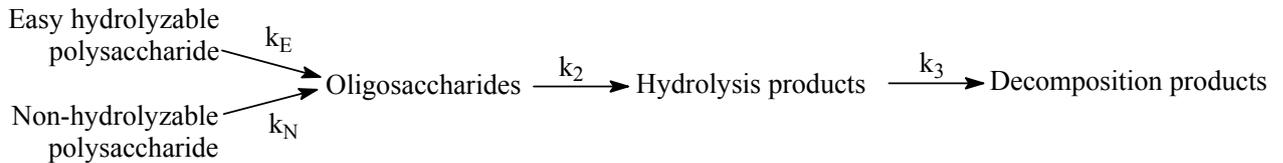
Model 2B



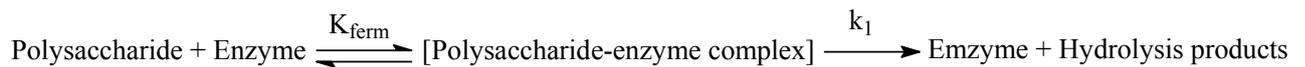
Model 3A



Model 3B



Model 4 (Enzymatic catalysis - Michaelis-Menten Model)



Scheme 5. Proposed models for kinetic modeling of polysaccharide hydrolysis

It should be noted that, while the solids in the kinetic equations of the processes occurring in the liquid phase, is not correct [13, 81]. However, water-insoluble cellulose polysaccharide typically is exception based on a complex mechanism of the first stage of its hydrolysis. On the one hand, the physical transition occurs from a solid substance into a liquid phase (i.e., dissolve). On the other hand, the cellulose dissolution is impossible without destroying the chemical, including covalent bonds (1,4-β-glycosidic linkages in the polymer chains and between) catalyzed H₂O, H⁺ or OH⁻ [81]. Thus, when considering the cellulose hydrolysis-dehydration authors take into account only the "hydrolytic" nature cellulose dissolution, neglecting the physical process of interfacial transition from the solid to the solution.

In a more complex kinetic model represented by the first [197], Abatogly et al. isolated by the steps of dissolving polysaccharide the raw material to form water soluble oligosaccharides and further hydrolysis (Scheme 5, Model 2A) [196-198]. At the third stage, the decomposition of the desired product happened. Authors of the works [129, 199], analyzed residues after acid hydrolysis of cellulose with sulfuric acid, have proposed to describe the transformation of cellulose model version 2 (Scheme 5, Model 2B), assuming cellulose conversion for the reaction by-route into insoluble compounds which are not subjected to further hydrolysis.

The third model takes into account that the structure of cellulose contains well and hard hydrolyzed domains. This model suggests the formation of a desired product or soluble oligosaccharides on the first step (in case of taking into account the cellulose dissolution) via two ways assigned for crystalline and amorphous regions of the polysaccharide, respectively (Scheme 5, Model 3A and 3B) [125, 127, 129, 200].

In drawing up the kinetic models, all the reactions are considered irreversible and first ordered [112, 125]. Kinetic equations written out for these models allow finding reaction rate constants, observed activation energies and pre-exponential factors of kinetic constants to be easy enough. The kinetic model could be further modified to more accurately describe the observed kinetic curves. In particular, reversibility may be administered at some stages [123, 197], as well as side reactions of decomposition of intermediates could be included [201]. Zhang et al. conducted a simulation of 5-HMF formation from cellulose via model 1 but included the stage of 5-HMF formation from glucose and 5-HMF decomposition [172]. The kinetic model proposed well described kinetics of 5-HMF formation at different temperatures. Conner et al. proposed a model of cellulose hydrolysis-dehydration based on 3A model, adding two reversible stages conversion of glucose in the disaccharide and anhydrosahara [202]. In work [203] kinetic parameters for the conversion of β -glucan and mannoproteins to 5-HMF were searched. Conversion of polysaccharides included five first order stages. The model used was supplemented with side reactions of destroying polysaccharide, glucose, and 5-HMF.

Enzymatic hydrolysis of polysaccharides, is outside the scope of our study and, is described by the Michaelis-Menten equation, which allows to very accurately predict the kinetic curves of conversion of sugars [204].

More complex kinetic schemes are rarely used, since they require the use of special computer programs. A group of authors under the direction of D.Yu. Murzin conducted modeling transformations hemicellulose - arabinogalactan with a rather complex kinetic model [23], consisting of 13 stages with the first order reaction observed. The kinetic scheme comprised: the formation of target products, furfural and 5-HMF, through the formation of soluble oligosaccharides and their subsequent hydrolysis-dehydration (model 2), but also the scheme takes into account the presence of

several ways of converting the intermediate and final products. To resolve the resulting scheme and determination of the rate constants, the authors used computer software.

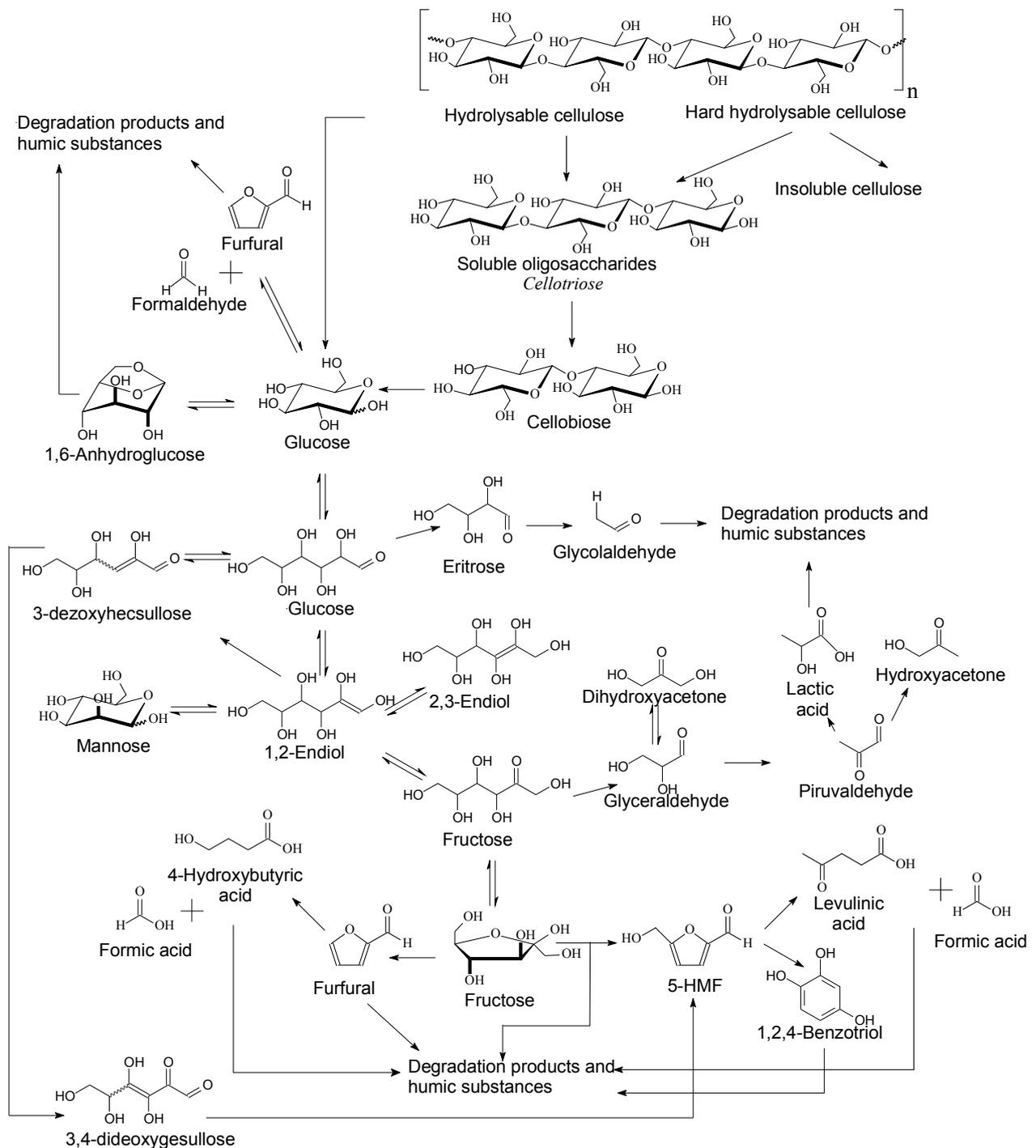


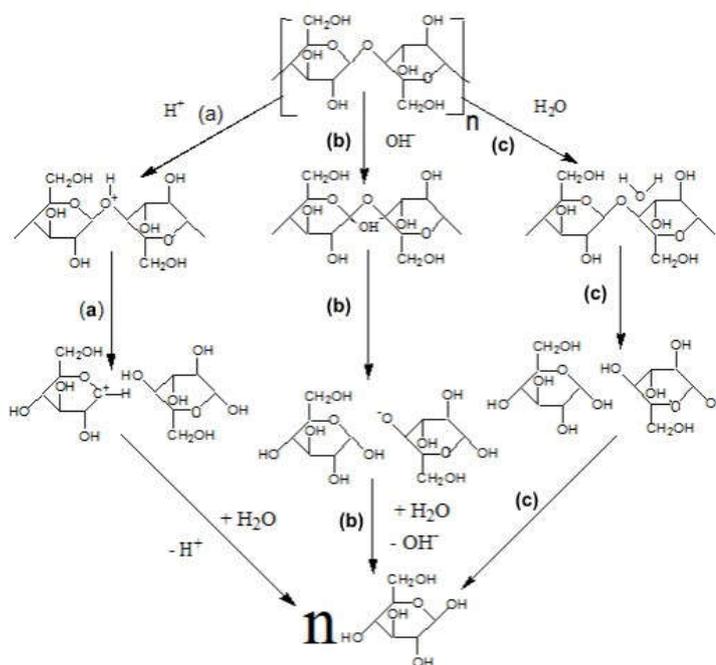
Figure 10. Possible paths of cellulose transformations

Besides the main products of the process, researchers found other intermediates and side connections. Total conversion circuit of cellulose and its intermediates including all found in the literature transformation is given in Figure 10 [100, 103, 104, 129, 191, 192, 205-208]. The product composition can depend on the type of catalyst. Thus, two main channels of fructose conversion are considered: 1) cleavage of fructose to glycerinaldehyde and further its conversion into lactic acid, 2)

sugar dehydration to 5-HMF and its further into levulinic acid. The first channel is the dominant one, under catalysis by bases and alkalis [209], and the second one - under the catalysis of acid solutions [128].

Authors [192] suggest the presence of at least two channels of the glucose conversion: isomerization to fructose and dehydration to 1,6-anhydroglucose and five ways of fructose conversion. Sasaki et al. conducted an extensive search for the depolymerization of cellulose intermediates in sub- and supercritical conditions [191]. Based on the research conducted by authors, a kinetic scheme has been proposed, which includes the possibility of converting glucose to 1,6-anhydroglucose and fructose and glucose erythrose, glyceraldehyde and 5-HMF [191].

Originating in the early stages of cellulose hydrolysis process can be catalyzed by both acids or bases, and water at elevated temperature [80, 81] (Scheme 6).



Scheme 6. Originating in the early stages of cellulose hydrolysis

Hydrolytic cleavage of water-insoluble cellulose to glucose may proceed via two ways. The first one involves dissolving cellulose to form soluble oligomers, which in turn are hydrolyzed in solution to form glucose. Along with this process, and a second route to glucose production may be - direct cleavage of a monosaccharide from a polysaccharide (Figure 11). However, previously it has been shown that the first channel formation of glucose through water-soluble oligosaccharides is dominant, although statistically there is no denying the presence of the second channel [125, 129, 193, 198]

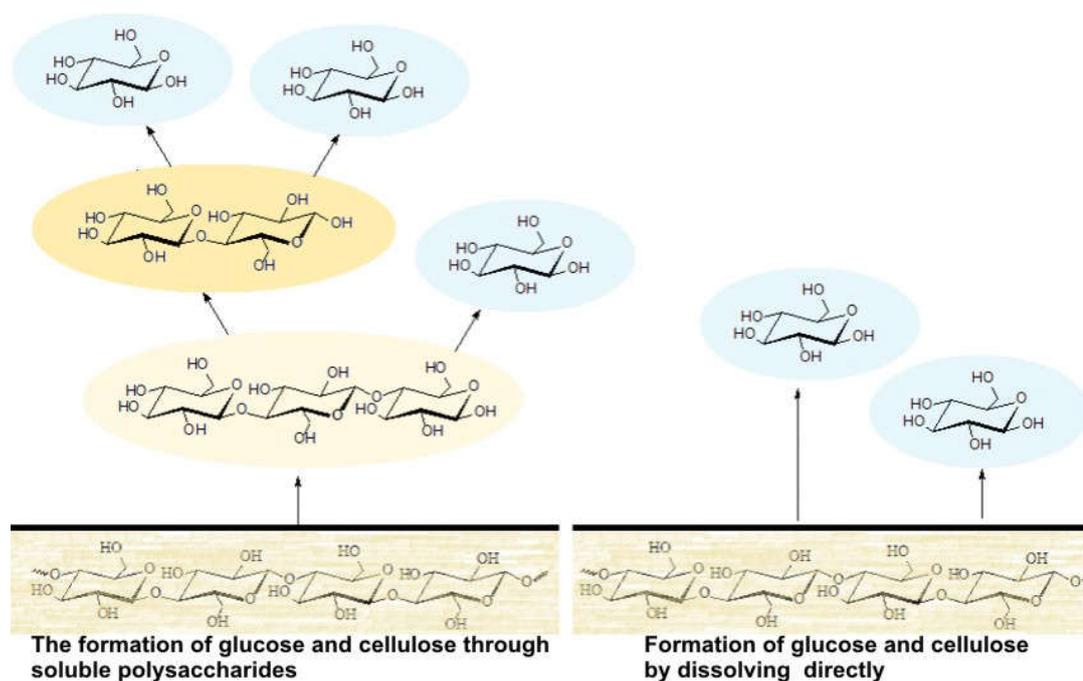
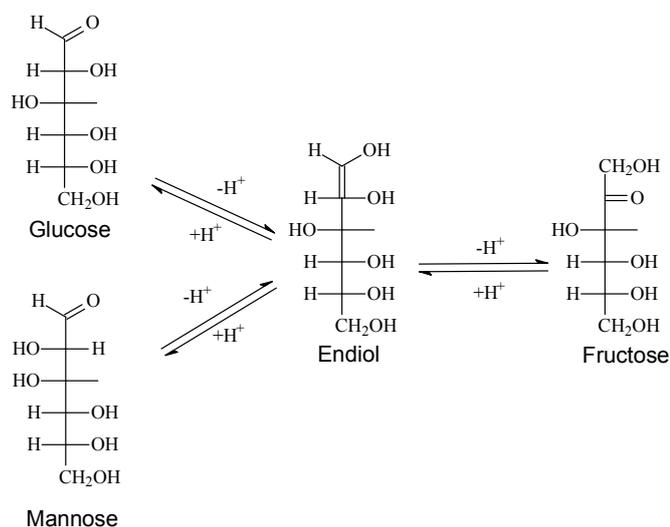


Figure 11. Two main ways of glucose formation from cellulose during polysaccharide solubilization: the first one, via oligosaccharides and, the second one from cellulose directly.

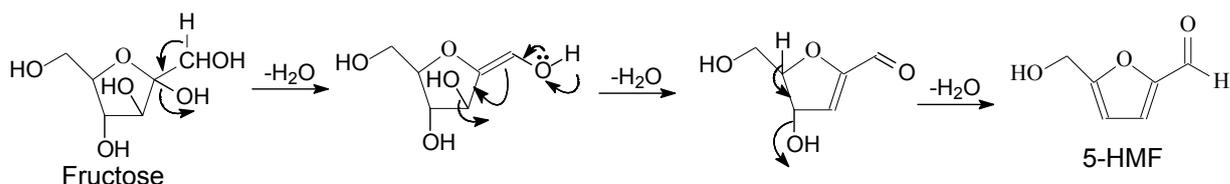
In aqueous media fructose and glucose exist in three different forms: linear, pyranose and furanose [100, 103]. Between all these forms there is a chemical equilibrium (cyclooxoautomeri). At room temperature and standard pressure the equilibrium is strongly shifted towards the cyclic forms. However, determining the equilibrium ratio of tautomeric forms at a high temperature is very difficult, since the equilibrium ratio is extremely sensitive to changes in the reaction conditions [210].

However, products of the further conversion of monosaccharides dependent on the ratio of the tautomeric forms of sugars. It is believed that compounds containing furan rings (5-HMF, furfural) are formed from furanose form of fructose. Similarly 1,6-anhydroglucose, by-product of dehydration, is obtained from pyranose form of glucose. At the same time sugar degradation products formed via breaking C-C bonds (lactic acid formation from fructose, erythrose formation from glucose, etc.), are formed from non-cyclic forms of sugars [100, 191]. It should be noted that this statement is true only for the processes conducted in the absence of catalysts capable to form complexes with the sugars and catalyze retroaldol cleavage [208, 209]. Formation of erythrose is fixed only in the conversion of glucose at high temperatures under near- or supercritical conditions [191]. Under soft conditions the main channel of glucose conversion is isomerization to fructose (Scheme 7) [211].



Scheme 7. Mechanism of glucose isomerisation to fructose

Fructose being formed undergoes further dehydration reactions to form 5-HMF (Scheme 8). Acid catalysts, both soluble and solid, appear to be most effective for this transformation [1].



Scheme 8. Mechanism of fructose dehydration to 5-HMF

Such mechanism of 5-HMF formation from glucose via transforming furanose form of fructose has become common in the second half of the XX century. It was firstly proposed by American chemist Nef in 1910 (see in [104] and [212]), and worded more explicitly in works of the Nobel Prize laureate Walter Norman Heuors [213]. The formation of 5-HMF and other furan compounds (furfural) from ketosugars at low temperatures (80-100 °C) exactly indicated this mechanism [214], in as much as the outputs of furan-based compounds from aldoses at the same conditions are extremely low [214, 215]. Alternative mechanism proposed in the 1930s of 5-HMF formation from sugar through a β -elimination reaction with the elimination of water from the linear form of sugars and formation 3-desoxyxullose and 3,4-dideoxyxullose-3-enes (see [104], Scheme 9) apparently occurs, but it is not the primary channel of transformations [207, 216].

1.4 Literature data conclusions

To conclude, significant increasing in the last 10 years the amount of scientific publications devoted to processing the main biomass components, especially cellulose, demonstrates that the cellulose transformation to valuable chemicals such as glucose, 5-HMF, FA is still a great challenge. By now, a lot of experimental data about cellulose hydrolysis to glucose have been accumulated but the amount of information about one-pot methods of 5-HMF and FA production is still insufficient.

According to literature data, carbon-based and oxide appear to be perspective to carry out hydrolytic transformation of cellulose. However there is no enough information about 5-HMF synthesis starting from cellulose using that promising catalysts. For cellulose hydrolysis-oxidation to be made bifunctional Mo-V-P HPA catalysts seem to be perspective and the information on using those catalysts is also negligible.

In the field of cellulose transformation there are some scientific tasks and solving them could be useful for developing catalytic technologies of cellulose transformation in pure water into valuable chemicals.

1. There is any denotes that systematic investigations on the dependence of an activity of Mo-V-P HPA on their composition and reaction conditions have been previously carried out.

2. The optimal way of carbon modification and the role of different chemical groups on the carbon surface as well as the stability of carbon catalysts under hydrothermal conditions are still unclear.

3. Oxides of Si, Al being unstable under hydrothermal conditions are still used as catalysts for cellulose hydrolysis. It causes a necessity to replace the oxides mentioned and investigations of more stable under hydrothermal conditions oxides, ZrO_2 for example, as a new catalyst of cellulose transformation.

4. To our knowledge, there is no information about kinetic investigations and kinetic modeling cellulose hydrolysis-dehydration using a complicated multistep process scheme.

In this work we made all the efforts to solve the tasks mentioned above.

CHAPTER 2.
EXPERIMENT

2.1 Chemicals and materials

The following chemical substances were used in this work without any preliminary purification.

Inorganic compounds: H_2SO_4 (high purity, Sigma Tek), H_3PO_4 (99.4%, Ekros); NaOH (high purity, Ekros), HNO_3 (high purity, 18-4, Reakhim), isopropoxide of zirconium $\text{Zr}(\text{OiPr})_4$ (70 vol% solution in iPrOH, Acros Organics), hydrate of niobium (V) oxalate $\text{C}_{10}\text{H}_5\text{NbO}_{20}\cdot x\text{H}_2\text{O}$ (Alfa Aesar), V_2O_5 (high purity, Vekton), MoO_3 (high purity), H_2O_2 (high purity 8-4), Na_2CO_3 (high purity), $\text{Co}(\text{CO}_3)_x(\text{OH})_{2-2x}$ (45.6% Co, pure.).

Organic compounds: acetic acid (Acros Organics), formic acid (98%, Panreac), D-glucose (Reahim, Moscow, Russia), D-fructose (Sigma-Aldrich), D-mannose (Sigma-Aldrich), D-cellobiose (Alfa Aesar), 5-hydroxymethylfurfural (Sigma-Aldrich), levulinic acid (Acros Organics), furfural (> 99 %, Sigma-Aldrich).

Solvents: methylisobutylketone (99.3%, Neva Reaktiv), butan-2-ol (99.3%, Reaktiv), iPrOH (Acros Organics).

Gases: air mixture 20% oxygen and 80% nitrogen (GOST 5583-78 and 9293-74), argon (GOST 10157-73).

Microcrystalline cellulose (fraction < 0.10 mm, Vekton, Saint-Petersburg, Russia) was used in all the investigations.

Mesoporous graphite-like carbon material Sibunit[®] (Omsk, Russia) (S_{BET} 379 $\text{m}^2\cdot\text{g}^{-1}$, average pore diameter 7 nm, pore volume 0.2 $\text{sm}^3\cdot\text{g}^{-1}$, micropore volume 0.000 $\text{sm}^3\cdot\text{g}^{-1}$) was used for preparation of all the catalysts.

Milli-Q water (Millipore, France) was used for preparing all the solutions.

2.2 Cellulose mechanical activation

2.2.1 Cellulose activation techniques

Method I. Grinding of cellulose in a ball mill was carried out during 10 h with a set of balls 10-30 mm in size. The grinding conditions: cylinder capacity 1 L, ball loading 330 mL, cellulose loading 330 mL, and rotating velocity 30-60 rpm.

Method II. Cellulose was activated in an Aktivator-4M planetary mill (ZAO Aktivator, Novosibirsk, Russia). The activation conditions: cylinder capacity 1300 mL, cellulose weight 50 g, weight of the balls 200 g, ball diameter 10 mm, acceleration of grinding bodies 75 g, and activation time 10 min [223].

Method III. Mechanical activation of cellulose was carried out in a planetary-type mill «Pulverizette 5» («Fristch», Germany). Activation conditions: drum volume 250 mL, cellulose mill feeding 15 g, ball diameter 20 mm, ball feeding 7 pcs., activation time 40 min.

2.2.2 Cellulose characterization

Humidity of cellulose was determined by the standart method GOST 16932-82. 5 g of cellulose were put into weighing bottle and dried for 4 hours at 103 ± 2 °C until no changes of the mass.

Humidity was recalculated according to the fomula:

$$W = \frac{m_1 - m_2}{m_1 - m} \cdot 100, \quad (1)$$

where m is the mass of empty weighing bottle (g); m_1 is the mass of weighing bottle with cellulose sample before drying (g); m_2 is the mass of weighing bottle with cellulose sample after drying (g).

Dryness coefficient K_{dry} of cellulose was evaluated from:

$$K_{dry} = \frac{100 - W}{100}. \quad (2)$$

Cellulose particle size was determined by optical microscope «Zeiss - Axiostar plus» (Germany) equipped with photcamera. Average diameter of cellulose particles was calculated as average value of diameters of a. 100 particles.

SEM was conducted with a scan electron microscope JSM-6460LV (JEOL, Japan).

XRD analysis of cellulose samples was carried out with BrukerD8 Advamced (Germany) diffractometer with monochromatic $CuK\alpha$ -radiation ($\lambda = 1,5418$ Å). Scanning was made in the 2θ range of 10 to 40°. All the diffraction patterns were distributed into individual peaks (101, 10 $\bar{1}$, 021, 002, 040 and amorphous cellulose) with 2θ values 15.2, 16.8, 20.6, 22.7, 34.1 and 21.5, respectively [224].

Crystallinity index (CI) was evaluated as a relation of the sum of 101, 10 $\bar{1}$, 021, 002, 040 peak squares subtracting the square of amorphous cellulose halo ($2\theta \sim 21.5^\circ$) to the total square of diffraction pattern ($2\theta = 10-40^\circ$) [225]:

$$CI = \frac{(I - I_a)}{I}, \quad (3)$$

where I is the integrated intensity of the crystal and amorphous phases, I_a is the intensity of the amorphous phase.

For amprphous cellulose samples (CI is less 30-50%) CI calculations were made is this way:

$$CI = \frac{(i^{002} - i^a)}{i}, \quad (4)$$

where i^{002} – peak intensity 002, i^a – intensity of amorphous halo.

Size of coherent-scattering region (CSR) was determined by Seliakov-Sherrer formula:

$$D_{hkl} = \frac{k\lambda}{\beta \cos\theta} \quad (5)$$

where $k \approx 1$ - Sherrer constant which depends on the crystal form, λ – X-ray length, β – half-height reflex width, θ – scattering angle.

2.3 Synthesis of heteropolyacid solutions – catalysts of hydrolysis-oxidation process

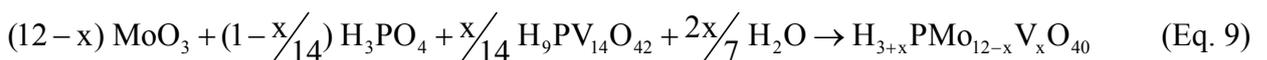
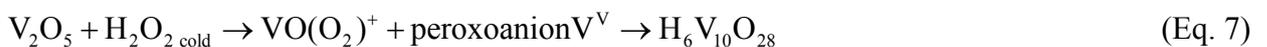
The solutions of HPAs have been prepared in the Department of the catalysts and the processes based on heteropolyacids of BIC.

An aqueous solution of HPA-x with the composition $H_3PMo_{10}V_2O_{40}$ (HPA-2) was obtained from stoichiometric amounts of V_2O_5 , MoO_3 , H_2O_2 and H_3PO_4 in two steps by the known technique [226]. At the first step, V_2O_5 was dissolved in a cold diluted H_2O_2 solution to form dark-red peroxo complexes of vanadium (V). Upon heating to room temperature, the resulting solution gradually decomposed with O_2 evolution to form ~ 0.0125 M of the orange solution of decavanadic acid $H_6V_{10}O_{28}$. The produced $H_6V_{10}O_{28}$ acid was immediately stabilized by adding an excess of H_3PO_4 , which led to the formation of a dark-brown aqueous solution of $H_9PV_{14}O_{42}$ by (Eq. 7) and (Eq. 8).

At the second step (Eq. 9), a freshly prepared aqueous solution of $H_9PV_{14}O_{42}$ was gradually introduced into the boiling suspension of $MoO_3 + H_3PO_4$. MoO_3 slowly dissolved under stirring of the resulting mixture to form a homogeneous HPA-x solution with a specified composition.

Aqueous HPA-x' solutions of composition $H_{11}P_3Mo_{16}V_6O_{76}$ (HPA-6') and $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10') with a high vanadium content were prepared in a similar way, the additional amount of vanadium being stabilized by an excess of H_3PO_4 according to the technique described in [227].

A solution of HPA-2 salt with the composition $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ (Co-HPA-2) was obtained by dissolution of cobalt carbonates in hot solutions of the produced salt.



The composition of freshly prepared solutions was investigated by ^{51}V and ^{31}P NMR spectroscopy on a Bruker AVANCE 400 high-resolution NMR spectrometer using 85% H_3PO_4 and $VOCl_3$ as external standards. According to the acquired data, both the HPA-x [228] and HPA-x' [227, 229] solutions are complex equilibrium mixtures of a close composition. Such solutions contain the

Keggin-type heteropolyanions with different numbers of vanadium atoms, H^+ ions, VO^{2+} cations, phosphoric acid, and possible products of their interaction with each other. Therewith, the number of lines corresponding to different HP anions increases with x (the number of vanadium atoms).

2.4 Synthesis of NbO_x/ZrO_2 oxide catalysts of cellulose hydrolysis-dehydration

2.4.1 Synthesis of NbO_x/ZrO_2

For zirconium oxide to be made, 5 mL of $Zr(O^iPr)_4$ solution (70% solution in iPrOH , Acros Organics) were diluted with 5 mL of iPrOH . The reaction solution was hydrolyzed by water steam and calcinated during 8 hours at 600 °C (heating rate 2.5 °C·min⁻¹).

For supporting niobium oxide, zirconia powder was placed into a thermostated reactor and vacuumized at 50 °C during 15 min. Calculated amount of niobium (V) oxalate was dissolved in a small volume of distilled water and placed into the thermostated reactor containing ZrO_2 . The catalyst was kept in the reactor during 30 min, dried under air for 24 hours, and calcined at 450 °C during 4 hours (heating rate 3.6 °C ·min⁻¹).

2.4.2 Characterization of NbO_x/ZrO_2

Texture characteristics of catalysts and zirconia support were investigated using low-temperature nitrogen absorption at -196 °C on ASAP-2400 device (“Micromeritics”, USA). All the catalysts were vacuumized up to pressure of 6 Torr before the analysis. The specific surface area (S_{BET}) was calculated from the adsorption curve of isotherms by BET method. Pore volume was determined by α_S –method. Pore size distribution was revealed by BJH method.

The content of Nb in the catalysts before and after the experiment as well as in the reaction media was measured by ICP-OES with Optima 4300 DV spectrophotometer (PerkinElmer Inc., USA).

X-ray diffraction analysis (XRD) of the catalysts was made with BrukerD8 Advanced (Germany) diffractometer (step $2\theta = 0,05^\circ$, signal accumulation time 1-3 seconds per point). Monochromatic $CuK\alpha$ -radiation ($\lambda = 1,5418 \text{ \AA}$) was used for recording spectra. Phase analysis was carried out using ICSD data base (2009). Calculation of theoretical XRD patterns and estimation of phase composition was made in PowderCell 2.3 program [230].

UV–vis diffuse reflectance spectra (UV–vis DRS) of the catalysts were recorded at ambient temperature without any pretreatment of the catalysts using UV-2501 PC Shimadzu spectrometer with IRS-250A diffusion reflection attachment in the 11000-54000 cm⁻¹ range using $BaSO_4$ as a reference. The UV-Vis edge energy (E_g) was determined by finding the intercept of the straight line for the low-energy rise of a plot of $[F(R_\infty)h\nu]^2$ versus $h\nu$, where $h\nu$ is the incident photon energy [231].

2.5 Synthesis of catalysts based on Sibunit-4[®] carbon material for cellulose hydrolysis-dehydration

2.5.1 Synthesis of carbon catalysts

Mesoporous graphite-like carbon material Sibunit-4[®] (hereafter Sibunit, Omsk, Russia) was used for the preparation of all the catalysts. Before any treatment the carbon was washed with boiling deionized water and air-dried. After cleaning the carbon was grinded and the fraction of 560-940 μm was used for the following treatments.

Samples of sulfonated carbon catalysts were prepared from pure Sibunit via sulfonation in fuming H_2SO_4 . 1 g of grinded Sibunit and 15 mL of H_2SO_4 were placed into a vessel and heated at an appropriate temperature for 10 hours. After cooling down the catalyst was decanted from the reaction mixture, washed with boiling water until constant pH of the wastewater and air-dried.

Oxidized samples were prepared by treating with HNO_3 solution and with wet air mixture [232].

The samples oxidized with HNO_3 were prepared as follows: 25 g of pure Sibunit were put into a vessel with 75 mL of aqueous HNO_3 solution (acid conc. 23 or 32 v/v.%). The mixture was heated at 90 °C during 2 hours. The treated catalysts were washed with hot deionized water until a negative reaction with sodium diphenylsulfonate for trace nitrates.

For catalysts to be prepared by oxidation with a wet air mixture, 50 g of Sibunit were placed into a quartz cell in an oven, and argon was passed through the cell for 30 min. Then the cell was heated at 450 °C and a gas mixture (20 v/v.% of O_2 in N_2) saturated with water steam at 90°C was blown through the cell for 4 hours. All the oxidized Sibunit samples were dried at 160 °C under Ar flow.

Oxidized-sulfonated samples were prepared by additional sulfonating at 200 °C of the oxidized catalysts during 10 h.

Before the catalytic experiments all the catalysts were treated at 190 °C under hydrothermal conditions for 3 hours to remove weakly fixed acidic groups. Whereupon the catalysts were additionally washed with boiling water until the constant pH of waste water and dried in air at 150 °C. The acidity of the catalysis was only measured with the catalysts after hydrothermal treatment.

Investigation of the catalyst stability was made with two samples: Sibunit sulfonated at 200 °C and carbon oxidized-sulfonated by wet air oxidation and subsequent sulfonation at 200 °C. The catalyst underwent hydrothermal treatment in pure water at 190, 250 and 300 °C during 3 hours under intensive stirring. After the treatment the catalysts were isolated from the solution by centrifugation (9000 rpm), washed by hot deionized water until a constant pH and dried at 150 °C.

2.5.2 Characterization of carbon catalysts

Texture characteristics of catalysts and non-treated Sibunit were investigated using low-temperature nitrogen absorption at $-196\text{ }^{\circ}\text{C}$ on ASAP-2400 device (“Micromeritics”, USA). All the catalysts to be analyzed were pre-evacuated down to 6 Torr at $130\text{--}150\text{ }^{\circ}\text{C}$. BET specific surface areas (S_{BET}) were calculated from adsorption isotherms. Pore volumes and pore surface areas were determined using the α_s –method. Pore size distributions were studied using QSDFT and NLDFT techniques.

Concentrations of strong acidic groups (phenolic, lactonic, carboxylic and sulfo-groups) on the surface of carbon catalysts were determined using acid-base titration with NaOH [233, 234]. The 0.5 g of Sibunit was stirred in a closed vessel with 20 mL of 0.2 M NaOH overnight. Next day the mixture was filtered and 5 mL aliquot was added to 25 mL of 0.1M HCl for the non-reacted alkali to be neutralized. The obtained acidic solution was back titrated with 0.2M NaOH using an automatic titrator (ATR-02 Akvilon, Russia). The amount of acidic groups on the surface was determined as a difference of NaOH quantities used for the blank titration (free of Sibunit) and that used for the titration of Sibunit samples.

Transmission electron microscope (TEM) studies were carried out using a JEM-2010 electron microscope (JEOL, Japan) with accelerating potential of 200 kV and a resolution of 1.4 \AA .

XRF analysis of samples of carbon catalyst sulfonated at $200\text{ }^{\circ}\text{C}$ and oxydized-sulfonated (oxydized by wet air and sulfonated at $200\text{ }^{\circ}\text{C}$) before and after hydrothermal treatment at 190, 250 and $300\text{ }^{\circ}\text{C}$ was made with ARL -Advant'x (Thermo Scientific) equipped Rh anode of the X-ray tube.

XPS was carried out with photoelectron spectrometer SPECS (Germany) with MgK_{α} radiation ($h\nu = 1253.6\text{ eV}$, 150 W). The scale of bonding energies was preliminarily calibrated via the gold and copper ground level positions: $\text{Au}^{4f}_{7/2} - 84.0\text{ eV}$ and $\text{Cu}^{2p}_{3/2} - 932.67\text{ eV}$. Vacuum was less than $8 \cdot 10^{-9}$ mbar. The samples were supported on the standart holder by double-side conductive sticky tape (Scotch 3M©). The received spectral data handling was made by XPS Peak 4.1 programm.

2.6 Catalytic tests

2.6.1 Cellulose hydrolysis-dehydration and hydrolysis-oxidation in a batch reactor

Cellulose hydrolysis-dehydration was made in an autoclave (Autoclave Engineers, USA) under intensive stirring 1500 rpm (Figure 12). Cellulose and catalyst, Sibunit or $\text{NbO}_x/\text{ZrO}_2$, (both $10\text{ g}\cdot\text{L}^{-1}$) and 45 mL of distilled water were put into the reactor. The reactor was purged with argon flow, and heated up to $180\text{ }^{\circ}\text{C}$ where the reaction time was started. At 0, 1, 2, 3 and 5 hours of reaction, aliquots of the reaction mixture ($\sim 1\text{ mL}$) having no influence on the process in the autoclave were taken from the reactor to monitor the evolution of concentrations by HPLC.

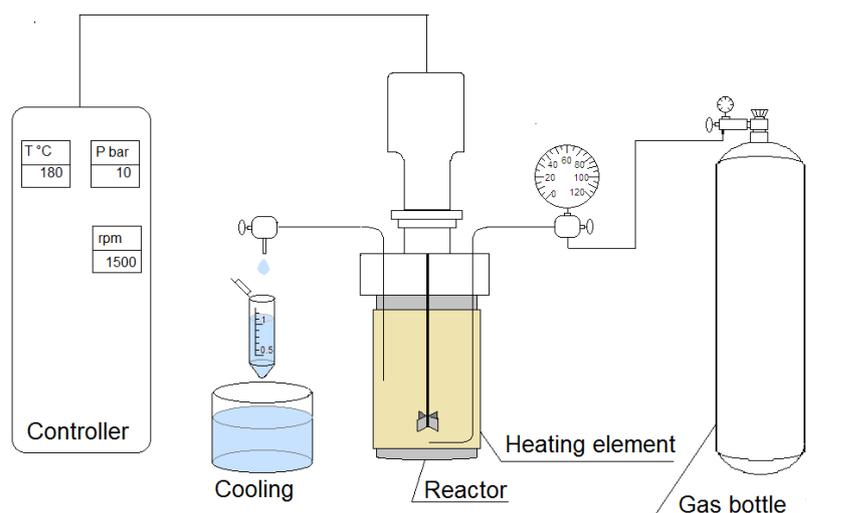


Figure 12. Scheme of the batch reactor.

Hydrolytic oxidation of cellulose was also carried out in a high-pressure autoclave (Autoclave Engineers, USA) under vigorous stirring (1500 rpm) with a mechanical propeller stirrer. The concentration of cellulose was $10 \text{ g}\cdot\text{L}^{-1}$, and the concentration of HPA referred to the number of vanadium atoms changed from 0.5 to 20 mmol. The experiments were performed at different temperatures (130, 140, 150 and 180 °C) and pressures (10, 20 and 50 bar) of the gas mixture containing 20% O_2 and 80% N_2 . In the course of the reaction, the reaction mixture was sampled periodically from an autoclave to analyze its composition. In the experiments with different concentrations of HPA salt of composition $\text{Co}_{0.6}\text{H}_{3.8}\text{PMo}_{10}\text{V}_2\text{O}_{40}$ and constant pH, the pH value in the prepared reaction solutions was adjusted to 1.5 by adding a 25% aqueous solution of H_2SO_4 .

Experiments on transformation of intermediates (cellobiose, glucose, fructose, 5-HMF, etc.) of cellulose hydrolysis-dehydration reaction were carried out similar to the experiments on cellulose processing.

2.6.2 Cellulose hydrolysis-dehydration in a flow reactor

Hydrolysis-dehydration of cellulose over Sibunit carbon catalysts has also been made in a flow system (Figure 13). The reactor is a tube made of stainless steel (length 200.00 mm, internal diameter 2.7 mm). The reactor was filled with mechanical uniform mixture of cellulose (250 mg) and the catalyst (200 mg). Deionized water was flowed with rate of 0.5 mL min^{-1} through the reactor thermostated at 200 °C. In the outlet, the cooled reaction mixture was collected into individual flask during each process hour (0-1 h, 1-2 h, etc.) for HPLC analysis.

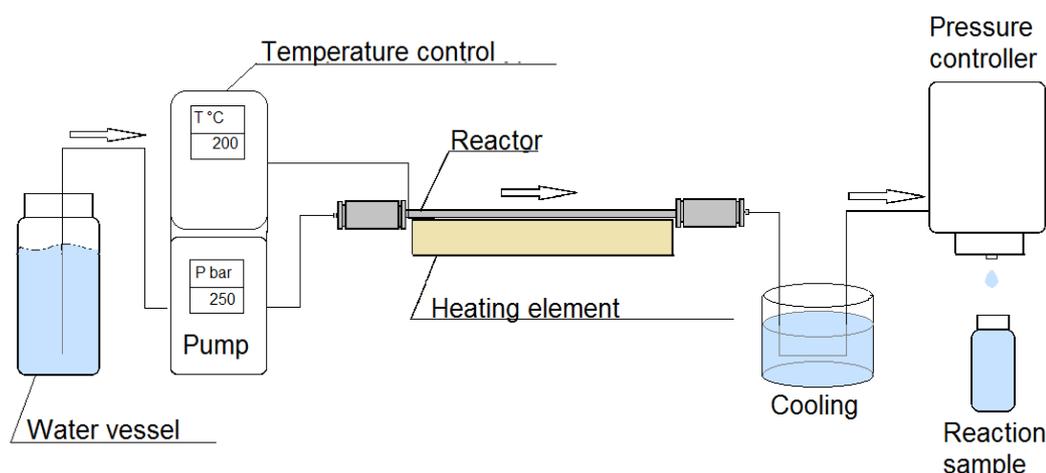


Figure 13. Scheme of the flow reactor.

Experiments on transformation of intermediates (cellobiose, glucose, fructose, 5-HMF, etc.) of cellulose hydrolysis-dehydration reaction were carried in the flow reactor in the following way. The reactor was filled with the catalyst (300 mg). 0.02 M substrate solution was flowed through the reactor with the rate $0.5 \text{ mL}\cdot\text{min}^{-1}$. The experiments were carried out at $200 \text{ }^\circ\text{C}$. The aliquots of cooled reaction media were collected similarly to cellulose experiment.

2.7 Analytical techniques

HPLC analysis

The samples were analyzed with Prominence LC-20A (Shimadzu) and Dionex Ultimate 3000 (Thermo Scientific) HPLC apparatus equipped with RI detector. Analysis of saccharides and acids was carried out on Rezex RPM-Monosaccharide Pb^{2+} or Rezex ROA-Organic Acids columns (both Phenomenex, $300 \text{ mm} \times 5.0 \text{ mm}$) thermostated at $40 \text{ }^\circ\text{C}$ and $70 \text{ }^\circ\text{C}$, respectively. Deionized water or $1.25 \text{ mM H}_2\text{SO}_4$ solution with flow rate $0.6 \text{ mL}\cdot\text{min}^{-1}$ were used for sugar and acid analysis, respectively.

The product yields were determined according to the formula:

$$Y = \frac{C_{\text{product}} V}{N_C \left(\frac{m_{\text{Cellulose}}}{M_{\text{Glucan}}} \right)} \cdot 100 \quad (6)$$

where Y is a product yield, C_{product} is the product concentration (mol L^{-1}), V is the reaction volume (L), N_C is a coefficient that takes into account the molar ratio carbon : glucan (for glucose $N_C=1$, for FA $N_C=6$, etc.), m_{Cell} is the cellulose mass (g), M_{Glucan} is molar mass of glucan in cellulose ($162 \text{ g}\cdot\text{mol}^{-1}$).

In the flow reactor Y for each reaction hour was measured by the formula (6) at that a V was the volume of a sample collected during 1 hour. The total product yield was determined as a sum of yields calculated for each hour of the process:

$$Y_{\Sigma} = \sum_{i=1}^4 Y_i, \quad (7)$$

In the experiments with water-soluble substrates (cellobiose, glucose, 5-HMF, etc.) the yields of products were calculated according to the fomula:

$$Y = \frac{C}{C_0} \cdot 100, \quad (8)$$

where Y is a product yield (%); C is the concentration of the product ($\text{mol} \cdot \text{L}^{-1}$); C_0 is the initial concentration of the substrate ($\text{mol} \cdot \text{L}^{-1}$). In the flow reactor the formula (7) was also used for calculating the total product yield.

The substrate conversions were calculated as follows:

$$X = \frac{C_0 - C}{C_0} \cdot 100, \quad (9)$$

where X is the conversion degree (%); C and C_0 are actual and initial concentrations of the substrate ($\text{mol} \cdot \text{L}^{-1}$).

Total organic carbon content (TOC) after the experiments with HPA and $\text{NbO}_x/\text{ZrO}_2$ was measured with Multi N/C 2100S TOC (Analytik Jena, Germany). A 500 μL aliquot of the reaction mixture was injected into the apparatus. TOC ($\text{g} \cdot \text{L}^{-1}$) was recalculated by calibration curves.

The cellulose conversion (X) has been determined from the TOC data by the following formula:

$$X = \frac{C_c \cdot V / (M_c \cdot N_c)}{m_{\text{Cellulose}} / M_{\text{Glucan}}} \cdot 100, \quad (10)$$

where X is the cellulose conversion (%), C_c is the concentration of carbon atoms ($\text{g} \cdot \text{L}^{-1}$), V is the reaction volume (L), M_c - carbon molar mass ($12.011 \text{ g} \cdot \text{mol}^{-1}$), N_c is a coefficient that takes into account the molar ration carbon : glucan ($N_c=6$), $m_{\text{Cellulose}}$ - mass of cellulose (g), M_{Glucan} is molar mass of glucan in cellulose ($162 \text{ g} \cdot \text{mol}^{-1}$).

Formaldehyde analysis was made by UV-spectrometry (wave length 570 nm, spectrophotometer Uvicon 923).

pH values of the solutions before and after the experiment were measured with a pH tester Anion 4100 (TD Anion, Russia).

5-HMF isolation

HMF was extracted from hydrolyzate solutions using methylisobutylketone (MIBK) and butanol-2 as the organic solvent. The ratio of butanol-2 or MIBK to hydrolyzate was 2:1 and 9:1, respectively. The extraction time was 10 min. The organic layer containing HMF was collected into a glass flask and dried by a vacuum evaporator (Laborota 4000, Heidolph). The solid residue was dissolved in water. The solutions as well as the post-extraction aqueous layer were analyzed by HPLC using the same technique as those for analyzing the reaction solutions.

CHAPTER 3.
CELLULOSE HYDROLYSIS-OXIDATION

3.1 Cellulose mechanical activation

As it was previously discussed in the literature review, cellulose is a polysaccharide containing crystal structures. It strongly decreases a reaction ability of cellulose and limits the cellulose transformation into valuable chemicals [17-19]. In this work the physical method of mechanical grinding was used to activate cellulose. This method was chosen not only for its high efficacy but also for its chemical inactivity.

Table 3. Cellulose parameters before and after the activation in different mills.

Cellulose sample	τ , min	Cellulose heating, °C	$\langle d_l \rangle$, μm	CI, %	CSR, nm	E_{AKT} , $\text{kJ}\cdot\text{kg}^{-1}$	$W_{\text{H}_2\text{O}}$, %	K_{dry}
Before	0	–	114±35	80-90	4-7	–	2,26	0.97
Activation in ball mill	600	25	30±11	75-85	4-6	60000	5,70	0.94
Activation in the planetary-type mill named Aktivator-4M	10	~100	5±4	30-60	2-3	216000	3,52	0.96
Activation in the planetary-type mill named Fritsch	40	~100	13±6	35-55	2-4	192000	–	–

In this work the activation of microcrystalline cellulose was conducted in three different mills: 1) roller mill, 2) planetary-type mill named Aktivator-4M (JSC Aktivator, Novosibirsk, Russia), 3) planetary-type mill named Fritsch (Germany).

The cellulose samples before and after grinding were investigated by optical microscopy to determine the average particle size and by XRD to evaluate the crystallinity degree (Table 3, Figure 14). Moreover, initial cellulose and the activated samples were investigated by SEM.

The average particle size for the initial sample was 114±35 μm . XRD diffraction pattern (Figure 14, 2A) is typical for cellulose crystal structure (101, 10-1, 021, 002, 040). Crystallinity index (CI) calculated from the XRD data was 80-90% and CSR 4-7 nm.

Grinding of cellulose during 10 hours in a ball mill decreased its average particle size to 30±11 μm . However, according to XRD data, the crystal structure of cellulose and its crystallinity index changed insignificantly (75-85%) and CSR was the same as for non-treated cellulose (Figure 14, 2B). Thus milling of cellulose in the ball mill caused pounding of big polysaccharide particles which contained several crystal domains. It is possible to conclude, that the power of this type of mills was not enough for destroying crystallites.

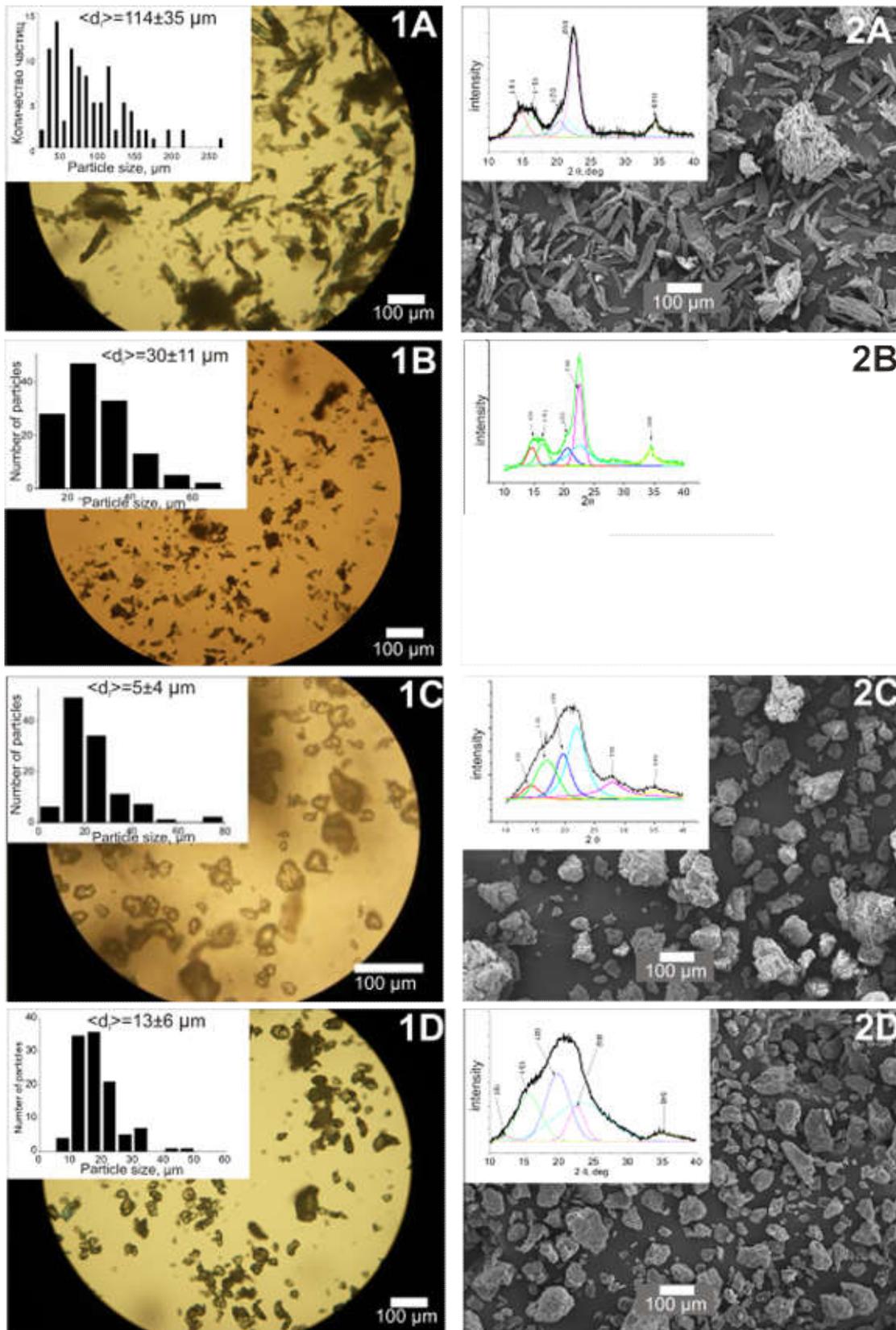


Figure 14. Cellulose samples characterisation. 1 - optic microscopy of cellulose particles (*insert* the size distribution of particles), 2 - SEM images (*insert* XRD patterns). A - initial cellulose, B - ball-milled cellulose, C - cellulose activated in Aktivator-4M planetary-type mill, D - cellulose activated in Fritsch planetary-type mill.

Analysis of the sample images made after 10-min grinding in a planetary mill Aktivator-4M showed that the particle size decreased to 5 ± 4 μm (Figure 14, 1C). XRD analysis confirmed the destruction of the crystal structure; this was indicated by the absence of reflections with 2θ angles equal to 22.7° , which are typical of crystalline cellulose, and by the appearance of a halo with the maximum at 21.5° . Calculated crystallinity index of the sample was about 30-60% and CSR was 2-3 nm (Figure 14, 2C).

Another planetary-type mill "Fritch" was also used for grinding cellulose. As this mill was less powerful than Aktivator-4M, the activation time was 40 min. Grinding cellulose led to a significant increasing of the amorphous halo ($2\theta \sim 21.5^\circ$) on the XRD pattern with simultaneous decreasing of CI (35-55%) and CSR values (2-4 nm) (Figure 14, 1D).

Cellulose is known to contain some moisture. The amount of uncombined water in the polysaccharide sample could impact the cellulose mass and decrease product yields in such a way. The moisture content in cellulose measured (GOST 16932-82, Table 3) was very low (K_{dry} was 0.94-0.97).

Thus, grinding in a ball mill has a low efficiency for mechanical activation and destruction of the crystal structure of cellulose. So, the sample activated in a planetary mill was chosen for investigation of the catalytic process of hydrolytic oxidation.

The importance of cellulose activation was confirmed by experiments. XRD of cellulose unsolved during hydrolysis-dehydration in the flow reactor showed an increase of the crystallinity of cellulose remained (Figure 15). Some crystal peaks appeared and amorphous halo disappeared what clearly confirmed the activation technique importance.

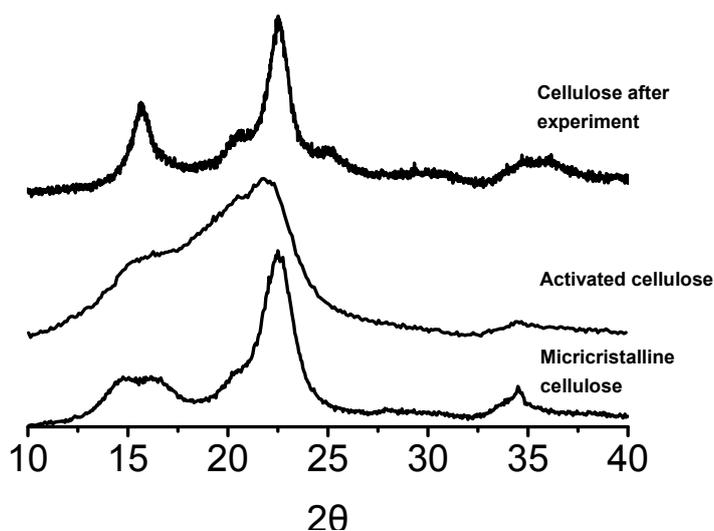


Figure 15. XRD patterns of cellulose before any treatment, after the activation in the planetary-type mill and after hydrolysis-dehydration experiment.

3.2 Cellulose hydrolysis-oxidation in the solution of HPA

The solutions of Mo-V-P Keggin-type HPA-x and non-Keggin HPA-x' heteropoly acids and their acidic salts ("x" refers to the amount of vanadium atoms included into one molecule of HPA) have been tested as catalysts for one-pot hydrolysis-oxidation of the ball-milled cellulose. The results of the experiments are presented in Table 4. HPAs HPA-2 – $H_5PMo_{10}V_2O_{40}$, Co-HPA-2 – $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$, HPA-6' – $H_{11}P_3Mo_{16}V_6O_{40}$, HPA-10' – $H_{17}P_3Mo_{16}V_{10}O_{40}$ were investigated in the process. Analysis of the reaction mixtures was made by HPLC. Yields were calculated according to the formula (6).

3.2.1 Analysis of the reaction mixtures

Significantly higher yield of formic acid (66 mol%) was obtained by using cellulose activated in the planetary mill. For initial cellulose and one activated in the ball mill FA yields appeared to be 18 and 23 mol%, respectively, under identical conditions. Hence we utilized cellulose activated in the planetary mill for subsequent experiments (Table 4).

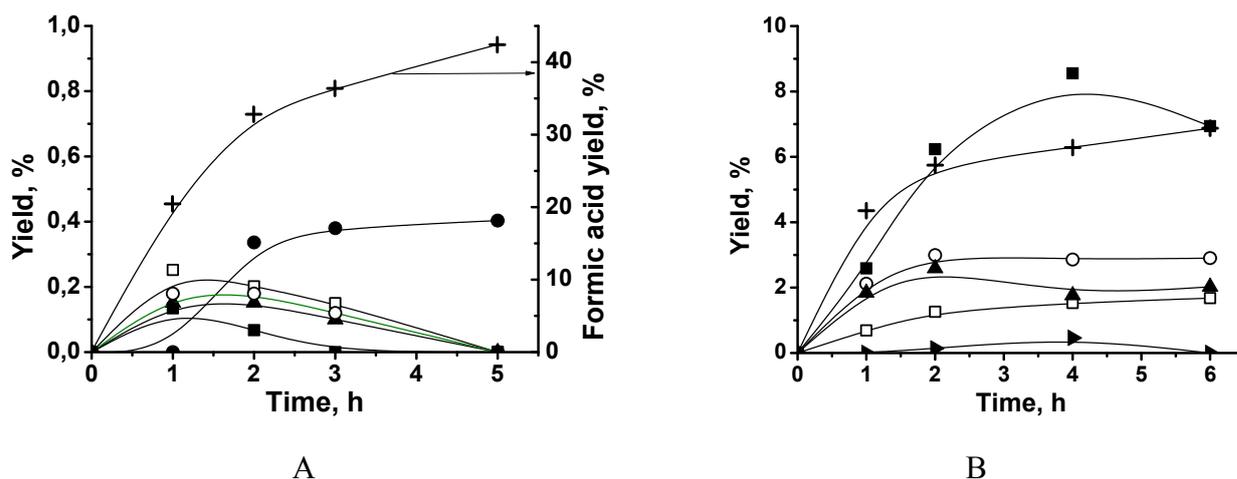


Figure 16. Kinetic curves of accumulating reaction products under oxidative ($O_2/N_2=1/4$) (A) or inert (Ar) (B) atmospheres in the presence of $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ (Co-HPA-2) as catalyst. Reaction conditions: cellulose $10\text{ g}\cdot\text{L}^{-1}$, catalyst $10\text{ mmol}\cdot\text{L}^{-1}$, gas pressure 10 bar, $150\text{ }^\circ\text{C}$. ■ – Glucose, ○ – Malic Acid, □ – Glycolic Acid, ▲ – Lactic Acid, ▶ - Levulinic Acid, ● – AA, + – FA.

Analysis of the reaction mixture components by HPLC showed (Table 4) that formic acid was the main product in all the experiments. Acetic acid as the final by-product was observed in the amounts not exceeding 1 mol %. It could be formed via oxidation of furan derivatives (5-HMF, furfural), according to [52]. Moreover, the formation of glucose and organic acids ($< 0.2\%$) was confirmed (Figure 16 A). UV-vis spectrometry [235] let to show the formaldehyde formation ($< 2\%$). Only the experiments performed in an argon atmosphere showed the formation of an appreciable amount of glucose (up to 8.0%) as an intermediate product of cellulose hydrolysis as well as small

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amounts of organic acids (malic, glycolic, lactic, levulinic and acetic) (Figure 16 B). The yield of formaldehyde achieved in the experiments did not exceed 1.3 mol %.

The TOC analysis of the reaction mixture after the reaction under the aerobic process conditions showed the organics and formic acid contents approximately equal (± 2 mol%) thus indicating no formation of high amount of side products. Therefore, the process kinetics was monitored from changes in the concentration of formic acid.

Table 4. Product composition of the activated cellulose hydrolytic oxidation by HPA solutions with different compositions against conditions of carrying out the process during its optimization. Reaction Conditions: cellulose activated in the planetary mill $10 \text{ g}\cdot\text{L}^{-1}$, catalyst $10 \text{ mmol}\cdot\text{L}^{-1}$. ¹Times of maximum formic acid yields are shown. ² Reaction was made under Ar (10 bar). ³pH was reduced to 1.5 by 25% H_2SO_4 solution. ⁴Initial cellulose was taken for the reaction. ⁵Cellulose activated in ball mill was taken for the reaction.

#	Acid ^a	C_{acid} , M	C_{Vatom} , M	pH	T,	$P_{25^\circ\text{C}}$,	Time ¹ ,	Product Yields, mol%		
								Glu	AA	FA
1 ²	Co-HPA-2	0.010	0.020	1.5	150	10	6	8.0	0.4	6
2	Co-HPA-2	0.010	0.020	1.5	130	10	7	0.0	0.2	20
3	Co-HPA-2	0.010	0.020	1.5	140	10	7	0.0	0.0	22
4	Co-HPA-2	0.010	0.020	1.5	150	10	5	0.0	0.4	42
5	Co-HPA-2	0.010	0.020	1.5	180	10	1	0.0	0.0	31
6	Co-HPA-2	0.010	0.020	1.5	150	20	7	0.0	0.8	66
7	Co-HPA-2	0.010	0.020	1.5	150	50	7	0.0	0.6	60
8	HPA-2	0.010	0.020	1.4	150	20	5	0.0	0.7	57
9	HPA-6'	0.010	0.020	1.6	150	20	7	0.0	0.9	51
10	HPA-10'	0.010	0.020	1.7	150	20	7	0.0	0.6	51
11 ³	Co-HPA-2	0.005	0.010	1.5	150	20	7	0.0	0.0	58
12 ³	Co-HPA-2	0.001	0.002	1.5	150	20	7	0.0	0.0	49
13 ³	Co-HPA-2	0.0005	0.001	1.5	150	20	5	0.0	0.0	23
14 ⁴	Co-HPA-2	0.010	0.020	1.5	150	20	7	0.0	0.0	18
15 ⁵	Co-HPA-2	0.010	0.020	1.5	150	20	7	0.0	0.0	23

3.2.2 Influence of reaction conditions on kinetics and product yields

The process parameters, in particular, temperature, gas phase composition and pressure, were optimized in the presence of a HPA-2 acid salt solution of composition $\text{Co}_{0.6}\text{H}_{3.8}\text{PMo}_{10}\text{V}_2\text{O}_{40}$.

The experiments at different temperatures (130, 140, 150, and 180 °C) were performed in a gaseous mixture $O_2/N_2 = 1/4$ (artificial air) at a pressure of 10 bar. The results presented in Figure 17 evidence that 150 °C was the optimal temperature; at this temperature the formic acid yield reaches 45 mol % after 3 hours. As seen from the plot, raising the process temperature to 180 °C does not improve the target product yield due to insufficient thermal stability of the HPA solution at this temperature, which decreases the oxidation power of the catalyst as a result of its partial decomposition accompanied by the precipitation of vanadium species. Moreover, at 180 °C the HCOOH concentration declines already after 1 hour of reaction, apparently, owing to instability of formic acid to further oxidation towards carbon dioxide and water at this temperature. At 130 °C the kinetic curve for the formic acid synthesis is S-shaped, which was not observed at higher temperatures. Acceleration of the reaction can be attributed to autocatalysis in the formic acid synthesis, because the first step of the one-pot process (hydrolysis of cellulose) occurs under the conditions of acid catalysis.

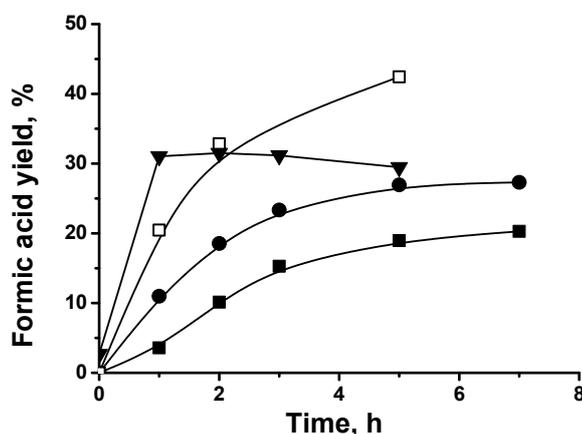


Figure 17. Kinetic curves of formic acid formation at different temperatures (● – 140 °C, ■ – 130 °C, □ – 150 °C, ▼ – 180 °C) in the presence of $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ (HPA-2) as catalyst. Cellulose $10\text{ g}\cdot\text{L}^{-1}$, catalyst $10\text{ mmol}\cdot\text{L}^{-1}$, oxidative atmosphere ($O_2/N_2 = 1/4$), gas pressure 10 bar.

The kinetic curves obtained for the formic acid accumulation were used to calculate the initial rates of reaction, W_0 , and to plot the dependence of the initial reaction rate on the inverse temperature of the reaction (Figure 18). The apparent activation energy of the process (E_a) equal to $78\text{ kJ}\cdot\text{mol}^{-1}$ was estimated from the linear dependence. This value is much lower as compared to the activation energy found for the processes of cellulose hydrolysis in the solution of sulfuric acid used as a catalyst ($170\text{--}180\text{ kJ}\cdot\text{mol}^{-1}$) [236], and somewhat lower than the activation energy in the presence of solid catalysts (sulfonated chloromethyl polystyrene resin, $83\text{ kJ}\cdot\text{mol}^{-1}$ [167], and sulfonated carbon materials, $110\text{ kJ}\cdot\text{mol}^{-1}$) [139]. The result obtained may indicate that the step of cellulose hydrolysis to glucose catalyzed by acidic HPA sites is the limiting step of the process. However, it proceeds by the

mechanism differing from the typical mechanism of glycoside bond cleavage catalyzed by dissolved hydrogen ions. A possible formation of the hydrogen or even complex bonds between hydroxyl groups of cellulose and polyoxometalates, which facilitates the hydrolysis of polysaccharide and decreases the apparent activation energy, can be hypothesized. A similar mechanism was proposed in [66] for the oxidation of 2-hydroxycyclohexanone (chapter 1.2.2 and Scheme 3).

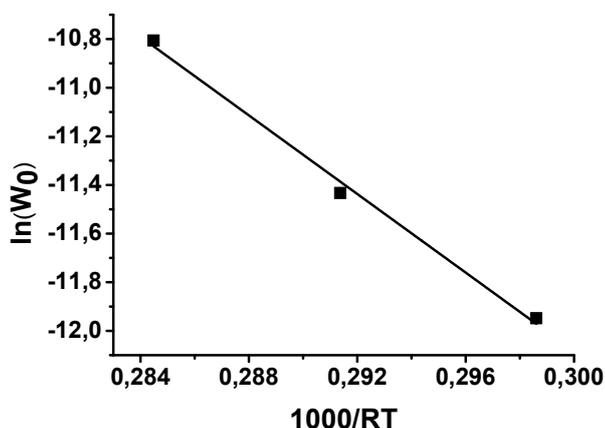


Figure 18. Arrhenius temperature dependence of initial rate in the presence of $\text{Co}_{0.6}\text{H}_{3.8}\text{PMo}_{10}\text{V}_2\text{O}_{40}$ (HPA-2) as catalyst. Reaction conditions: cellulose $10 \text{ g}\cdot\text{L}^{-1}$, catalyst $10 \text{ mmol}\cdot\text{L}^{-1}$, oxidative atmosphere ($\text{O}_2/\text{N}_2 = 1/4$), gas pressure 10 bar.

However, the second step of the one-pot process — oxidation of glucose to formic acid — proceeds at the oxidation sites of Mo-V-P HPA (V^{5+}), which are reduced to (V^{4+}) during the substrate oxidation. In order to obtain the steady-state process and high yields of formic acid, the indicated sites should be reoxidized, which would provide quite a high oxidation potential (E) of the HPA solution. Hence it is clear that the gas phase composition should exert a substantial effect on the yields of reaction products. Indeed, in the experiment performed in inert Ar atmosphere for 5 hours at a temperature of $150 \text{ }^\circ\text{C}$ in the presence of $\text{Co}_{0.6}\text{H}_{3.8}\text{PMo}_{10}\text{V}_2\text{O}_{40}$ catalyst, a maximum yield of formic acid was as low as 6 mol % (Table 4, line 1, Figure 16 B). The formation of comparable amounts (8 mol %) of glucose was also observed, which may indicate a low rate of the oxidation as compared to the rate of cellulose hydrolysis. In addition, noticeable amounts of acetic, glycolic, malic, lactic and levulinic acids were observed. Note that in the course of an experiment in an inert atmosphere, the catalyst solution changed its color from brown-orange to dark-blue already within the first hour of the reaction. This justifies that the oxidation of the cellulose hydrolysis products in an Ar atmosphere led to a deep reduction of the HPA solution, i.e., the concentration of V^{5+} strongly decreased and the concentration of V^{4+} increased. Since the reduced form of the catalyst cannot serve as an oxidant due to a considerable decrease in the oxidation potential (U) of HPA solution, a definite conclusion can be made from this experiment indicating that the catalyst regeneration in the one-pot process requires an

oxidizing atmosphere in the autoclave reactor. This provides quite a high U value for the catalyst, its elevated oxidative capacity, and thus a higher yield of FA without the formation of substantial amounts of by-products, which was observed under similar conditions but in the presence of gaseous mixture $O_2/N_2= 1/4$ (artificial air) (Figure 16 A).

After that, we investigated the effect of artificial air pressure on the observable kinetics of the process at 150 °C. The study was conducted at the gas mixture pressures equal to 10, 20 and 50 bar. The gas pressure was found to exert no effect on the reaction rate in the initial region of kinetic curve. However, changes in the pressure and hence in the autoclave oxygen content affected the ultimate yield of formic acid. In particular, the prolonged 11-hour experiments carried out at 150 °C demonstrated that the generation of formic acid stopped after 5 hours at a pressure of 10 bar, whereas at 20 and 50 bar it stopped only after 7 hours with FA yield 60-66 mol % (Figure 19). When the reaction stopped, the reaction mixture composition did not change.

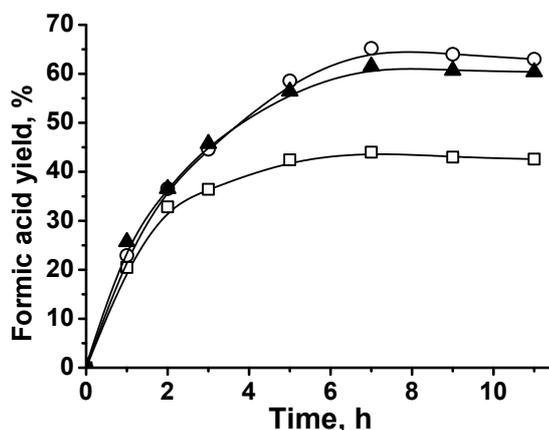


Figure 19. Kinetic curves of formic acid accumulation under different air ($O_2/N_2= 1/4$) pressures (▲ – 50 bar, ○ – 20 bar, □ – 10 bar) in the presence of $C_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ (HPA-2) as catalyst. Cellulose $10\text{ g}\cdot\text{L}^{-1}$, catalyst $10\text{ mmol}\cdot\text{L}^{-1}$, oxidative atmosphere ($O_2/N_2= 1/4$), temperature 150 °C.

The highest yield of formic acid equal to 66% was obtained at 20 bar. Over the entire time of experiments at 20 and 50 bar, the catalyst did not change its color and remained brown, which may evidence a sufficient oxygen amount in the reactor, which provided regenerability of the catalyst and its stationary state.

Hence, the optimal conditions are 150 °C and air pressure equal to 20 bar. This conditions let to reach maximal FA yields during relative short time.

3.2.3 Influence of HPA composition (acidity and vanadium content) on reaction kinetics and product yields

Taking into account the crucial role of the catalyst acidity that is responsible for the hydrolysis step of the examined process, we investigated the cellulose transformation in the presence of heteropoly acids varied in the H^+ content: $H_5PMo_{10}V_2O_{40}$ (HPA-2), $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ (Co-HPA-2), $H_{11}P_3Mo_{16}V_6O_{76}$ (HPA-6') and $H_{17}P_3Mo_{16}V_{10}O_{89}$ (HPA-10'), differing in the number of both the vanadium and hydrogen atoms, were carried out under the optimal conditions that were found earlier (process temperature of 150 °C and gas mixture pressure of 20 bar). As was noted above, the HPA solutions have bifunctional properties (acidic and oxidizing), which affect the observable reaction kinetics. So, the effect of HPA solution acidity on the hydrolytic oxidation of cellulose was determined in experiments where the HPA concentration was calculated in such a manner that provided a constant concentration of vanadium atoms in the solution equal to 20 $mmol \cdot L^{-1}$. Thus, the concentrations were as follows: 10 $mmol \cdot L^{-1}$ for HPA-2 and Co-HPA-2, 3.33 $mmol \cdot L^{-1}$ for HPA-6', and 2 $mmol \cdot L^{-1}$ for HPA-10'. The curves of formic acid accumulation in the presence of the indicated catalysts are displayed in Figure 20 A. Both the yields and the initial rate (A_0) of the process decrease in the series HPA-2 > Co-HPA-2 > HPA-6' > HPA-10'.

The calculation of hydrogen ions concentration in HPA solution (or determination of the pH value) is a nontrivial problem, since the HPA hydrolysis in solution is a complicated process including several tens of equilibrium steps, which equilibrium constants are often unknown. So, the pH values created by different HPA in solutions were measured before the reaction and used to calculate the concentrations of hydrogen ions. This allowed us to determine with sufficient accuracy the effect of solution acidity on the rate of the overall process of cellulose oxidative hydrolysis. It was found that dependence of the process initial rate on the number of protons had a linear form (Figure 20 B). The highest initial rate of the reaction was observed in the presence of catalyst Co-HPA-2, which provided the lowest pH value of the medium, i.e. the highest acidity at the same vanadium content. This observation confirms once more our earlier hypothesis that hydrolysis is the limiting step of the overall process.

The effect of vanadium content on the process kinetics was studied in the presence of catalyst $Co_{0.6}H_{3.8}PMo_{10}V_2O_{40}$ (Co-HPA-2) (Table 4, entries 11, 12, 13). To exclude the effect of changes in the solution acidity with changes in the HPA concentration, all the experiments were conducted at a constant pH equal to 1.5, which was controlled by the addition of sulfuric acid. Therewith, the vanadium concentration was varied over the range of 1 to 20 $mmol \cdot L^{-1}$. The amount of cellulose in the reaction mixture in terms of the glucose monomer was about 60 $mmol \cdot L^{-1}$ in all the experiments, and hence the ratio of glucose unit to V ranged from 60 : 1 to 3 : 1. The results of kinetic studies presented in Figure 21 show that at a decrease in vanadium concentration from 20 to 10 $mmol \cdot L^{-1}$ the kinetic

curves for the formic acid accumulation coincide. A further decrease of vanadium concentration in the solution to 2 and 1 $\text{mmol}\cdot\text{L}^{-1}$ decreases both the initial rate and the formic acid yields. At that, the ultimate yield of the target product decreases from 58 to 23%. Thus, it can be concluded that the yields of the target product decrease when the ratio of glucose unit to vanadium is below 6 : 1. However, additional studies are needed to explain the revealed experimental fact.

The data obtained on the effect of acidity and vanadium content in the HPA composition on the process rate and yields of the target product suggest that HPA-10' taken in the same amount as Co-HPA-2, i.e. 10 $\text{mmol}\cdot\text{V}\cdot\text{L}^{-1}$ or 100 $\text{mmol}\cdot\text{V}\cdot\text{L}^{-1}$, will be even more active than Co-HPA-2. The reason is that such concentration of HPA-10' will provide a sufficient acidity of the medium, and vanadium concentration will certainly exceed the found threshold value. However, for practical application the catalyst cost is important. It should be noted that HPA-2 is the most widely used and commercially produced catalyst.

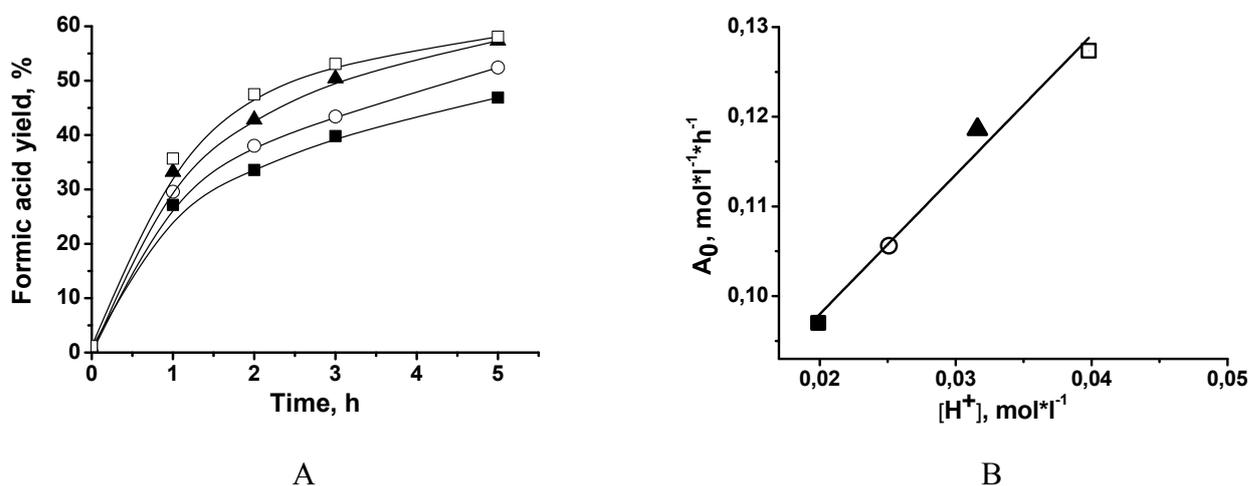


Figure 20. Kinetic curves of formic acid accumulation in the presence of different heteropoly acids: ■ – $\text{H}_{17}\text{P}_3\text{Mo}_{16}\text{V}_{10}\text{O}_{89}$, ○ – $\text{H}_{11}\text{P}_3\text{Mo}_{16}\text{V}_6\text{O}_{76}$, ▲ – $\text{Co}_{0.6}\text{H}_{3.8}\text{PMo}_{10}\text{V}_2\text{O}_{40}$, □ – $\text{H}_5\text{PMo}_{10}\text{V}_2\text{O}_{40}$ (A) and initial rate dependence from the environment acidity at vanadium concentration $[\text{V}] = 20 \text{ mmol}\cdot\text{L}^{-1}$ (B). Cellulose 10 $\text{g}\cdot\text{L}^{-1}$, catalyst 10 $\text{mmol}\cdot\text{L}^{-1}$, oxidative atmosphere ($\text{O}_2/\text{N}_2 = 1/4$), pressure 20 bar, 150 °C.

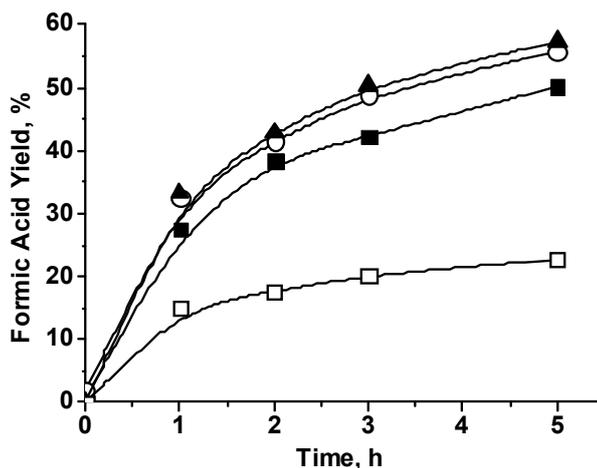


Figure 21. Reaction time dependence of formic acid yield in the presence of different concentrations of Co-HPA-2: □ – 0.5 mmol·L⁻¹ (1 mmol·L⁻¹ vanadium atoms), ■ – 1 mmol L⁻¹ (2 mmol L⁻¹ vanadium atoms), ○ – 5 mmol·L⁻¹ (10 mmol·L⁻¹ vanadium atoms), ▲ – 10 mmol·L⁻¹ (20 mmol·L⁻¹ vanadium atoms). pH = 1.5, cellulose 10 g·L⁻¹, oxidative atmosphere (O₂/N₂=1/4), gas pressure 20 bar, 150 °C.

3.2.4 Reaction pathways and process mechanism

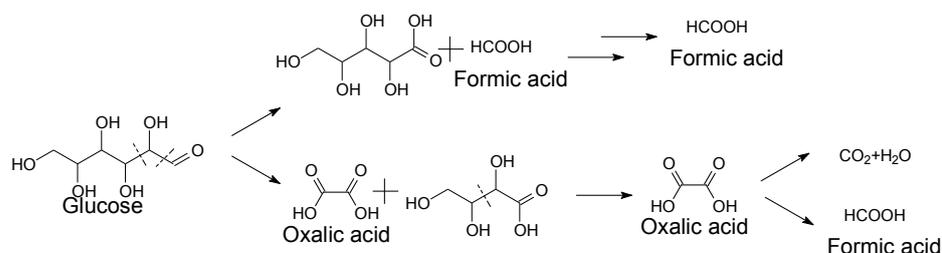
The following possible mechanisms of cellulose hydrolysis-dehydration could be discussed.

First, the mechanism close to peroxide oxidation (chapter 1.2.2) is possible [52, 64]. However, conducting the cellulose hydrolysis-oxidation via this path would be followed by the formation of a big number of side products which have not been detected in the present work. Also low selectivity of FA would be but in here this parameter is quite high.

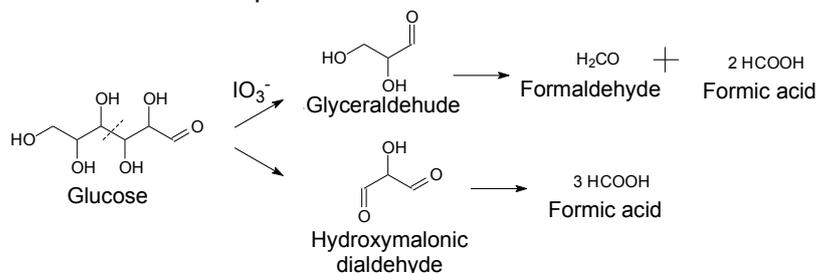
Secondly, the reaction of periodate oxidation is well known for carbohydrates. It is used in lab for determining the structure of oligo- and polysaccharides [237]. When reacting 1 mol of periodate with a saccharide the oxidation of a diol group takes place. A cleavage of C-C bond and a formation of two aldehyde groups are simultaneously observed. During the oxidation of 1 mole of triols 2 moles of periodate are used. It causes the formation of 2 aldehyds and 1 FA. The oxidation of carbonyls and ketones is a special case of transformations of diols meaning that undergoes oxidation when it is hydrated. Cellulose is oxidized by periodate at the ambient temperature. 1 mol of periodate is used to oxidize 1 mol of glucose units. During the reaction the cleavage of C₂-C₃ carbon bond takes place and polyaldehyde is formed. According to [237], oxidation of glucose goes through the following steps. C₃-C₄ carbon bond is decomposed and one molecule of glyceraldehyde and one hydroximalonic dialdehyde are formed. These two substances undergo the following oxidation as it was described for diols, triols and carbonyls (Scheme 12, mechanism II). Hence, during oxidation of glucose formed after the cellulose hydrolysis five molecules of FA and one molecule of formaldehyde are formed. If the oxidation of glucose over HPA was similar to that one, the ratio of FA to formaldehyde would be

close to 5 : 1. It means the the yields of FA and formaldehyde would be 83 and 17% after the full conversion. However in the present work the highest FA yield is 66% while the yield of formaldehyde is very low (5%), i.e. the FA : formaldehyde ratio is 13 : 1. Investigating the stability of FA and formaldehyde has demonstrated low rate of product oxidation, so the oxidation of the products could not explain completely decreasing the experimental yields compared to theoretical ones.

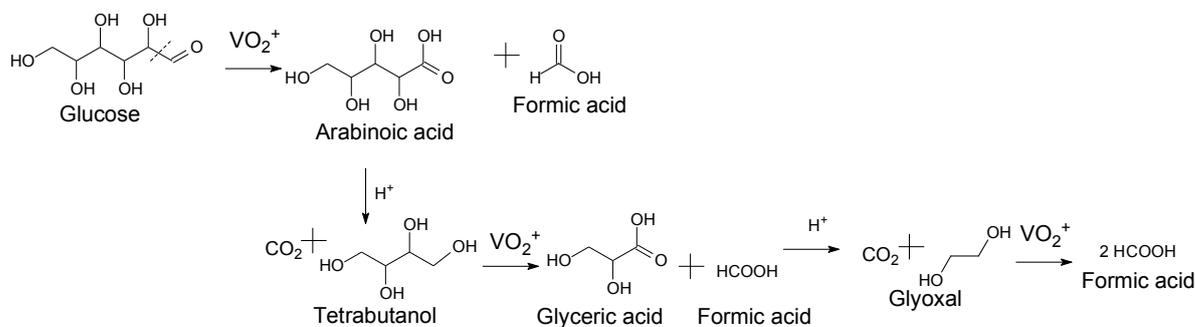
I. Subsequent oxidation mechanism



II. The mechanism of periodate oxidation of saccharides



III. Electron transfer - oxygen transfer mechanism



Scheme 12. Possible paths of glucose oxidation

Third, the mechanisms of electron transfer-oxygen transfer (ET-OT mechanisms) are described in oxidation of oxygen-containing organic substrates over HPA catalysts. These reactions are also followed by the cleavage of C-C carbon bond [66, 67]. In [66, 67, 71] the oxidation of diols and 2-hydroxycyclohexanon is investigated. During the cleavage of C-C bond the carboxylic acids are formed. This transformation is catalyzed by VO_2^+ species which are formed through the dissociation of heteropolyacid molecules in delutied solutions of fresh HPA catalysts or during the reduction of vanadium to V(IV). VO_2^+ are more active catalytic particles compared to HPA itself [62]. The

formation of such compounds in the present study has been confirmed by NMR. Oxidation of glucose via this path (Scheme 12, mechanism III) would form one FA and one arabinoic acid. Arabinoic acid could undergo decarboxylation in acidic solution under high temperature. This reaction led to the formation of one CO₂ and tetrabutanol. Its oxidation would cause the formation of FA and glyceric acid according to ET-OT mechanism. Decarboxylation of glyceric acid would form CO₂ and ethylene glycol. The last product could be oxidized into two FA. Thus, during glucose decomposition FA and CO₂ would be accumulated in the ratio FA : CO₂ = 4 : 2 what would decrease the FA yield.

In the present work only formaldehyde product was detected in the reaction system. Therefore the mechanism similar to periodate oxidation seems to be more likely than ET-OT. At the same time it is not possible to exclude completely other possible reaction paths like ET-OT. Besides, high ratio of FA to formaldehyde seen in this work could be explained by the oxidation of glucans in the structure of cellulose, like cellulose periodate oxidation [237]. Oxidation of polymer structures could facilitate cellulose solubilization and decrease the activation energy of hydrolysis-oxidation compared to the energy values observed in cellulose transformation over soluble acid catalysts (chapter 3.2.2).

3.3 Chapter conclusions

The possibility of formic acid synthesis from cellulose with high yields (66 mol %) via the single-step catalytic process of hydrolytic oxidation in the presence of bifunctional homogeneous Mo-V-P heteropoly acid catalysts has been demonstrated. A temperature of 150 °C and air pressure of 10-20 bar are the optimal reaction conditions. Pressure was found to exert no effect on the initial rate of the process, however, it affects the yield of the target product. An increased oxygen content in the reaction medium provides regenerability of the catalyst solution and a high yield of formic acid.

As shown by the search for optimal HPA composition with the use of H₅PMo₁₀V₂O₄₀, Co_{0.6}H_{3.8}PMo₁₀V₂O₄₀, H₁₁P₃Mo₁₆V₆O₇₆ and H₁₇P₃Mo₁₆V₁₀O₈₉, the highest reaction rate was observed in the presence of HPA solutions that provide a greater acidity of the reaction medium. A linear dependence of the reaction rate on the concentration of H⁺ ions in the solution was established. The dependence of the process rate and formic acid yields on the vanadium content is linear up to the point at which the ratio of glucose unit to vanadium becomes equal to 6:1, and then the dependence goes to a plateau. Thus, three criteria should be used when choosing a bifunctional catalyst for practical application in the process under consideration: high acidity, vanadium amount greater than 1:6 with respect to glucose monomers, and the catalyst cost.

Formic acid obtained from vegetable lignocellulosic feedstock can be used as a reductant or hydrogen source for the production of valuable raw materials and fuel from vegetable biomass.

CHAPTER 4.
CELLULOSE HYDROLYSIS-DEHYDRATION

4.1 Cellulose hydrolysis-dehydration over NbO_x/ZrO₂ catalysts

The oxide catalysts were prepared in the Department of template synthesis of BIC. The catalysts are bulk zirconia and contains 0, 0.5, 1.1 and 2.8% of Nb element. All the catalysts were characterized and tested in the cellulose hydrolysis-dehydration reaction. Cellulose was previously activated in the "Fritch" planetary-type mill. Experiments have been conducted in a batch reactor at 180 °C. The working temperature has been chosen with the help of literature data. This temperature seems to be high enough for cellulose conversion with high product yields [80, 81].

4.1.1 Catalyst characterization

Elemental analysis of the fresh catalysts by ICP-OES has confirmed the content of Nb impregnated into the samples. Analysis of the spent catalysts as well as the solutions after the reaction has shown no leaching neither Nb nor Zr during the reaction in the hydrothermal reaction media.

Table 5. Texture (specific surface area S_{BET} , total pore volume V_{PORE} , average mesopore diameter $\langle d_{PORE} \rangle$) parameters of NbO_x/ZrO₂ catalysts determined by nitrogen adsorption method and ZrO₂ phase composition revealed by XRD.

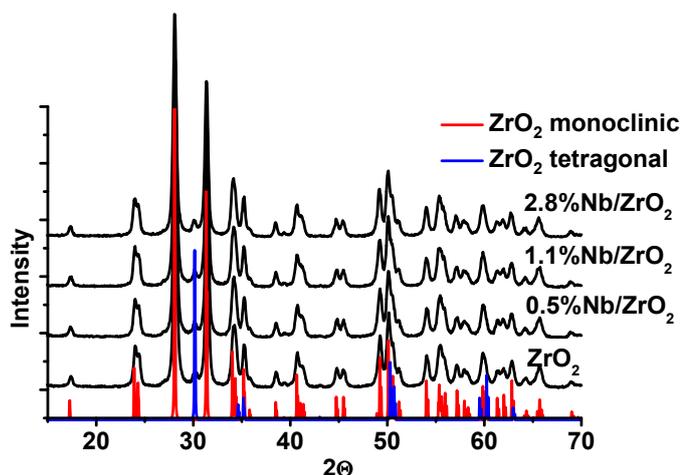
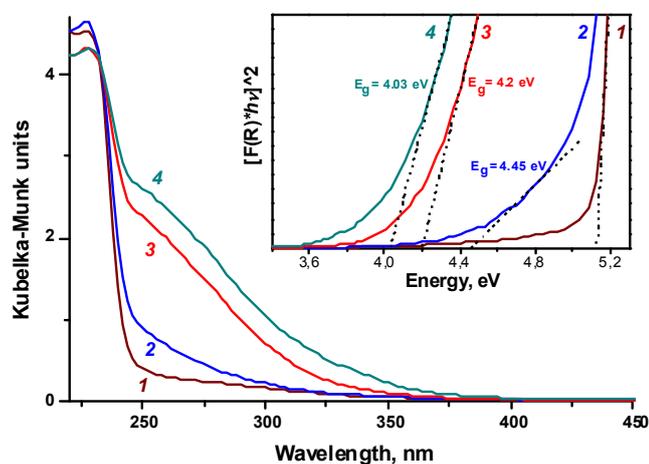
Sample	Texture parameters			Phase composition ZrO ₂ , %	
	S_{BET} , m ² ·g ⁻¹	V_{PORE} , cm ³ ·g ⁻¹	d_{PORE} , nm	<i>Monoclinic</i>	<i>Tetragonal</i>
ZrO ₂	16	0.08	20	99	1
0.5%Nb/ZrO ₂	12	0.09	30	97	3
1.1%Nb/ZrO ₂	11	0.08	29	97	3
2.8%Nb/ZrO ₂	12	0.09	29	97	3

Texture properties of the catalysts have been revealed by a low-temperature nitrogen adsorption (Table 5). Specific surface area (S_{BET}) of non-modified ZrO₂ is 16 m²·g⁻¹, and total pore volume (V_{PORE}) is extremely low. Isotherms are identified as an example of the III type which is typical of non-porous and/or macroporous materials having no micro/mesopores. Low S_{BET} of ZrO₂ has been expected as the values of S_{BET} for such kind of materials are often not higher than 10-20 m²·g⁻¹ because of agglomeration during the calcination [82]. Addition of niobium to the catalyst leads to decreasing S_{BET} by ~ 25% to 11-12 m²·g⁻¹ and to increasing the average pore diameter ($\langle d_{PORE} \rangle$) by 50% from 20 to 30 nm. At the same time, V_{PORE} remains unchanged. S_{BET} and $\langle d_{PORE} \rangle$ do not depend on the amount of Nb added to the catalysts in the range of 0.5-2.8 wt%. Decreasing surface area after Nb precipitation could be explained by partial blockage of an internal space of catalyst grains by high-dispersed Nb species.

CHAPTER 4. CELLULOSE HYDROLYSIS-DEHYDRATION

From XRD data, the ZrO_2 and $\text{NbO}_x/\text{ZrO}_2$ catalysts contain mainly monoclinic phase of zirconia (99% for pure ZrO_2 and 97% for $\text{NbO}_x/\text{ZrO}_2$) (Table 5, Figure 22). This confirms the monoclinic structure is more thermally stable than the tetragonal one [238, 239]. XRD data obtained confirm the amorphous state of the active component but not the formation of the crystalline niobium oxide (Figure 22). The absence of crystalline phases of niobia after the immobilization on the surface of other oxide supports was previously shown in literature [239].

The coordination geometry and the chemical arrangement of the Nb species in the catalysts have been studied by UV-vis DRS spectroscopy (Figure 23). This method is the only appropriate one for investigating acid surface sites over $\text{NbO}_x/\text{ZrO}_2$ catalysts as these catalytic systems have low specific surface area and Nb content. Traditional technique being used to study Brønsted acid sites by pyridine adsorption followed by IR spectroscopy has low sensitivity for the catalysts with a loading of niobium less than 5 wt.% [240]. Also the ammonia adsorption method of $\text{NbO}_x/\text{ZrO}_2$ analysis has not revealed any appropriate results. Thus, we have used UV-vis DRS spectroscopy. This technique has been chosen since, a relationship between the absorption edge energy and the degree of condensation of niobium oxide species have been previously shown [241, 242]. The zirconia absorption edge energy ($E_g=5.13$ eV) due to the charge transfer transition $\text{O}^{2-} \rightarrow \text{Zr}^{4+}$ is consistent with the reported data [242]. The absorption edge energy for niobate species in $\text{NbO}_x/\text{ZrO}_2$ for 0.5%Nb/ ZrO_2 ($E_g = 4.45$ eV) is close to that reported for isolated NbO_4 species in Nb-MCM-41 [241] and to that of niobium oxalate [242] what indicates the formation of isolated NbO_4 mainly. The UV-vis absorption edge energy for 1.1%Nb/ ZrO_2 and 2.8%Nb/ ZrO_2 decreases to 4.20 and 4.03 eV (Figure 23, *inset*) towards the typical value of polymeric Nb structures (for example, niobic acid, $\text{Nb}_2\text{O}_5 \cdot n\text{H}_2\text{O}$, $E_g = 3.9$ eV [242]). However, these values remain higher than that measured for niobium oxide ($E_g = 3.42\text{-}3.2$ eV). The red shift of edge energy with increasing Nb loading indicates a higher degree of polymerization: the Nb cations in the 0.5%Nb/ ZrO_2 sample are predominantly isolated NbO_4 species, while polymerized surface niobia NbO_x (NbO_6) species are formed in the 1.1-2.8 %Nb/ ZrO_2 catalysts [241, 242].


 Figure 22. XRD patterns of $\text{NbO}_x/\text{ZrO}_2$ catalysts

 Figure 23. Diffuse reflectance UV-Vis spectra of ZrO_2 (1) and $\text{NbO}_x/\text{ZrO}_2$ catalysts: 0.5 wt% Nb (2), 1.1 wt% Nb (3), 2.8 wt% Nb (4); inset shows the Kubelka-Munk function vs. energy of the excitation source.

4.1.2 Cellulose one-pot hydrothermal hydrolysis-dehydration over $\text{NbO}_x/\text{ZrO}_2$ catalysts

The results of the catalytic hydrothermal hydrolysis-dehydration of mechanically-activated cellulose in the autoclave at 453 K and inert argon atmosphere are shown in Table 6. The main reaction products are glucose and 5-HMF. The formation of low amounts of mannose and fructose (via glucose isomerization), formic and levulinic acids (caused by 5-HMF decomposition), and furfural (the side-product of fructose transformation) have been observed in this study and, previously in literature [92, 243]. The formation of oligosaccharides is observed in 0 and 1h HPLC aliquots. Then the yields of soluble oligomers are decreased to zero. Under the reaction conditions used, some humins being the solid side products of 5-HMF degradation are also formed. Formatting humins is unavoidable at high

temperature which is indispensable for the effective transformation of cellulose possessing a structure, one is very steady to hydrolytic impact [81].

A problem of cellulose treatment is that both cellulose and an oxide catalyst are solids and a way is needed to form water soluble oligosaccharides which could be transformed into glucose and HMF on a catalyst surface. It is well known that ion product of water (K_w) is increased with increasing temperature. At the temperature near 200 °C $-\lg K_w$ increases from 14 (at 273 K) to 11 what also increases the concentrations of H^+ and OH^- ions [89]. Such changes of water properties let the liquid to play a role of co-catalyst in cellulose hydrolysis-dehydration [91]. Also pH measurements confirm the mediate formation of some H^+ when adding a solid acid catalyst to the reaction mixture (Table 6).

Using HPLC data the yields (Y) of the products were calculated via the formula in Chapter 2. Turnover frequency, TOF (s^{-1}), i.e. the combined amount of glucose and 5-HMF (mol) produced by NbO_x/ZrO_2 of the catalyst (mol) per second was calculated according to the formula:

$$TOF = \frac{A_0 \cdot V}{m_{cat} \cdot \left(\frac{\omega_{Nb}}{M_{Nb}} + \frac{\omega_{ZrO_2}}{M_{ZrO_2}} \right)}, \quad (11)$$

where A_0 is the initial reaction rate of combined glucose and HMF formation ($mol\ L^{-1}\ s^{-1}$); V is the volume of the reaction mixture (L); m_{cat} is the mass of the catalyst (g); M_{Nb} is the molar mass of niobium ($92\ g\ mol^{-1}$); M_{ZrO_2} is the molar mass of zirconium oxide ($132.222\ g\ mol^{-1}$); ω_{Nb} and ω_{ZrO_2} are the mass portions of niobium and zirconia, respectively.

The initial reaction rate A_0 ($mol\ L^{-1}\ c^{-1}$) was determined from the kinetic data as follows:

$$A_0 = \frac{(C_{Glu} + C_{HMF}) - (C_{Glu}^0 + C_{HMF}^0)}{\tau}, \quad (12)$$

where A_0 is the rate of combined glucose and 5-HMF formation ($mol\ L^{-1}\ s^{-1}$); C_{Glu} and C_{HMF} are the concentrations of glucose and 5-HMF ($mol \cdot L^{-1}$), respectively, achieved at the second kinetic point (1 h reaction time); C_{Glu}^0 and C_{5-HMF}^0 are the concentrations of glucose and 5-HMF ($mol \cdot L^{-1}$), respectively, at the first kinetic point (0 h reaction time, C_{5-HMF}^0 is zero); τ is the reaction time measured in seconds.

Maximum yields of all the side-products usually are no more than 1-1.5 mol% except the yield of levulinic acid that reaches 1.8 mol% and 2.5 mol% after 5 h of the reaction over 1.1%Nb/ZrO₂ and 2.8%Nb/ZrO₂, respectively (Table 6).

All the catalysts are highly active to the formation of 5-HMF, while it is not formed in the blank experiment at all. It is also interesting that in the blank experiment maximal glucose yield is only 7.0 mol% after 5 h of the reaction when in the presence of all the catalysts the maximal yields of glucose are 12.7-22.0 mol%. These yields are achieved at 3 h for all the catalysts except 0.5%Nb/ZrO₂.

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Increasing of glucose yields in the presence of solid catalysts demonstrates that the cellulose depolymerization occurs not only because of catalysis by hot water. A mediate catalytic action of the solid catalysts takes place. The mediate acidity of the reaction mixture is confirmed by pH. In the experiment with pure water pH is 5.5. In the mixtures with catalysts pH is 3.6-4.5 and it decreases with increasing Nb loading.

Initial reaction rates A_0 calculated from combined glucose and 5-HMF formation are 5-20 times higher in the presence of the catalysts compared to the blank experiment. The activity of pure zirconia (without Nb) is high enough. Maximum yields of glucose and 5-HMF over ZrO_2 are 12.7 mol% and 13.3 mol%, respectively. The observed activity of this catalyst to cellulose treatment is higher than that described in the literature [180]. Thus Wang and co-authors reached 9 mol% glucose and 15.8 mol% total yield from cellulose over pure ZrO_2 after 12 h of reaction at 160 °C. Pure ZrO_2 developed in this work also demonstrates comparable activity to mixed ZrO_2 - TiO_2 (8.6 mol% 5-HMF yield at 300 °C [176]) and sulfated ZrO_2 (14 mol% of glucose at 150 °C and 24 h [90]).

However, almost two-fold decrease in the catalytic activity (initial reaction rate A_0 and TOF) is observed upon addition of small amount of NbO_x to the catalyst. The close yield of glucose (12.9 mol%) is reached only at 5 h of reaction (Table 6). Decreasing the activity of 0.5%Nb/ ZrO_2 takes place in spite of increasing the reaction medium acidity as compared to one occurred with ZrO_2 . Further increasing the Nb loading up to 1.1 and 2.8 wt% leads to a. 2 times rising the activity against that observed with ZrO_2 . Close activities of 1.1%Nb/ ZrO_2 and 2.8%Nb/ ZrO_2 and close yields of glucose and HMF over these catalysts (21-22 mol% and 16 mol%, respectively, see Table 6) are revealed. However the yield of levulinic acid formed via HMF decomposition is somewhat higher over 2.8%Nb/ ZrO_2 than over 1.1%Nb/ ZrO_2 indicating that the catalytic activity of 2.8%Nb/ ZrO_2 is a little bit higher. This similar results could be accounted for close pH values of the reaction media which takes place in spite of double difference of Nb loading.

To our knowledge, the NbO_x / ZrO_2 catalytic system has not been used before for direct cellulose transformation to glucose and HMF in pure water. Concerning the utilization of niobium for cellulose depolymerization, Takagaki et al. investigated this process over $HNbMoO_6$ oxide [183]. The authors have found 1 mol% Glucose yield and 8.5 mol% total yield of the main products (cellobiose and glucose). So low yields of monomers and an absence of HMF could be explained by a low temperature equal to 100 °C [183].

The activity changes can be interpreted in the following manner. Zirconia is known to be an acid-base bifunctional catalyst and the cooperation of weak Lewis acid and weak base sites (acid-base pairs are suitably oriented on ZrO_2) plays an important role in the achievement of high selectivity to some reactions [244]. Previously, the concentration of Lewis acid sites on the zirconia surface was shown not to be decreased when niobium oxide was supported on a surface [242]. Thus we guided by

the literature information could assume that in spite of small increasing total acidity (according to pH) of the reaction medium decreasing the activity of 0.5%Nb/ZrO₂ compared to ZrO₂ could be accounted for by forming basically dispersed isolated NbO₄ species which isolate spatially the acid and base centers (according to UV-vis DRS). This also let us to suppose that the catalyst surface plays some role in the hydrolysis of cellulose to glucose. Unfortunately, as mentioned above in chapter 4.1.1, the direct techniques for measuring acidity of catalysts could not be used. The formation of additional Brönsted sites was observed upon supporting niobium at concentrations higher than 0.69 wt%, 3.4 wt% and 5 wt% on zirconia [242], titania [245], and alumina [246], respectively. Analysis of the Nb phase structure has shown that the Brönsted acidity was associated with polymeric NbO_x species while isolated species had no acidity [242]. In the catalysts under investigation polymerized NbO_x (NbO₆) species are formed, as shown above by UV-vis DRS, when 1.1-2.8 wt% Nb are impregnated. Obviously, additional acid sites causes increasing activity to cellulose depolymerization.

When the reaction finished the TOC analysis of the solutions has been made. The results are shown in Table 6. TOC of all the reaction mixtures are quite close to each other. However TOC values (g·L⁻¹) increase as following: 2.01 < 2.16 < 2.26 ~ 2.29. This order is similar to the catalyst activity 0.5%Nb/ZrO₂ < ZrO₂ << 1.1%Nb/ZrO₂ ~ 2.8%Nb/ZrO₂.

The cellulose conversion (X) has been determined from the TOC data by the formula (10). The cellulose conversion (X) is shown in Table 3. In the blank experiment the cellulose conversion are 14.1% only while in the catalytic experiments X values are close to 50%. The highest conversion equal 52.3% is observed in the presence of 1.1%Nb/ZrO₂ and 2.8%Nb/ZrO₂.

The most active catalyst 2.8%Nb/ZrO₂ has been tested in dehydration of the main cellulose transformation intermediates: glucose and fructose, and 5-HMF degradation has been also studied under the conditions used for cellulose treatment (Table 7). Using HPLC results the yields and substrat conversions were calculated by formula (8) and (9). TOF of the catalyst was determined by the formula (11). The initial reaction rate (A_0) was calculated as the rate of the substrate consumption:

$$A_0 = -(C - C^0) \cdot \tau^{-1} . \quad (13)$$

where A_0 is the rate of glucose and 5-HMF formation (mol L⁻¹ s⁻¹); C and C^0 are the actual and initial concentrations of a substrate, respectively (mol L⁻¹); τ is the reaction time measured in seconds.

Table 6. Cellulose hydrolysis-dehydration in the presence of $\text{NbO}_x/\text{ZrO}_2$. Conditions: $[\text{Cell}]=[\text{Cat}]=10\text{g}\cdot\text{L}^{-1}$, 45 mL, 180 °C, P_{Ar} 10 bar, 1500 rpm, reaction time 5 h.

Catalyst sample	pH of the reaction solution		A_0 , $\text{mol}\cdot\text{L}^{-1}\cdot\text{c}^{-1}\cdot 10^6$	TOF, $\text{s}^{-1}\cdot 10^{7*}$	TOC, $\text{g}\cdot\text{L}^{-1}$	X , %	Yields of the products identified							
	before	after					Glu Maximal		Glu	5-HMF	Fr	FA	LA	Total
							τ , h	Y , %						
blank	5.5	n.d.	0.2	-	n.d.	14.1	7.0	5	7.0	0.0	0.0	0.0	0.0	7.0
ZrO_2	4.5	2.7	2.3	2.8	2.16	50.0	12.7	3	12.6	13.3	0.0	0.5	0.0	26.4
0.5%Nb/ ZrO_2	4.0	3.0	1.1	1.4	2.01	45.5	12.9	5	12.9	12.9	0.0	0.1	0.0	25.9
1.1%Nb/ ZrO_2	3.6	2.8	4.0	4.8	2.26	52.3	21.3	3	17.9	16.3	0.0	0.0	1.8	36.0
2.8%Nb/ ZrO_2	3.6	2.7	4.3	5.2	2.29	52.3	22.0	3	16.3	16.1	0.0	0.0	2.5	34.9

Table 7. Dehydration of the main cellulose transformation intermediates in the presence of 2.8%Nb/ ZrO_2 . Conditions: $[\text{Cat}]=10\text{g}\cdot\text{L}^{-1}$, $[\text{Substrate}]=50\text{mM}\cdot\text{L}^{-1}$, 45 mL, 180 °C, P_{Ar} 10 bar, 1500 rpm, reaction time 5 h.

Substrate	pH of the reaction solution		A_0 , $\text{mol}\cdot\text{L}^{-1}\cdot\text{c}^{-1}\cdot 10^6$	TOF $\cdot 10^7$	X , % before	Yields of the products identified						
	before	after				5-HMF Maximal		Glu	Fr	5-HMF	FA	LA
						τ , h	Y , %					
Glucose	3.6	2.7	5.0	6.3	84.3	22.6	3	-	2.7	20.6	1.4	2.4
Fructose	3.6	2.7	9.4	11.8	100.0	31.8	0.5	16.4	-	10.5	3.2	8.2
5-HMF	3.6	2.7	1.0	0.1	56.7	-	-	0.0	0.0	-	2.2	4.2

The highest yields of HMF obtained from glucose and fructose equal to 22.6 and 31.8 wt.%, respectively, are achieved after 3 and 0.5 h of the reaction. The fructose transformation is the fast reaction (X of Fructose is 100% at 1 h) while glucose treatment is slower as it is limited by isomerization of glucose to fructose. We have not achieved a very high yield of HMF from monosaccharides due to its degradation (X equal to 56.7 wt.% at 5 h) at 180 °C. The yields of Levulinic and Formic acids derived from HMF and furfural are very low in all the experiments made as they are unstable under the reaction conditions.

NbO_x/ZrO₂ catalysts underwent hydrothermal treatment at 200, 250 and 300 °C to investigate the catalyst stability under harsh conditions. XRD and ICP demonstrated excellent stability of the oxide catalytic system.

4.2 Cellulose hydrolysis-dehydration over the catalysts based on carbon material Sibunit-4[®]

4.2.1 Catalyst characterization

As stated above, carbon materials seem to be perspective catalysts for hydrolytic cellulose transformations. Advantages of carbons, including Sibunit, are high specific surface area, stability, low costs [1, 141, 247]. A common feature of these materials is that their surface acidity is insufficient for depolymerization of the chemically stable polysaccharide such as cellulose. In our studies, we used carbon material Sibunit (fraction 56 – 94 μm) to prepare catalysts for cellulose hydrolysis. Low-temperature nitrogen adsorption was used for determining the surface area of the initial non-modified carbon material, and titration with alkali for determining the content of acid species (phenolic, lactonic, carboxylic); these were 379 m²·g⁻¹ and 0.042 mmol·g⁻¹, respectively (Table 8).

Three methods were investigated for studying the effect of various treatment procedures on the catalyst properties.

1) Sulfonation of Sibunit by concentrated sulfuric acid at 80, 150, 200 and 250 °C. The catalysts developed were named C-S80, C-S150, C-S200 and C-S250, respectively.

2) Oxidation by wet air mixture or 32 and 23% nitric acid solutions (catalysts C-O, C-N32 and C-N23, respectively).

3) The third method is a combination of the first and the second techniques. The oxydized catalysts were then sulfonated at 200 °C. The catalysts were named as C-O-S200, C-N32-S200 and C-N23-S200.

Three series of catalysts were thus prepared. The catalysts were characterized, tested in the reaction conditions in pure water and in the reaction itself. Our aim was to identify optimal conditions of the Sibunit treatment for not only anchoring the maximal quantity of acid species but also preventing considerable changes in the carbon morphology.

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Table 8. Textural characteristics of Sibunit catalysts determined by low temperature N₂ adsorption, the content of acid groups on the surface of the catalysts measured by titration with NaOH.

#	Catalyst	S _{BET} , m ² ·g ⁻¹	V _{mesopore} , cm ³ ·g ⁻¹	C _{acid groups} , mmol·g ⁻¹	C _{acid groups} , μmol·m ⁻²
1	C	379	0.213	0.042	0.11
2	C-S80	344	0.200	0.14	0.41
3	C-S150	360	0.222	0.32	0.88
4	C-S200	400	0.240	0.40	1.00
5	C-S250	221	0.069	0.62	2.68
6	C-O	348	0.33	0.28	0.80
7	C-N32	320	0.27	0.36	1.12
8	C-N23	306	0.22	0.33	1.08
9	C-O-S200	343	0.30	0.49	1.43
10	C-N32-S200	290	0.27	0.51	1.76
11	C-N23-S200	299	0.23	0.49	1.64

The low temperature adsorption studies (Table 8) demonstrated that sulfonation at 200 °C does not result in a considerable decrease in the surface area (S_{BET}) and mesopore volume (V_{mesopore}), both S_{BET} and V_{mesopore} being even slightly increased at 200 °C. At 250 °C, there is observed ca. 30 % decrease in S_{BET} while the mesopore volume decreases down to less than one third of the mesopore volumes of the other sulfonated samples and of initial Sibunit. This is an evidence of the destruction of the carbon texture, probably, due to collapsing mesopores. Nitrogen adsorption studies of the oxidized and oxidize-sulfonated catalysts demonstrated that all the treatment procedures used result in a partial destruction of the carbon structure. The oxidation with wet air appeared a more structure-friendly procedure than oxidation with nitric acid (Table 8). Generally, the surface areas and pore volumes decrease in the series: C > C-O > C-O-S200 > C-N32 > C-N23 > C-N23-S200 > C-N32-S200, i.e. additional sulfonation of oxidized catalysts causes more damage to the carbon structure (Table 8).

A total of phenolic, lactonic, carboxylic and sulfo-group contents was determined by titration with NaOH (Table 8). In the sulfonated samples after hydrothermal treatment and washing with water, the content of acid groups increases upon temperature elevation to as high as 3 to 15 times of the content in the initial Sibunit samples. The maximal content of acid species (0.62 mmol·g_{catalyst}⁻¹) was characteristics of the C-S250 sample. Concentrations of acid groups per surface area of samples C-S200 and C-S250 (1.00 and 2.68 μmol·m⁻², respectively) were comparable to the concentrations of acid groups in activated carbons referred to in literature (1.1 to 2.0 μmol·m⁻²) [32, 90, 140]. The contents of the acid groups vary from 0.80 to 1.12 μmol·m⁻² after the oxidation and increase up to 1.43

– $1.76 \mu\text{mol}\cdot\text{m}^{-2}$ after the following sulfonation. Generally, we can conclude that the total content of acid groups is comparable in the oxidized samples but 1.5-2 times higher in the oxidized-sulfonated samples than in the sulfonated Sibunit sample C-S200 (Table 8).

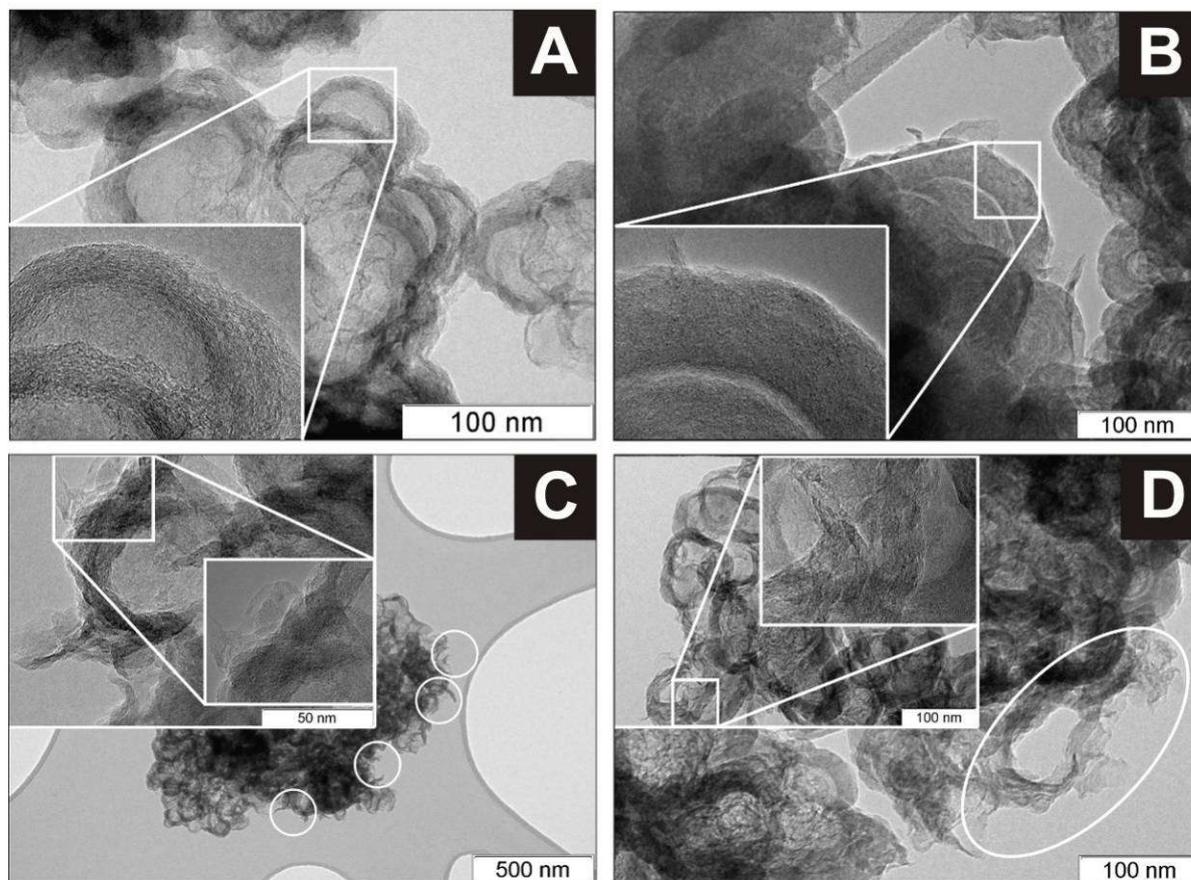


Figure 24. TEM images of Sibunit carbon samples: a) non-treated Sibunit (C), b) Sibunit sulfonated at 200 °C (C-S200), c) Sibunit sulfonated at 250 °C (C-S250), and d) Sibunit oxidized by 32% HNO_3 (C-N32).

The obtained TEM data indicate similar morphologies of all the catalysts under study and of initial Sibunit (Figure 24). They consist of hollow globules agglomerated into coarser particles of up to several microns in size. The linear globule size varies over a wide range between 50 and 300 nm. The globule walls are built up by several azimuthally oriented graphite layers. Apparently, the Sibunit morphology is a stable enough graphite-like material and does not undergo profound rearrangement during oxidation and sulfonation (see C and C-S200, Figure 24, A and B). The modification touches mainly the carbon surface due to chemical bonding of acid groups. Changes in the specific surface areas of the treated carbons are accounted for by complete (C-S250 and C-N32, Figure 24 C and D) or partial (C-S200, Figure 24 B) destruction of some Sibunit globules under the action of strong oxidants (sulfuric or nitric acid). Strongly destroyed Sibunit globules are clearly seen in TEM images of catalysts C-S250 and C-N32 (Figure 24 C and D). The surface area and mesopore volume decrease

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upon complete destruction of the globules (C-S250, Table 8, line 5) but increase upon their partial destruction (C-S200, Table 8, line 4). The latter may result from the partial destruction of the globule walls and “opening” of closed voids that are formed during synthesis of Sibunit via soot burning from globules of pyrolytic carbon [247].

Table 9. Atom concentrations of different element states of the sample surface.

#	Catalyst	C	S		O	N		Na
			S ²⁻	-SO ₃ ⁻		(C-N)	NO ₂ ⁻ /NO ₃ ⁻	
1	C	92928	33	0	3511	0	0	0
2	C-S80	81517	19	45	3414	0	0	0
3	C-S150	82259	27	82	4528	0	0	0
4	C-S200	78981	27	51	5502	0	0	728
5	C-S250	92146	24	42	6534	0	0	0
6	C-O	85856	42	0	4396	0	0	0
7	C-O20-S200	89989	26	31	6257	0	0	0
8	C-N32	80857	21	0	4566	192	111	0
9	C-N32-S200	77757	24	19	5272	112	0	0

XPS analysis was used for determining sulfur and oxygen content in sulfonated Sibunit samples (Table 9). There are only observed the lines assigned to carbon and oxygen in the panoramic spectra of all the samples under study. In order to identify chemical states of the elements on the sample surface, S2p, C1s and O1s spectra were acquired. The Na1s spectrum was acquired additionally for C-S200, and N1s spectrum for samples C-N32 and C-N32-S200. The C1s line (at 284.5 eV) of carbon in Sibunit was used for calibration [248].

In the S2p spectra (Figure 25) of samples C, C-S80, C-S150, C-S200, C-S250, C-O, C-O-S200, two states of sulfur are identified with all the samples except the Sibunit support (C) and C-O where an only sulfur state is identified. The peak at $E_b \sim 164$ eV can be assigned to the sulfur constituent of sulfides (S²⁻). The peak at 168.3 eV is characteristic of oxygen-bound sulfur with a high oxidation state and assigned usually either to sulfate-ion (-SO₄⁻) (free [249-251] or on the surface of various oxides [252, 253]) or to sulfo-group (-SO₃⁻) [254, 255]. While the difference in bond energies of sulfates and sulfites is no more than 1 eV [253], it is hardly possible to use XPS to identify more precisely the sulfur state on the surface. Seemingly, sulfur is as the sulfide impurity in the initial Sibunit support. The presence of sulfur in the form of sulfate leads to suppose two types of sulfur-containing species on

the Sibunit surface (Figure 26). The first assumes the Van-der-Waals forces between free sulfate-ions and the surface (physical adsorption) or weak hydrogen bonds between sulfate-ions and the hydrophobic carbon surface [31, 157] (Figure 26 IA and IB, respectively). The second implies the covalent interaction of oxygen-surrounded sulfur atoms with the carbon surface through bridge oxygen ($-\text{SO}_4^-$) or direct C-S bond of the sulfo-group ($-\text{SO}_3^-$) (Figure 26 IIA and IIB, respectively) resulted from an attack of the sulfating electrophilic agents to oxygen atoms bound through the C-O bond to the surface or to the negatively charged Sibunit surface, respectively.

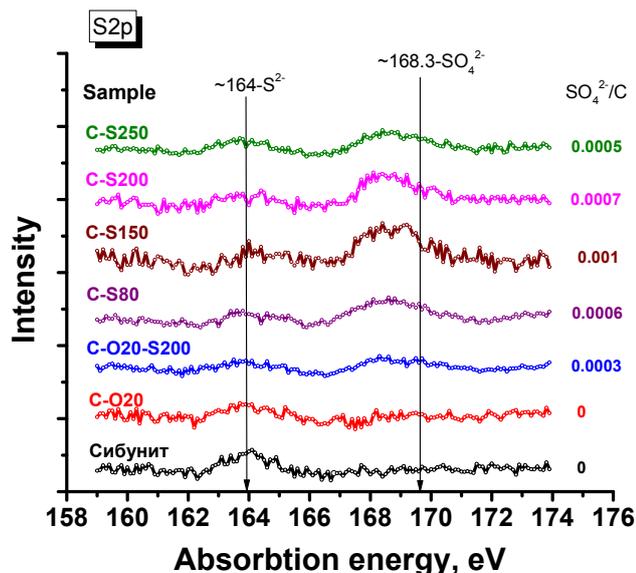


Figure 25. XPS spectra of S2p line measured for the C, C-S80, C-S150, C-S200, C-S250, C-O20, C-O20-S200 catalysts.

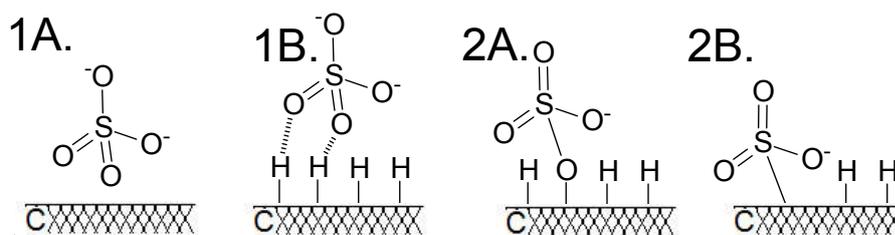


Figure 26. Possible models of interaction between carbon material and S-containing particles.

Table 10. XRF analysis of sulfur content in C-S200 and C-O-S200 samples before and after hydrothermal treatment at 200, 250 and 300 °C.

Catalyst	Sulfur content, %			
	Before treatment	After hydrothermal treatment		
		200 °C	250 °C	300 °C
C-S200	0.24	0.25	0.15	0.13
C-O-S200	0.17	0.16	0.14	0.10

The type of bonding sulfur-containing species to the surface determines directly the catalyst stability in the aggressive reaction medium. In order to characterize the catalyst stability, the samples were subjected to hydrothermal treatment at 200 °C, 250 and 300 °C followed by XRF analysis for the sulfur content (Table 10). Analysis of the treated catalysts revealed the sulfur content closed to the initial content to indicate clearly the catalyst stability under the strong conditions at 200 °C. When the temperature is higher than 200 °C, decreasing sulfur content takes place. Hence, we can conclude about the chemical interaction between the sulfur-containing species and the carbon surface: otherwise, the sulfur would be leached from the catalyst. Again, sulfo-groups should be namely connected to the surface because of the common knowledge that sulfoacids ($C-SO_3^-$ type compounds) are stable in aqueous media but sulfoperoxides ($C-O-SO_3^-$) are very unstable and easily hydrolyzed in aqueous media or upon temperature elevation.

Sulfur in the sulfide state was only observed in the S2p spectrum of C-N32 sample but an additional sulfur bound with oxygen (as sulfate-ions $-SO_4^{2-}$ or sulfo-groups $-SO_3^-$) in the S2p spectrum of C-N32-S200 sample (Figure 27). In the N1s spectra, there are observed two nitrogen states with bond energies 339.6 and 405.7 eV, which are characteristic of nitrogen bound with carbon (C-N) [256] and of nitrogen in nitrate groups (NO_3^-) [257], respectively. Supposedly, nitrogen bound to oxygen is formed upon treatment of the carbon material with nitric acid similar to the process of sulfonation. This is a feasible interaction because rather strong δ^+ charge is accumulated in nitrogen in the nitric acid molecule but the non-modified carbon surface is negatively charged [258]. Hence, the electrophilic attack to the negatively charged surface may happen. The presence of nitrates on the surface of the oxidized catalyst may be accounted for by incomplete washing of the sample from oxidizing agent HNO_3 after the surface modification.

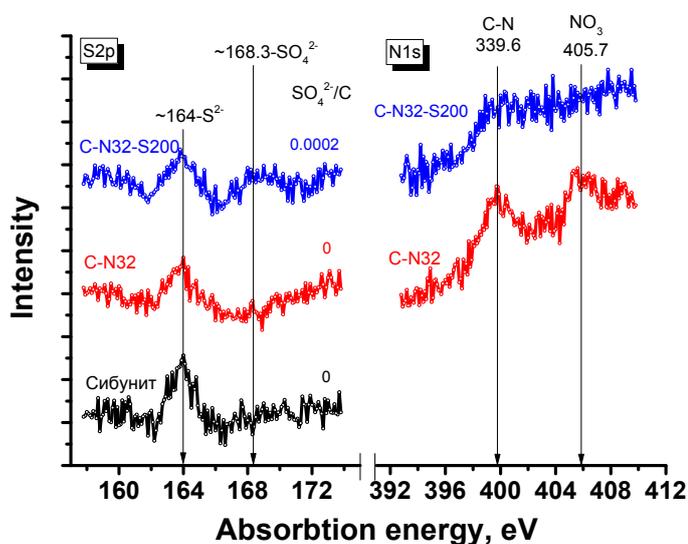


Figure 27. XPS spectra of S2p and N1s lines measured for C-N32 and C-N32-S200 catalysts.

Unfortunately, it is difficult to inspect the states of oxygen bound to sulfur and nitrogen due to the presence of an intense O1s signal from the initial Sibunit support. Nevertheless, atomic O/C ratios on the sample surfaces were analyzed (Table 11).

Relative surface contents of elements and their atomic concentration ratios were determined from integral intensities photoelectron lines in C1s, S2p, N1s and O1s regions corrected for the coefficients of atomic response [259]. The weight proportions (ω_i , %) of surface sulfur and oxygen given in Table 11 were calculated according to the formula:

$$\omega_i = \frac{N_i \cdot a_i}{\sum_i N_i \cdot a_i} \cdot 100, \quad (14)$$

where ω_i is a weight proportion of an element, N_i is the atom concentration of the element, a_i is the element atom weight.

Table 11. Atom ratio of the elements on the sample surface as well as evaluative wait amount of sulfur element being in sulfate state ($-\text{SO}_3^-$).

#	Catalyst	$-\text{SO}_3^-/\text{C}$	O/C	ω_i , %		
				S	O	S+O
1	C	0	0.038	0	5.02	5.02
2	C-S80	0.00056	0.042	0.14	5.28	5.42
3	C-S150	0.00100	0.055	0.25	6.81	7.06
4	C-S200	0.00064	0.070	0.15	8.34	8.49
5	C-S250	0.00045	0.071	0.11	8.63	8.74
6	C-O	0	0.051	0	6.38	6.38
7	C-O20-S200	0.00034	0.070	0.08	8.47	8.55
8	C-N32	0	0.056	0	6.97	6.97
9	C-N32-S200	0.00024	0.068	0.06	8.27	8.33

The XPS data showed that the non-modified Sibunit and oxidized catalyst samples were free of sulfo-groups. The relative weight contents of sulfur in the form of sulfo-groups on the surface of sulfonated carbon were almost doubled, from 0.14 wt % to 0.25 wt %, as the sulfonation temperature rose from 80 to 150 °C. However, the quantity of supported sulfur in the form of $-\text{SO}_3^-$ was then decreased down to 0.15 and 0.11 wt % at 200 and 250 °C, respectively. It is interesting that the sulfonation was accompanied by a noticeable increase in the oxygen atomic proportion as the sulfonation temperature rose. The increase in the oxygen proportion cannot be accounted by

sulfonation only. The quantity of sulfur-bonded oxygen could not be measured but only estimated in assumption that, upon supporting one sulfo-group ($-\text{SO}_3^-$), three oxygen atoms are fixed with one sulfur atom. Since the atomic mass ratio of one sulfur atom and three oxygen atoms is equal to $3 \cdot a_o / a_s = 3 \cdot 15.999 / 32.059 = 1.50$, the quantities of oxygen in sulfo-groups supported on the surface are estimated as 0.21, 0.37, 0.22 and 0.16 wt.% in C-S80, C-S150, C-S200, C-S250, respectively. That these estimations are lower than the related XPS data (except those for C-S80 with almost identical XPS and estimated quantities) indicates the absence, practically, of oxidation processes during sulfonation at 80 °C. At higher treatment temperature, the oxidation of the Sibunit surface by sulfuric acid is accompanied, along with the sulfonation, by the formation of surface acid species (hydroxyl, carboxylic, lactic, carbonylic).

Comparison of carbons oxidized with a wet air mixture and 32 v/v.% nitric acid solution (C-O and C-N32, respectively) showed a smaller number of oxygen-containing species supported on the surface in the former case than in the latter. However, comparative analysis of the XPS data on oxidized and oxidized-sulfonated samples gave rather surprising result: sulfonation at 200 °C produced as low quantity of supported sulfo-groups as a half of those in the C-S200 sample.

The sulfonation degree of the carbon material and oxidation depth are obviously opposite to one another: the higher acidity of the Sibunit surface, the lower number of sulfo-groups are supported on the surface. The phenomenon can be explained based on the mechanism of the sulfonation reaction [260].

The active species of sulfonation is sulphurous anhydride, SO_3 ; this is an electron-deficient compound which behaves as an electrophilic agent during sulfonation. The hydrophobic poorly oxidized carbon surface with C-H groups [31, 157] is negatively charged [258]; therefore, the electrophilic anhydride can attack the carbon surface to produce sulfoacid (a C-SO_3^- compound) (Figure 28). However, if the surface is strongly oxidized, electron density is drawn towards the oxygen-containing groups that results in localization of the positive charge on the carbon surface and, therefore, in impossibility of the nucleophilic attack followed by sulfonation (Figure 28).

In general, the developed acid catalysts based on carbon material Sibunit are, unlike untreated carbon, strongly oxidized material which bear preferably acidic oxidized species.

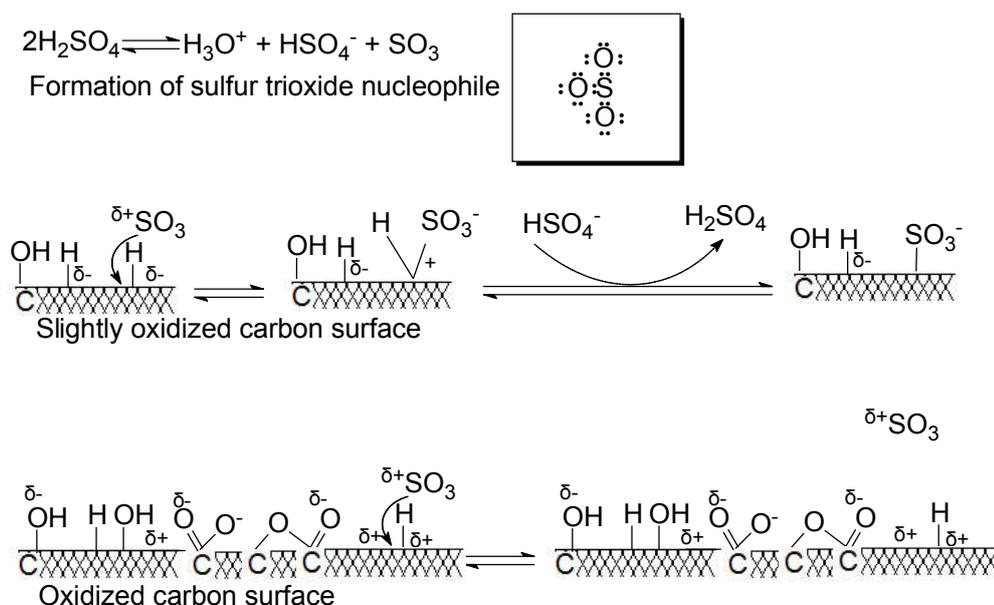


Figure 28. The possible ways of carbon surface sulfonation depending on the surface oxidizing degree.

4.2.2 Cellulose one-pot hydrolysis-dehydration over Sibunit catalysts in a batch reactor

The prepared solid acid catalysts were tested for hydrothermal depolymerization of mechanically activated cellulose at 180 °C in argon atmosphere (Table 12). The yields of the reaction products were calculated according to the formula (6) and the initial reaction rate (A_0) with the formula (12) (see both formulae in Chapter 2). TOF of the carbon catalysts was determined as a ratio of the reaction rate to the total amount of acid groups in the reaction system:

$$\text{TOF} = \frac{A_0 \cdot V \cdot 10^3}{C_{\text{acid groups}} \cdot m_{\text{cat}}} \quad (15)$$

Where $C_{\text{acid groups}}$ is the amount acid groups in the catalyst ($\text{mmol} \cdot \text{g}^{-1}$), m_{cat} is the mass of a catalyst (g).

In addition, three experiments – a blank run (the reaction without catalyst), a run with the catalyst C-S200 amount decreased in 2 times, and a run with $0.02 \text{ mol} \cdot \text{L}^{-1}$ sulfuric acid solution as the catalyst – were conducted for comparison (Table 12, Figure 29). The sulfuric acid concentration was chosen for the content of acid centers H^+ in the reaction medium to be identical to that in the run with the most active carbon catalyst C-S200.

Table 12. Yields of cellulose hydrolysis-dehydration over Sibunit carbon catalysts. Cellulose and catalyst $10 \text{ g}\cdot\text{L}^{-1}$, 45 mL, 180 °C, 10 atm (Ar), 1500 rpm, reaction time 7 h.

#	Catalyst	Yield, %												$A_0,$ $\text{mol}\cdot\text{L}^{-1}\cdot\text{s}^{-1}\cdot 10^7$	TOF, $\text{s}^{-1}\cdot 10^7$	
		Glu		HMF		Celb	Glu	Fr	Mn	HMF	Furf	FA	LA			Total
		Y, %	t, h	Y, %	t, h											
1	blank	7.0	5	0	7	0	6.0	0	0	0	0	0	0	7.0	-	-
2	$0.02 \text{ mol}\cdot\text{L}^{-1}$ H_2SO_4	29.3	1	12.0	3	0	12.9	0	6.7	6.4	1.6	14.0	14.6	61.8	-	-
3	C	0	5	0	7	0	0	0	0	0	0	0	0	0	0	0
4	C-S80	12.1	3	8.7	5	0	5.8	0.5	2.6	6.0	0	0	0	17.6	14.4	1.02
5	C-S150	33.5	2	18.3	7	1.2	23.5	3.6	4.0	18.3	1.5	0	0	50.8	43.1	1.34
6	C-S200	45.9	2	21.5	5	1.0	18.9	6.0	9.7	16.7	5.9	0	0	63.0	55.8	1.39
7	C-S250	30.7	2	16.2	7	1.1	26.7	7.5	9.0	23.4	1.4	0	0	64.7	40.5	0.65
8	C-O	40.7	3	17.8	5	3.1	27.4	1.1	8.4	14.3	0	1.6	1.1	60.5	59.2	2.11
9	C-N32	38.6	2	20.3	5	1.1	22.3	0.1	2.8	15.3	0	1.2	0.0	47.8	47.5	1.31
10	C-N23	40.0	2	18.0	7	0.6	23.7	0.4	7.7	18.0	0	1.7	0.0	52.1	57.7	1.23
11	C-O-S200	43.7	2	17.2	5	0	34.5	0.5	6.6	15.9	0	1.3	1.6	61.7	60.3	1.74
12	C-N32-S200	42.8	3	17.6	7	1.1	31.9	0	4.8	17.6	0	1.2	4.6	61.2	44.9	0.88
13	C-N23-S200	42.6	3	15.9	7	2.9	15.3	0	7.6	15.9	0	2.5	0.6	44.8	47.2	0.96
14 ¹	C-S200	22.8	3	15.9	7	0	15.4	0	0	15.9	0.9	0.8	0	33.0	22.0	0.88

1 - catalyst loading $5 \text{ g}\cdot\text{L}^{-1}$.

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5-HMF and glucose were the main reaction products. Apart from these products, the formation of intermediate (cellobiose and fructose) and side (mannose) products was observed. Formic and levulinic acids were formed in minor quantities (maximal yields 2.5 and 4.6 wt %, respectively) due to decomposition of 5-HMF (Table 12). Furfural at the yield of 1–6 wt % was detected in the reactions over sulfonated carbon. The formation of water-soluble oligosaccharides was only observed during the first hour of the reaction. Note that the total yield of dissolved products of no more than 65 % was observed both with active solid and with dissolved catalysts (Table 12). This may result from incomplete dissolution of cellulose, specifically, the crystal cellulose fraction (ca. 37 %). At the present stage of our study, we failed to isolate unreacted cellulose from the catalyst.

In the blank run, the yield of glucose was no more than 7 wt % at 180 °C, any other product including 5-HMF being not detected.

In the presence of the dissolved acid catalyst (H_2SO_4) (Table 12), the rate of glucose formation was much higher than in the blank run. The maximal yield (29.3 wt %) was observed in one hour but then the glucose concentration decreased. 5-HMF was formed in a noticeable quantity; the maximal yield (12.0 wt %) was reached in 3 h and then the concentration decreased again but levulinic and formic acids were formed as the main reaction products. The yields of these acids (14.6 and 14.0 wt %, respectively) were higher than the yield of 5-HMF.

Studies of the initial Sibunit revealed its absolute catalytic inactivity. Moreover, neither target nor side products were detected in the reaction medium, even though glucose formed in pure water. All the modified catalysts were highly active to the process under study. With all the catalysts, the main products were glucose and its dehydration product – 5-hydroxymethylfurfural (5-HMF). The yields of levulinic and formic acids were no more than 2.5 and 4.6 wt %, respectively.

Kinetic curves of accumulation of the target products in the presence of the sulfonated catalysts are plotted in Figure 30. The maximal yields of glucose and 5-HMF equal to 45.9 wt % and 21.5 wt % were observed in 2 and 5 h, respectively, in the presence of C-S200 (Table 12, Figure 30). When the C-S200 catalyst weight was reduced by half, the rates of formation and the yields of glucose also were halved but the yield of 5-HMF was a factor of ~ 1.4 lower (Figure 29). When the time of hydrolysis lengthened from 2 to 5 h in all the experiments, the yields of glucose decreased several times due to the conversion of glucose to 5-HMF through dehydration (Table 12). It is interesting that the maximal yield of the target reaction products – glucose and 5-HMF – increased upon substitution of C-S80 for C-S200, probably, because of an increase in the number of acid groups. At the same time, the yields were lower in the presence of C-S250 than C-S200, even though the concentration of acid groups was higher on the surface of C-S250 (Table 12, Figure 31). This phenomenon may be accounted for by the strong rupture of the C-S250 surface during its synthesis. The decrease in the specific surface area results in a decrease in the number of the sites exposed to intermediates that are adsorbed and converted

within the surface layer of the catalyst. When so, the observed catalyst activity is limited by the external diffusion of intermediates towards the catalyst surface.

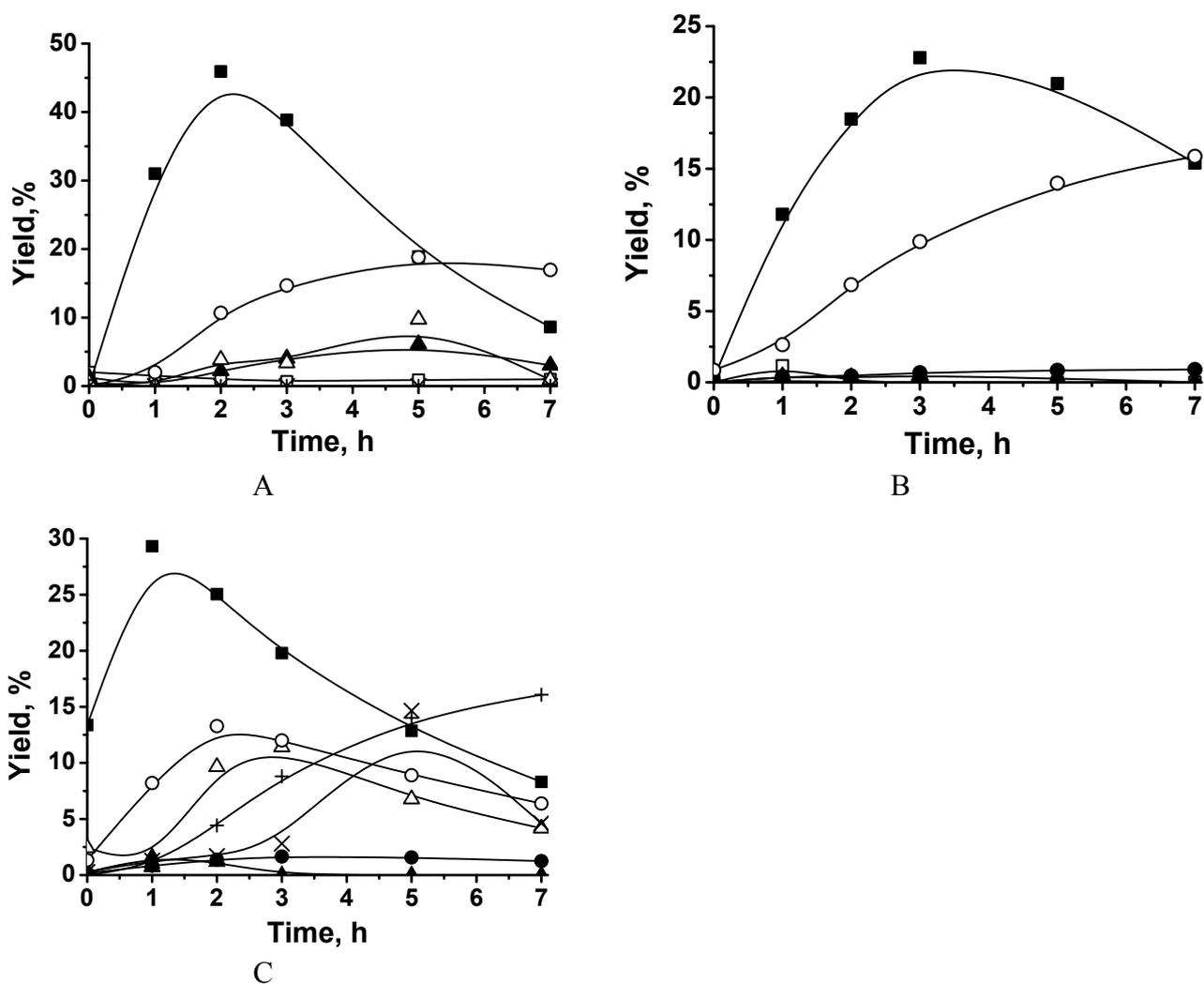


Figure 29. Kinetics of the transformation of the cellulose hydrolysis-dehydration products (□ - Cellobiose, ■ - Glucose, ○ - 5-HMF, △ - Mannose, ▲ - Fructose, ● - Furfural, + - Levulinic acid, × - Formic acid) in the presence A - 450 mg of C-S200, B - 225 mg of C-S200, C - catalyst 4mM solution H₂SO₄. Cellulose 10 g·L⁻¹, 45 mL, 180 °C, 10 atm (Ar), 1500 rpm, reaction time 7 h.

The yields of glucose and the target product, 5-HMF, were observed not to differ considerably over the Sibunit samples oxidized using different methods, probably, due to comparable contents of acid groups on their surfaces (Table 12, Figure 32). However, about the same yields of glucose and 5-HMF were obtained with the oxidized-sulfonated samples, even though the total contents of the surface acid groups were as high as 1.5 times of those in the oxidized catalysts. Averagely, the yields of 5-HMF and glucose varied diversely between 17–20 and 38–40 %, respectively (Table 12). The maximal yield (20.3%) of 5-HMF was obtained over the C-N32 sample oxidized with 32% nitric acid solution, while the maximal yield of glucose (43.7%) in the presence of C-O-S200 oxidized with wet

air and sulfonated. However, these yields were no more than those in the presence of C-S200 sulfonated at 200 °C.

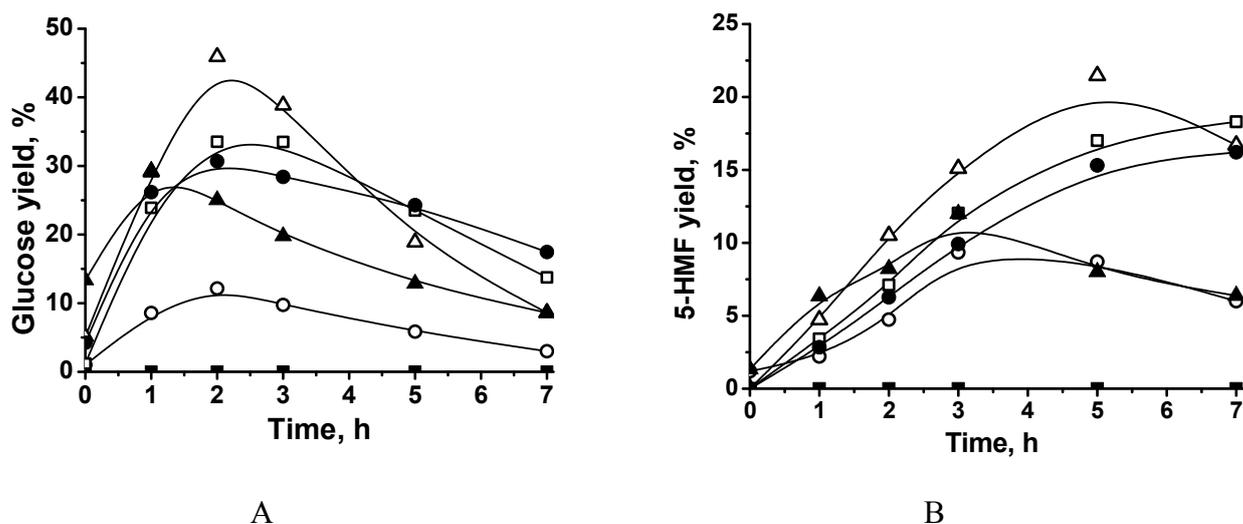


Figure 30. Kinetic curves of glucose (A) and 5-HMF (B) evolution in cellulose hydrolysis-dehydration over sulfonated Sibunit catalysts and in 0.02 M H₂SO₄. ■ – C, ○ - C-S80, □ – C-S150, △ - C-S200, ● – C-S200, ▲ - H₂SO₄. Cellulose and catalyst 10 g·L⁻¹, 45 mL, 180 °C, 10 atm (Ar), 1500 rpm, reaction time 7 h.

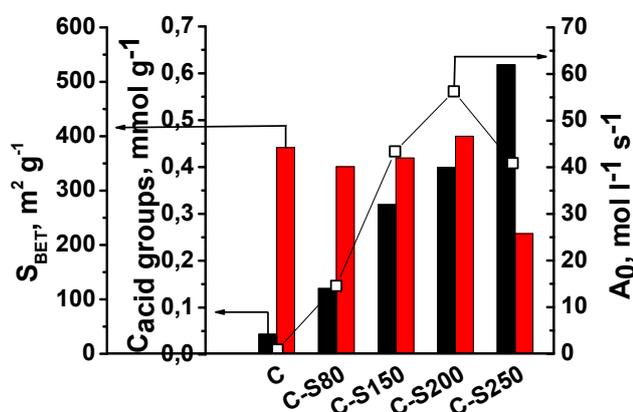


Figure 31. Dependence of the initial reaction rate of combined glucose and 5-HMF formation on specific surface area (S_{BET}) and the content of acid groups on the surface ($C_{acid\ group}$) in the case of sulfonated Sibunit samples.

While close maximal yields of the target products were observed, the catalyst activities can be compared based on the initial rates of a total of the formation of glucose and 5-HMF, A_0 and TOF, determined as the ratio of the rate to the total content of acid groups ($\text{mmol}\cdot\text{g}^{-1}$). The highest A_0 and TOF were observed with a couple of catalysts prepared using the wet air mixture as the oxidant. The least active two catalysts were prepared by oxidation of the surface with 32% HNO₃. TOFs of the oxidized and oxidized-sulfonated carbons prepared using HNO₃ were comparable to those of

sulfonated carbons but 50–90 % lower of those of the catalysts prepared by oxidation with the wet air mixture (Table 12). The carbons prepared with HNO₃ were less active than the carbons prepared with the wet air mixture, and the oxidized-sulfonated carbons less active than oxidized carbons; these observations can be accounted for by a decrease in the specific surface area similar to the case of C-S250. Even though TOF of the oxidized-sulfonated catalysts was some lower than TOF of the oxidized catalysts, the former provided high yields of glucose. The results obtained agree with literature data. For example, a minor (1.6 %) difference in the glucose yields was observed over the most active carbon sulfonated at 250 °C and the carbon oxidized with nitric acid and then sulfonated at the same temperature [32]. It is interesting that the C-O sample provided the highest TOF equal to 2.1 among all the carbon catalysts under study; this was 1.7 more than TOF observed with the most active sulfonated carbon C-S200.

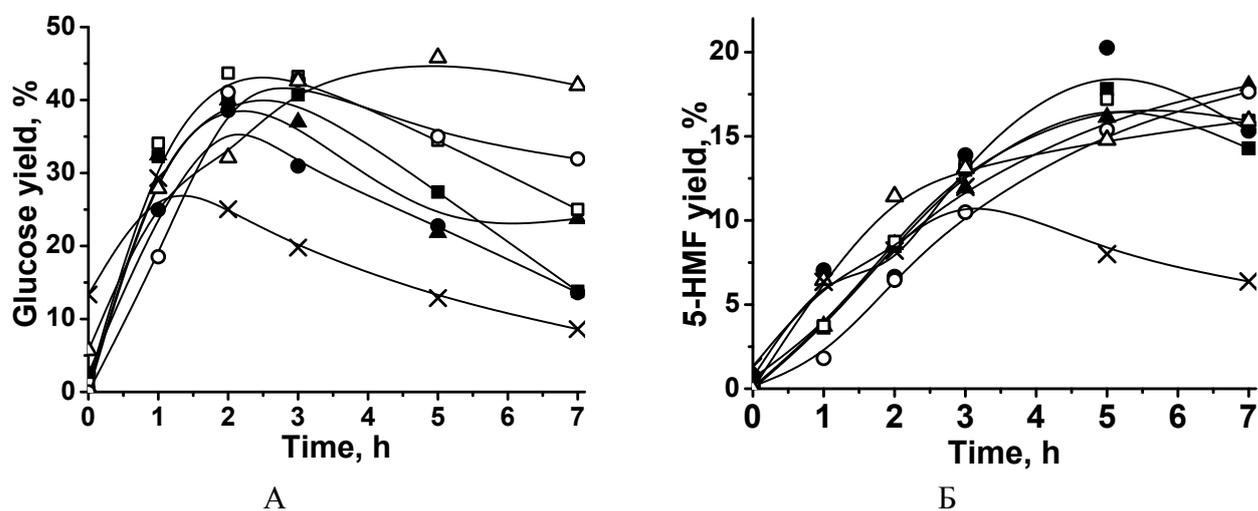


Figure 32. Kinetic curves of glucose (A) and 5-HMF (B) evolution in cellulose hydrolysis-dehydration over oxidized and oxidized-sulfonated Sibunit samples and in 0.02 M H₂SO₄. ■ – C-O, □ – C-O-S200, ● – C-N32, ○ – C-N32-S200, ▲ – C-N23, △ – C-N23-S200, + – 0.02M H₂SO₄. Cellulose and catalyst 10 g·L⁻¹, 45 mL, 180 °C, 10 atm (Ar), 1500 rpm, reaction time 7 h.

Comparative inspection of the data obtained leads to conclude about correlation between the catalyst activities and, on the other hand, their total acidity, contents of sulfur- and oxygen-containing groups, and the catalyst morphology. First, the activity of the carbon catalyst does not depend directly on the sulfonation degree but, thoughtfully, on the total acidity. For example, C-S200 contains 1.6 less sulfo-groups than C-S150 but is most active. This means that acidity is the factor determining the catalyst activity. The activity of samples C-S80, C-S150 and C-S200 increases with the increasing activity. Second, morphology affects considerably the carbon activity. Samples C-S250, C-N32-S200 and C-N23-S200, with the largest proportions of acid groups but considerably destroyed structures

characteristic of them, were less or comparably active than C-S200. The rate decreases noticeably when S_{BET} decreases below $300 \text{ m}^2 \cdot \text{g}^{-1}$. Third, the surface oxidation with the wet air mixture, rather than sulfonation or oxidation with HNO_3 , allows more active acid groups or group combinations to be supported on the carbon surface. Catalysts C-O and C-O-S200, with the total acidities close to those of C-S150 and C-S200, were more active than the sulfonated catalysts. In fact, titration with NaOH does not let the quantities of very weak carboxylic groups be determined, while these groups can be formed on the catalyst surface during oxidation [261] and contribute to the catalytic activity. Fourth, the oxidized carbon surface bearing large number of oxygen-containing groups is oxidized ineffectively. The oxidized-sulfonated catalysts are less active in a static reactor than the oxidized catalysts.

The obtained experimental dependencies of the catalyst activity on the chemical composition and morphology allow some conclusions concerning the mechanism of the transformations. Two reaction pathways of hydrolysis of water-soluble oligosaccharides in the presence of a solid acid catalyst are supposed. The first pathway is hydrolysis of oligosaccharides and dehydration of monosaccharides over the surface acid centers, the second is H^+ mediated catalysis in the solution. The heterogeneous reaction mechanism and an important role of glucosane adsorption on the surface are supposed in literature [31, 139, 152, 157]. Supposedly, both catalytic pathways contribute to the saccharide transformations observed in the case. The influence of pH of the solutions (3.0–4.0 against 5.5 of pure water) on the reaction rate argues for the mechanism of the mediated catalysis. The heterogeneous mechanism is supported by the influence of the catalyst morphology on the catalytic activity. Shrinkage of surface area leads to a decrease in the number of exposed adsorption centers and to a decrease in the activity. Experiments with C-S200 and sulfuric acid at an identical quantities of NaOH titrated acid centers ($40 \text{ mmol} \cdot \text{L}^{-1}$) also argue for a heterogeneous mechanism. High yields of 5-HMF were observed in the presence of the solid catalysts, while LA and FA were the main products in the H_2SO_4 solution. It is thought that glucose and/or oligosaccharides can be adsorbed on the carbon catalysts and transformed further on the hydrophobic surface of the catalyst to stabilize 5-HMF, which is more hydrophobic compound than LA and FA: in the experiments with a half-weight catalyst sample, the reaction rate and glucose yield were halved but the yield of 5-HMF did not decrease considerably. The catalytic behavior of water can also be observed during dehydration of glucose to 5-HMF. When the C-S200 catalyst weight was reduced by half, the rates of formation and the yields of glucose also were halved but the yield of 5-HMF was a factor of ~ 1.4 lower. While the number of acid centers here was reduced by half, the formation of 5-HMF was accounted for by the catalytic action of water.

4.2.3 Cellulose one-pot hydrolysis-dehydration over Sibunit catalysts in a flow reactor

Investigations of carbon catalyst activity have been also conducted in a flow reactor (Figure 13). The experiments without catalysts were carried out to optimize reaction parameters (temperature and water pressure). The appropriate temperature was defined under a water pressure of 50 atm and water flow of 0.5 mL min⁻¹. First, cellulose hydrolysis-dehydration was carried out without any catalyst at 180 °C but this temperature shown low efficiency (Table 13). The reason of lower yields in the flow reactor compared to ones in the batch reactor consists of small reaction times in the flow system. Thus, in this work the reaction contact time determined with the formula 16 was 2.0 min.

$$\tau_{\text{contact}} = \frac{V_{\text{react}}}{u_{\text{volume}}} \cdot \frac{\rho_{\text{conditions}}^{\text{H}_2\text{O}}}{\rho_{\text{syringe}}^{\text{H}_2\text{O}}} = \frac{\pi \cdot r^2 \cdot L}{u_{\text{volume}}} \cdot \rho_{\text{conditions}}^{\text{H}_2\text{O}}, \quad (16)$$

where τ_{contact} - reaction contact time, V_{react} - the volume of the reactor (mL or cm³) determined from the size parameters: length (L) and radius (r), u_{volume} - the volume flow rate, $\rho_{\text{conditions}}^{\text{H}_2\text{O}}$ and $\rho_{\text{syringe}}^{\text{H}_2\text{O}}$ are the densities of water under reaction (200 °C and 250 bar) and the ambient conditions and they are 0.88 and 1 g·mL⁻¹, respectively.

Because of that, all the experiments were carried out under a higher temperature of 200 °C what let to increase the product yields but not rise the amount of side products. Previously, it was found that the temperature 200-220 °C were optimal to produce water-soluble products under flow conditions [111]. The experiments were carried out at 200 °C in the flow reactor with a cellulose fixed bed to evaluate the best water pressure. Water pressures of 50 and 250 bar were investigated. The results showed the positive influence of high pressure on the yields of glucose, 5-HMF and total yield. HPLC analysis of the reaction mixtures demonstrated that a lot of oligosaccharides were formed. Cellotriose, cellotetraose, and cellopentose were identified. The oligomers were the main products at 200 °C and 250 bar. The experiments were carried out under stop-slow for 10, 20 and 40 min to hydrolyze oligosaccharides and to increase the main product yields. The stop-flow conditions provided high conversion of oligomers. However, when 40 min stop-flow was used, appreciable yields of the side-products and humins. Therefore, all the catalytic experiments were carried out under 20 min stop-flow each half-an-hour. Under optimal conditions (200 °C, 250 bar, 20 min stop-flow) in the blank experiment the total yields of glucose and 5-HMF were 13.5 and 3.5%, respectively.

Under the optimal reaction conditions the carbon catalysts have been tested (Table 13). The yields of products per hour and the total product yield were determined by the formulae 7 and 8. The values of the initial reaction rate (A_0) of the common formation of glucose and 5-HMF were revealed. TOF of the catalysts was found by the equation 15 as a ratio of A_0 to the total catalyst acidity. Moreover, the initial reaction rate of 5-HMF formation was found separately.

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According to HPLC, the main products were glucose and 5-HMF. The highest formation of the products was observed during the first hour of the reaction (about 70-80% of the total yield). All the catalysts could be divided into three groups in terms of the catalyst activity (Figure 33A). Only one catalyst - untreated pure Sibunit - was in the group characterized by the lowest activity. The activity of pure carbon was slightly higher than water action. The yield of glucose was 20% and one of 5-HMF 4.8%. In fact, catalytic action of water noticeably influenced TOF of low-active catalyst samples C and C-S80, therefore the "activity" of these two samples was higher than it should be.

The second group consisted of sulfonated and oxidized catalysts. The activity of sulfonated carbons increased as follows $C-S150 < C-S200$ what was similar to the batch experiments. Hydrolytic activity of oxidized carbons was close to C-S150 and C-S200 as it was in the autoclave too. C-O was the most active carbon although this catalyst had the lowest acidity among all the sulfonated and oxidized samples. The activities of Sibunit samples prepared by the treatment with HNO_3 solutions were close to each other and to sulfonated carbon C-S200.

The third group was composed of oxidized-sulfonated carbons. They were noticeably (about 1.5-2 times) more active compared to oxidized and sulfonated samples. Such a difference of the activities was in agreement with the total acidity of the catalysts.

The highest yield of glucose obtained under the flow conditions equal to **74%** was reached in the presence of C-N32-S200 catalyst.

Thus, it makes us possible to conclude the carbon solid acid catalysts are highly effective to obtain glucose from cellulose in a flow reactor. The best glucose yields received in this work exceed the literature data by a factor of 1.1-1.3 [32, 90]. The total acidity of catalyst is the crucial factor of the activity in the cellulose hydrolysis-dehydration. The hydrolysis seems to have weak dependence on the chemical nature of the acidic surface groups.

According to HPLC, the total yield of 5-HMF was found to be very low and equal to 2-10% after the end of all the experiments. So low yields indicated the dehydration of glucose was a slow process. It could not proceed with high 5-HMF yields during the reaction contact time 20 min in the flow system. The dependence of the catalyst activity on the catalyst pretreatment method was not so clear (Figure 33B). However, it was possible to conclude that the activity of the sulfonated carbons increased as follows $C-S150 > C-S80 > C-S200$. Interestingly note, the C-S150 possessing the highest amount of sulfo groups on the surface (according to XPS) was the most active sulfonated catalyst. Oxidized-sulfonated samples were much less active in the glucose dehydration compared to oxidized ones. C-O-S200 had the lowest activity in the dehydration which was comparable to non-treated carbon.

Table 13. Yields of cellulose hydrolysis-dehydration products reached over solid Sibunit catalysts in the flow reactor . Cellulose 0.25 g, catalyst 0.2 g, flow rate 0.5 mL·min⁻¹, experimental time 5 h. 1 - τ - stop-flow time.

#	Catalyst	T, °C	P, bar	τ , min ¹	Celb	Glu	Fru	5-HMF	Furf	FA	LA	Total	A_0 mol·s ⁻¹ ·10 ⁸	TOF, s ⁻¹ ·10 ⁴	A_0^{5-HMF} МОЛЬ·С ⁻¹ ·10 ⁸
1	blank	180	50	-	1.8	1.2	0	0.3	0	0	0	3.3	-	-	-
2	blank	200	50	-	2.6	6.0	0	1.2	0	0	0	9.8	-	-	-
3	blank	200	250	-	2.3	8.0	0	1.7	0	0.1	0	12.1	-	-	-
4	blank	200	250	10	2.7	10.2	0.4	2.6	0.1	0	0	16.0	-	-	-
5	blank	200	250	20	2.4	13.5	0.4	3.5	0.1	0	0	19.9	-	-	-
6	blank	200	250	40	2.0	17.1	0.9	4.8	0.3	0	0	33.2	-	-	-
7	C	200	250	20	4.5	20.2	2.5	4.8	0.3	0.4	0	32.7	2.23	5.3	0.40
8	C-S80	200	250	20	5.3	37.8	3.6	9.3	0.8	0.5	0.1	57.4	6.09	4.3	1.24
9	C-S150	200	250	20	5.4	39.8	3.5	10.3	0.9	0.7	0.2	60.8	6.11	1.9	1.38
10	C-S200	200	250	20	11.8	48.0	2.1	7.5	0.9	0.5	0.2	71.0	8.34	2.0	1.04
11	C-O	200	250	20	5.7	44.2	2.4	5.7	0.7	0.4	0	59.1	7.11	2.5	0.74
12	C-N32	200	250	20	7.3	49.4	4.4	7.7	0.8	0.9	0	70.5	6.41	1.8	0.88
13	C-N23	200	250	20	6.2	49.1	4.7	8.7	0.5	0.8	0	70.0	6.75	2.0	1.03
14	C-O-S200	200	250	20	5.5	71.0	1.7	3.0	0.2	0.4	0	81.2	13.8	2.8	0.52
15	C-N32-S200	200	250	20	5.4	74.1	3.2	5.8	1.0	0.6	0	90.1	12.6	2.4	0.72
16	C-N23-S200	200	250	20	5.2	66.5	1.9	4.9	0.3	0.3	0	79.1	11.3	2.3	0.62

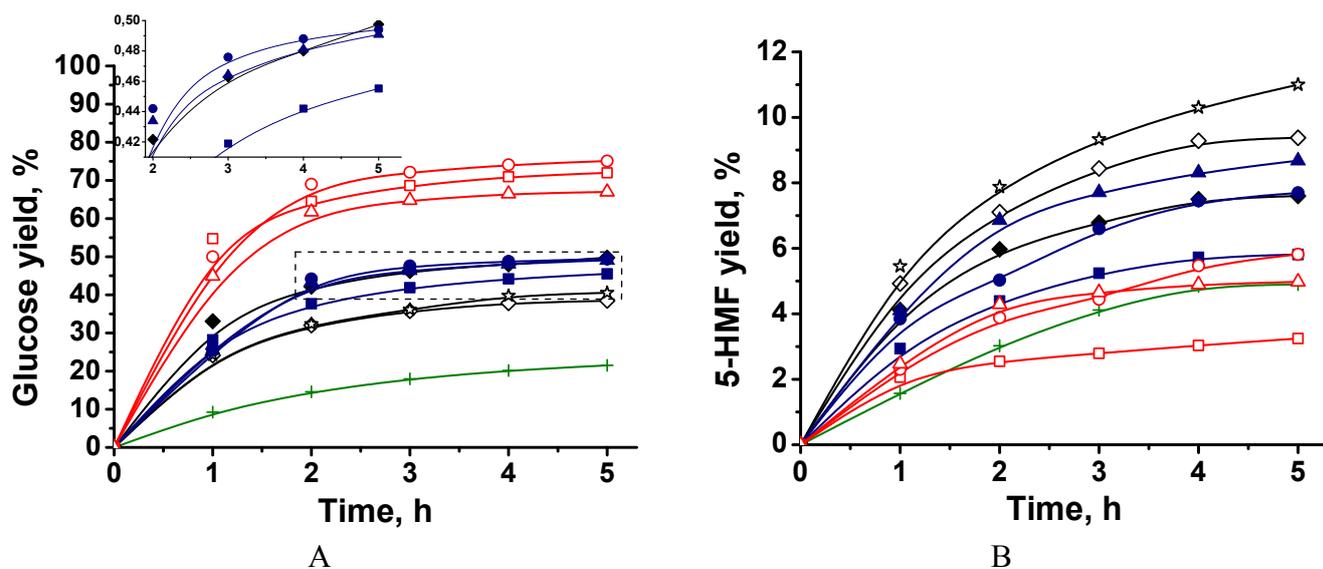


Figure 33. Kinetic curves of glucose (A) and 5-HMF (B) accumulation in cellulose hydrolysis-dehydration over Sibunit solid acid catalysts and in the flow reactor. Cellulose 0.25 g, catalyst 0.2 g, 200 °C, 250 bar, flow rate 0.5 mL·min⁻¹, stop flow 20 min, reaction time 5 h. + – C, \diamond – C-S80, \star – C-S150, \blacklozenge – C-S200, \blacksquare – C-O, \square – C-O-S200, \bullet – C-N32, \circ – C-N32-S200, \blacktriangle – C-N23, \triangle – C-N23-S200.

Thus, the following remarks based on the analysis of the results obtained are possible.

1) Both acid and sulfo groups are active in dehydration. 2) The activity of sulfo groups is noticeably high. Sulfonated catalysts are more active in the dehydration than other samples. And among sulfonated Sibunits, C-S150 possessing the highest amount of sulfo groups on the surface was the most active catalyst. 3) Additional sulfonation of oxidized carbons caused decreasing the catalyst activity in the dehydration process. The activity of oxidized-sulfonated samples in the dehydration was close to non-treated Sibunit.

When comparing the experimental results obtained in the autoclave and the flow reactor, some differences could be found. 1) In the flow reactor non zero yields of the main products were observed in the presence of non-modified carbon sample. Moreover, glucose yield over pure Sibunit was somewhat higher than in the blank experiment (20 and 17%, respectively). At the same time, in the autoclave glucose yield was 7% in the blank experiment and 0% in the presence of pure carbon. No other products were formed. Also the influence of water activity made impossible revealing the real activity of low-active catalysts C and C-S80 in the flow reactor. 2) In the flow reactor, TOFs of oxidized-sulfonated carbons were higher compared to oxidized samples. And the yields of glucose were also greater over oxidized-sulfonated carbons in 1.5-2 times. In the batch reactor, the glucose

yields in the presence of oxidized and oxidized-sulfonated carbons were close to each other and the TOF of oxidized carbons was higher.

The differences between the catalyst activities in flow and batch reactors could be explained via different reaction conditions: the temperature (180 and 200 °C), the volume of the reaction mixture (45 and 1.1 mL). The influence of the reaction volume is especially important. The concentration of acid centers in the reaction system is much more higher in the flow reactor compared to the autoclave due to the loading of solid catalyst is 450 mg in the batch and 200 mg in the flow. Moreover, very small reaction volume in the flow system causes decreasing diffusion limitations. As in the batch reactor cellulose and a catalyst are under intensive stirring in a big volume of water while in the flow reactor there is no stirring and uniform mechanical mixture of cellulose and a catalyst are in the fixed bed. This layer is just wetted and stated under high temperature.

4.2.4 5-Hydroxymethylfurfural extraction

An important problem to be solved in developing any effective technology is separation of the reaction products and isolation of pure products. Our studies dealt with the possibility of separation of 5-HMF and monosaccharide mixtures. From literature, extraction is one of the most promising methods for isolation of 5-HMF [4].

Table 14. HMF extraction. Volumes of water and organic phases 5 mL. Extraction time 10 min.

Sample	Organic phase	Ratio of phases water : organic	Extraction degree, %	
			Glucose	5-HMF
Solution 5 mmol·L ⁻¹ 5-HMF	MIBK	1:5	-	86
		1:9	-	95
	Butanol-2	1:1.5	-	71
		1:2	-	85
	Butanol-2: MIBK (3:7)	1:1	-	67
	Butanol	1:5	-	80
	Hexane	1:9	-	14
	Dimethylmethane	1:1	-	35
Dimethyl ether	1:9	-	73	
Hydrolyzate after the experiment with C-S200	MIBK	1:9	13	98
	Butanol-2l	1:2	40	83

The most effective extractive system was searched for using a model $5 \text{ mmol}\cdot\text{L}^{-1}$ 5-HMF solution. Based on literature data [4], the following most often used and most effective extragents were chosen: methylisobutylketone (MIBK), isobutanol, a mixtures of MIBK and isobutanol at the ratio of 7:3, butanol, hexane, diethylmethane, dimethyl ether. The used ratios of aqueous and organic phases were identical to the best results reported in literature (Table 14).

MIBK was the most effective among the tested extragents. At the ratio of water to organic phase equal to 1:9, 95 % of 5-HMF was extracted during single step from the aqueous medium. MIBK is, indeed, the most often used agent for separation of 5-HMF during experiments in two-phase catalytic systems [4]. Butanol and isobutanol, which can be produced biotechnologically from cellulose, also seem promising [262-267]. They allow 80 and 85 % of 5-HMF, respectively, to be extracted by lower quantities of the solvents (1:2). The other systems (dimethyl ether, isobutanol:MIBK (3:7), dimethylmethane, hexane) did not provide high extraction degrees.

The most promising extractive systems (MIBK and isobutanol) were tried for separation of the reaction mixture obtained with C-S200. The quantities of extracted 5-HMF from the hydrolyzate were comparable to those observed during the model experiments (98% with MIBK; 83% with isobutanol). However, the quantity of glucose extracted from the reaction solution to the organic phase was as low as 13 % with MIBK but 40 % with isobutanol. Thus, MIBK is the best extragent, while isobutanol and butanol seem promising in terms of the biorefinery concept

4.3 Simulation of cellulose hydrolysis-dehydration process

To model the process, we suggested the kinetic scheme of the cellulose hydrolysis-dehydration to relate reaction equations to all the process intermediates detected by HPLC (Figure 34). The scheme is based on literature data on interconversions of compounds involved in the process of cellulose depolymerization and on experimental data obtained in the present study (Figure 34). Kinetics of individual stages of the process was studied with main process intermediates as the substrates in the presence of the carbon catalyst C-S200 using a static reactor.

Reactions of hydrolysis of disaccharide cellobiose, isomerization-dehydration of glucose and mannose, as well as destruction of 5-HMF and furfural were studied (Figure 35).

Cellobiose was used as the substrate in order to determine the rate of hydrolysis of the glycoside bond in the presence of the carbon catalyst. It was established that the disaccharide is very quickly consumed (Figure 35 A). At zero point (the moment of achieving the required temperature of $180 \text{ }^{\circ}\text{C}$ in the autoclave), the cellulose conversion reaches 55 %, and the disaccharide is not detected in 30 min in the reaction medium. These data demonstrate that the hydrolysis is a very fast process, and the overall kinetics of the cellulose transformation is limited by the cellulose dissolution.

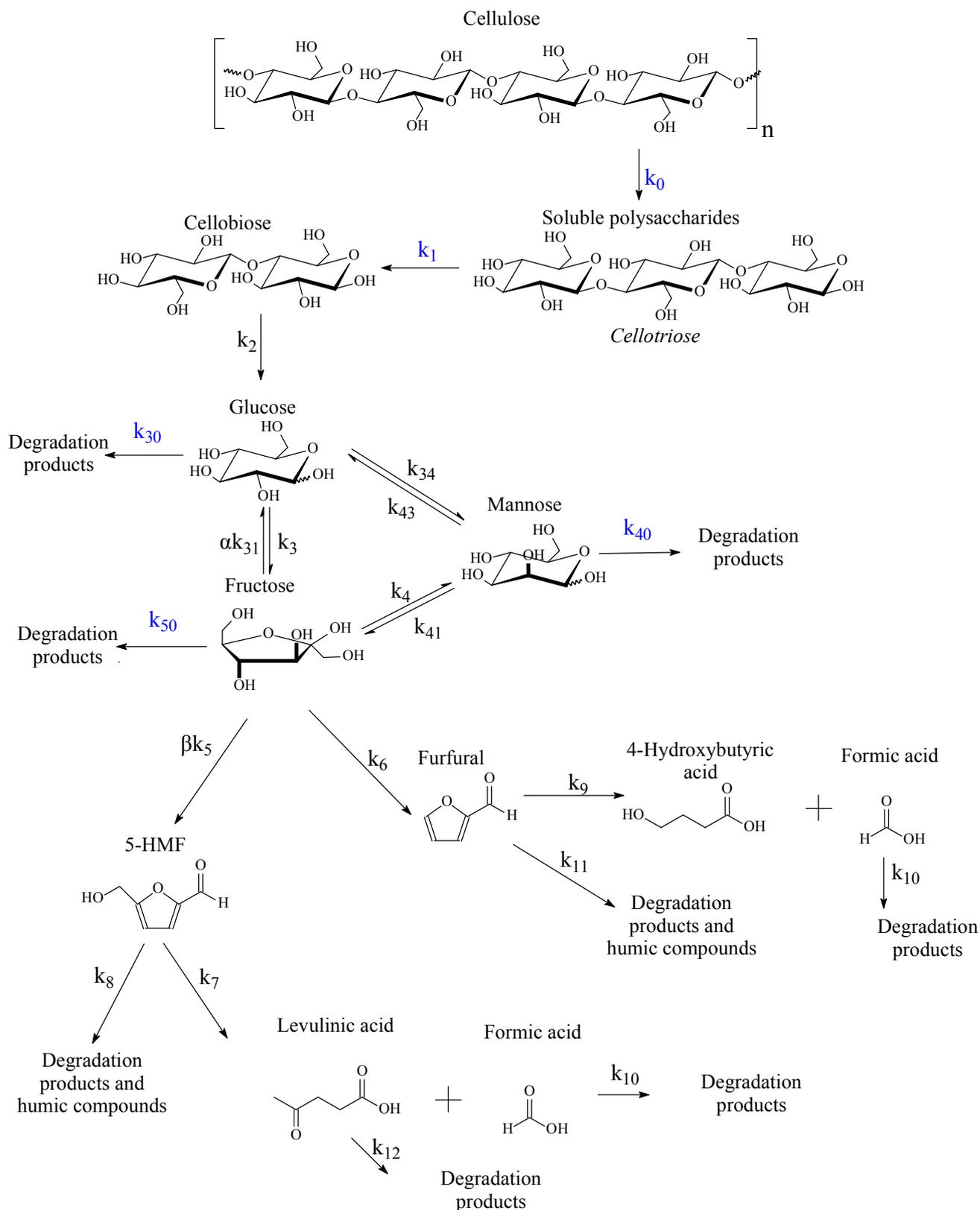


Figure 34. Kinetic scheme of the cellulose hydrolysis-dehydration process. The blue colored constants cannot be estimated based on experimental data.

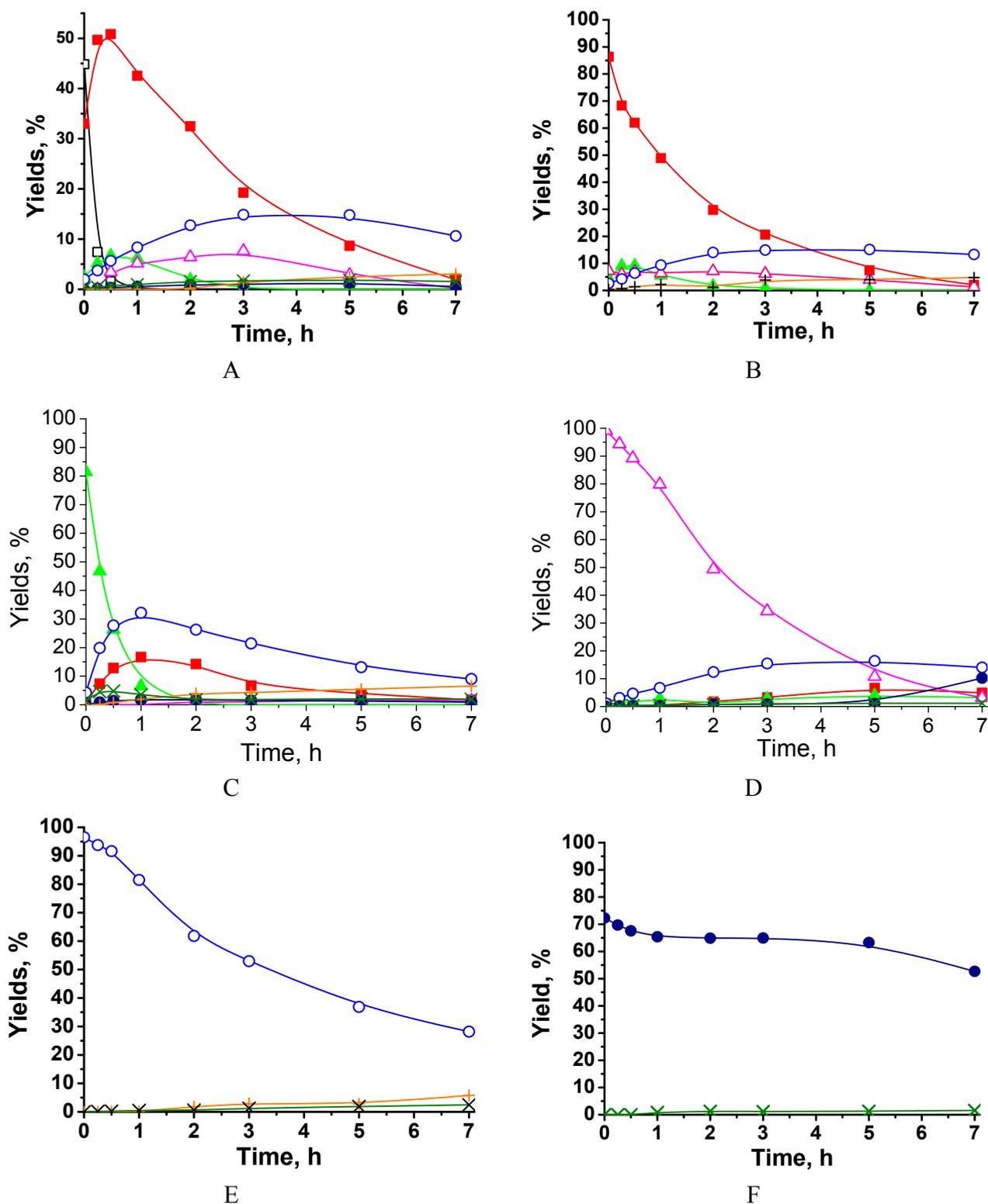


Figure 35. Kinetic curves of treating cellulose hydrolysis-dehydration intermediates in the presence of Sibunit carbon catalyst in the batch reactor. (□ - Cellobiose, ■ - Glucose, ○ - 5-HMF, △ - Mannose, ▲ - Fructose, ● - Furfural, + - Levulinic acid, × - Formic acid). Substrates: A - Cellobiose, B - Glucose, C - Fructose, D - Mannose, E - 5-HMF, F - Furfural. Substrate 10 g·L⁻¹, 45 mL, 180 °C, 10 atm (Ar), 1500 rpm, reaction time 7 hs.

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Experimental studies of cellobiose hydrolysis revealed that this is an irreversible reaction. Reversibility of saccharide hydrolysis was studied earlier [197] using the kinetic model close to Model 2 of cellulose transformations (Scheme 5). Calculations showed that the kinetic model did not fit the experimental data but only when repolymerization constant tends to zero (that means the high energy barrier and practical irreversibility of the process). Saeman [112] showed that the reaction orders of hydrolytic cellulose transformations range between 0.7 and 1.3. The first order of the reaction of cellobiose conversion to glucose was demonstrated by Bobleter and Bonn [268]. Thus, the first order of the hydrolysis reactions determined by our calculations agrees with the literature data.

Comparison of kinetic curves shows that glucose is consumed much slower than fructose. It has been stated above in the present work that fructose transforms faster than glucose in the presence of 2.8%Nb/ZrO₂ catalyst (Table 7). In the hydrolysis of glucose, fructose is practically not accumulated but consumed rapidly for the formation of 5-HMF. Besides, 5-HMF yield is higher if fructose is a substrate and not glucose (Figure 35 B and C). The maximal yield of 5-HMF was 15.1 % from glucose in 3–5 h of the reaction and 32.2 % from fructose in one hour. As soon as fructose is fully consumed, 5-HMF stops accumulating but glucose formed from fructose starts consuming. The transformation of glucose to fructose proceeds at a low rate and limit the process that results in a decrease in the yield of 5-HMF. The high yields of 5-HMF from fructose were reported before [128, 269]. The kinetic curves are linearized in semilog coordinates ($\ln(C/C_0) - \tau$) that indicates the first reaction order of sugar conversions reported elsewhere [100, 112, 209, 270]. These results agree with the known fact that 5-HMF is from fructose [128, 269], while fructose from glucose through isomerization [128, 209], the latter being the limiting stage of the process.

In describing chemical transformations of monosaccharides during cellulose depolymerization, it is typically accepted that glucose, fructose and mannose are in the following relation: Glucose \rightleftharpoons Fructose \rightleftharpoons Mannose [103, 192]. However, the reaction mechanism is more complicated, it implies interconversion of the sugars through their common endiol intermediate (Scheme 7) [211], i.e. glucose may transform to mannose directly but not through fructose. We added the reaction of glucose conversion to mannose (k_{34} and k_{43}) to our kinetic scheme. The occurrence of this route was supported by experimental studies of fructose transformation using a static reactor (Figure 35 C). The formation of mannose was not observed during the first hour of the reaction until fructose was consumed completely but detected in the chromatograms as soon as glucose started consuming. These results allowed us to suppose that the constant of fructose isomerization is very low ($k_4 \rightarrow 0$), and mannose is formed through isomerization of glucose.

The stability and potential transformations of 5-HMF were studied using 5-HMF as the substrate. The substrate appeared unstable under the reaction conditions. The conversion was more than 70 % in 7 h (Figure 35 E). The kinetic curve of 5-HMF transformation is aligned in semilog

coordinates, and the induction period is observed at the initial region (0–0.5 h). Sugars were not detected to form; hence, dehydration of fructose to 5-HMF is an irreversible reaction. While LA and FA were not accumulated in considerable amounts, 5-HMF was supposed to transform thorough high-temperature polycondensation to give water-insoluble side products. It is interesting that LA usually is detected in trace amount, if any, upon hydrothermal treatment of sugars in the absence of soluble catalysts [191, 192, 271].

The formation of furfural in minor quantities (1–2 %) was observed in all the experiments; from literature data [192], furfural is formed from fructose with the release of formaldehyde. Again, furfural may be a product of 5-HMF transformation. When fructose and 5-HMF were used as substrates (Figure 35 E and F), furfural was demonstrated only to form from fructose but not from 5-HMF.

The kinetics of furfural consumption was studied in the presence of the catalyst (Figure 35 F). Furfural was more stable than 5-HMF, its conversion was no more than 20 %. In the run, the formation of FA in small quantity but not accumulation of sugars was observed.

Kinetics of transformations of intermediates of cellulose hydrolysis-dehydration also was studied at 200 °C and 250 bar using a flow system in the *stop-flow* mode (the flow was stopped for 20 min). Kinetic curves were obtained for transformation of cellobiose, glucose, fructose, mannose and 5-HMF in the presence of the catalyst C-S200 (Figure 36). Inspection of the kinetic data on transformations of intermediates in the flow mode supports, in general, conclusions made with the data obtained using the static reactor: polysaccharide dissolution and sugar isomerization as the rate-limiting stages, very high rates of hydrolysis and dehydration, low stability of 5-HMF under the reaction conditions.

Kinetic models were suggested for hydrolysis-depolymerization of cellulose in flow and static reactors. Note that cellulose depolymerization is a very complex process involving a large number of intermediate compounds and stages. When all the transformations are taken into consideration, the model becomes too intricate and the rate expressions very complex. On the other hand, strong simplification of the system, even though experimental and calculated data coincide, may lead to wrong understanding of the kinetic regularities and, therefore, to errors in scaling-up from the laboratory reactor to the pilot and industrial plants. Thus, the reasonable simplification is an essential part of the work.

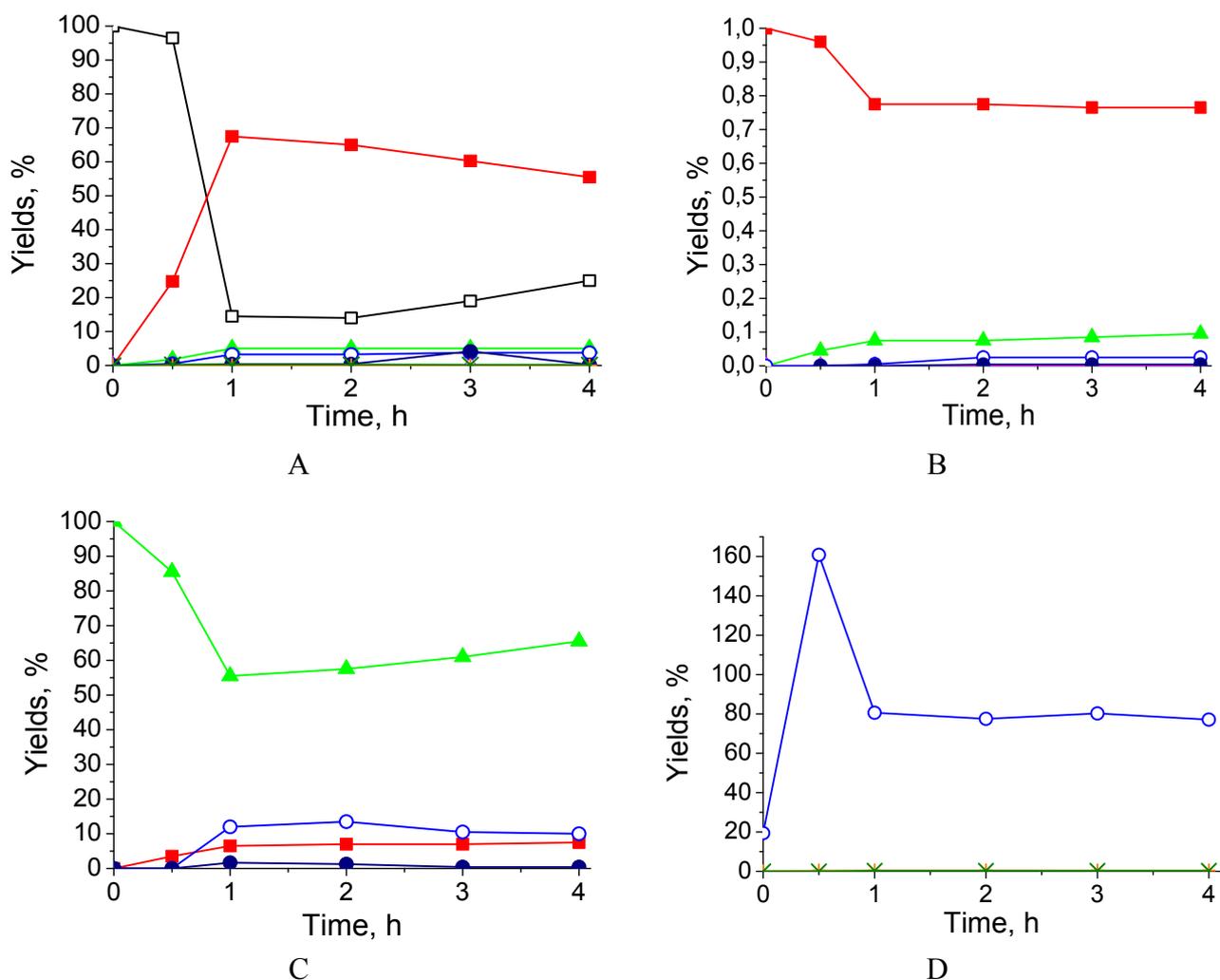


Figure 36. Kinetic curves of treating cellulose hydrolysis-dehydration intermediates in the presence of Sibunit carbon catalyst in the flow reactor (□ - Cellobiose, ■ - Glucose, ○ - 5-HMF, △ - Mannose, ▲ - Fructose, ● - Furfural, + - Levulinic acid, × - Formic acid). A - Cellobiose, B - Glucose, C - Fructose, D - 5-HMF. Substrate 0.02M, catalyst 300 mg, 200 °C, 250 bar, скорость flow rate 0.5 mL min⁻¹.

The model used in the present work describes interaction of all the identified reaction intermediates and products (Figure 34). The kinetic curves of the formation or consumption of the intermediates and products under static conditions are linear in semilog coordinates ($\ln(C/C_0)$ vs time) that leads to conclude about the first order of all the stages. The reaction constants were determined from the slope of the kinetic curves in the semilog coordinates (Figure 37). Rate constants of the reversible equilibrium of sugars were calculated using experimental data on the flow system, the stages being considered quasi-equilibrium. The kinetic modeling was based on the assumptions that the rates of proton adsorption/desorption at the stage of cellulose dissolution and the rates of diffusion processes to/from the surface of the solid catalyst are high enough, and the measured constants are the constants of intrinsic chemical transformations. The calculated constants are given in Table 15.

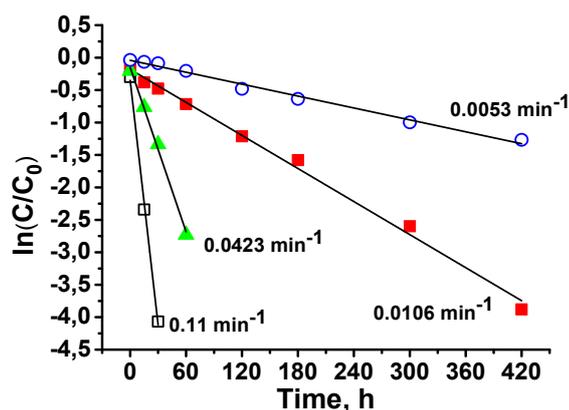


Figure 37. Kinetic curves of cellobiose (□), glucose (■), 5-HMF (○) and fructose (▲) transformations in the presence of carbon catalyst in the batch reactor. Substrate and the catalyst $10 \text{ g}\cdot\text{L}^{-1}$, 45 mL, $180 \text{ }^\circ\text{C}$, 10 atm (Ar), 1500 rpm, reaction time 7 hs.

Table 15. Values of the reaction constants in the cellulose hydrolysis-dehydration, 1 – constants calculated from the results of kinetic investigations, 2 – constants used for simulation, 3 – constants presented in the literature. The blue colored constants cannot be estimated based on experimental data.

Constant	Reaction	Constant value, min^{-1}			Ref.
		1	2	3	
k_0	Cellulose solubilization	-	$16 \cdot 10^{-3}$		
k_1	Hydrolysis of oligosaccharides	-	0.11		
k_2	Cellobiose hydrolysis to glucose	0.11	0.11	0.356	[272]
k_{glu}	Total constant of glucose consumption	$10.6 \cdot 10^{-3}$	$10.6 \cdot 10^{-3}$	$4.4 \cdot 10^{-3}$	[272]
				$8.0 \cdot 10^{-3}$	[270]
				$3.0 \cdot 10^{-3}$	[194]
k_3	Glucose isomerization to fructose	$8.0 \cdot 10^{-3}$	$8.0 \cdot 10^{-3}$		
k_{31}	Fructose izomerization to glucose	$76.0 \cdot 10^{-3}$	$11.0 \cdot 10^{-3}$		
k_{30}	Glucose decomposition to side products	-	$1.0 \cdot 10^{-3}$		
k_{man}	Total constant of mannose consumption	$6.22 \cdot 10^{-3}$	$6.22 \cdot 10^{-3}$	$9.8 \cdot 10^{-3}$	[270]
k_{34}	Glucose isomerization to mannose	$1.6 \cdot 10^{-3}$	$1.6 \cdot 10^{-3}$		
k_{43}	Mannose izomerization to glucose	$0.4 \cdot 10^{-3}$	$0.4 \cdot 10^{-3}$		
k_{40}	Mannose decomposition to side products	-	$1.0 \cdot 10^{-3}$		
k_{fru}	Total constant of fructose consumption	$4.23 \cdot 10^{-2}$	$4.23 \cdot 10^{-2}$		
k_4	Fructose izomerization to mannose	~ 0	0		
k_{41}	Mannose izomerization to fructose	$4.82 \cdot 10^{-3}$	$4.82 \cdot 10^{-3}$		

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Constant	Reaction	Constant value, min ⁻¹			Ref.
		1	2	3	
k ₅₀	Fructose decomposition to side products	-	9.5·10 ⁻³		
k ₅	Fructose dehydration to 5-HMF	6.0 -	1.9·10 ⁻²	1.6·10 ⁻³	[270]
		9.6·10 ⁻²		8.2·10 ⁻³	[270]
k ₆	Fructose dehydration to furfural	2.23·10 ⁻³	2.23·10 ⁻³		
k ₇	5-HMF transformation to levulinic and formic acids	2.06·10 ⁻⁴	2.06·10 ⁻⁴		
k ₈	Formation of humic compounds from 5-HMF	5.1·10 ⁻³	5.1·10 ⁻³		
k ₉	Furfural decomposition to formic and 4-hydro butyric acids	2.3·10 ⁻³	2.3·10 ⁻³		
k ₁₀	Formic acid decomposition	1.7·10 ⁻³	1.7·10 ⁻³		
k ₁₁	Formation of humic compounds from furfural	2.1·10 ⁻³	2.1·10 ⁻³		
k ₁₂	Levulinic acid decomposition	1·10 ⁻⁴	1·10 ⁻⁴		

Based on the process scheme (Figure 34) a system of differential equations was made for subsequent modeling of the kinetics. As cellulose is solid matter, its concentration in the system was replaced by the cellulose conversion value (X) [112, 172]:

$$X = \frac{m_0 - m}{m_0},$$

where X is the cellulose conversion degree and m is the cellulose weight.

The following system of differential equations was composed:

$$(I) \quad \frac{d}{dt} X(t) = -k_0 \cdot (1 - X(t)),$$

$$(II) \quad \frac{d}{dt} \text{Olig}(t) = k_0 \cdot X(t) - k_1 \cdot \text{Olig}(t),$$

$$(III) \quad \frac{d}{dt} \text{Celb}(t) = k_1 \cdot \text{Olig}(t) - k_2 \cdot \text{Celb}(t),$$

$$(IV) \quad \frac{d}{dt} \text{Glu}(t) = k_2 \cdot \text{Celb}(t) + k_{31} \cdot \text{Fru}(t) + k_{43} \cdot \text{Mann}(t) - (k_3 + k_{34} + k_{30}) \cdot \text{Glu}(t),$$

$$(V) \quad \frac{d}{dt} \text{Fru}(t) = k_3 \cdot \text{Glu}(t) + k_{41} \cdot \text{Man}(t) - (k_{31} + k_4 + k_5 + k_6 + k_{50}) \cdot \text{Fru}(t),$$

$$(VI) \quad \frac{d}{dt} \text{Man}(t) = k_4 \cdot \text{Fru}(t) + k_{34} \cdot \text{Glu}(t) - (k_{41} + k_{43} + k_{40}) \cdot \text{Man}(t),$$

$$(VII) \quad \frac{d}{dt}5HMF(t) = k_5 \cdot Fru(t) - (k_7 + k_8) \cdot 5HMF(t),$$

$$(VIII) \quad \frac{d}{dt}Furf(t) = k_6 \cdot Fru(t) - (k_9 + k_{11}) \cdot Furf(t),$$

$$(IX) \quad \frac{d}{dt}Lev(t) = k_7 \cdot 5HMF(t) - k_{12} \cdot Lev(t),$$

$$(X) \quad \frac{d}{dt}Form(t) = k_7 \cdot 5HMF(t) + k_9 \cdot Furf(t) - k_{10} \cdot Form(t),$$

where Cell – cellulose, Celb – cellobiose, Glu – glucose, Fru – fructose, Man – mannose, HMF - 5-hydroxymethylfurfural, Furf – furfural, Lev – levulinic acid, Form – formic acid.

The system was solved using the Mathcad 15.0 software with function Odesolve. An advantage of the function is that the differential equation is written in its true mathematical form. Odesolve is based on the Runge–Kutta method with an automatic step-size for solving the problem.

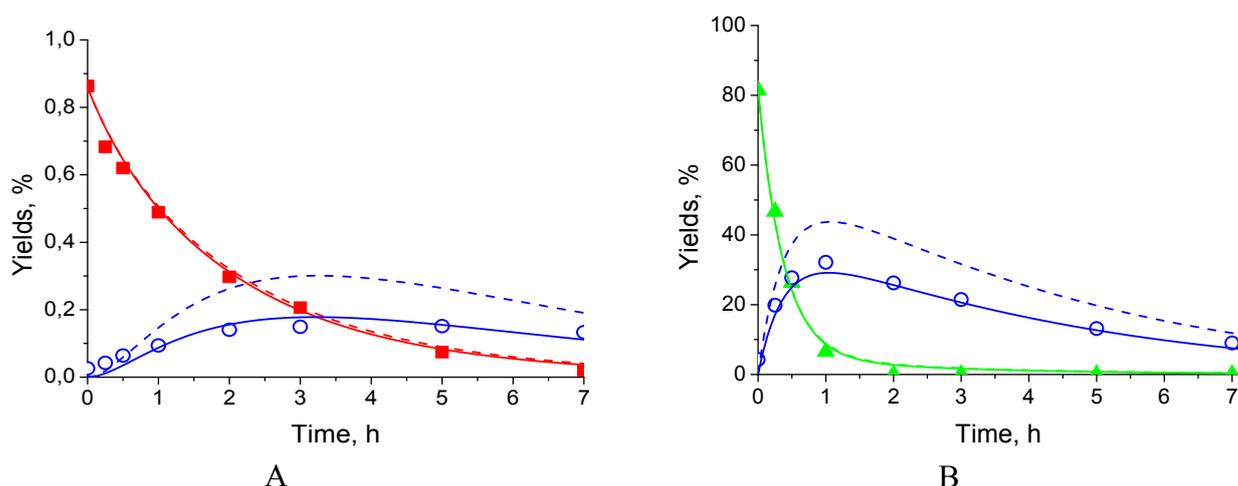


Figure 38. Experimental and simulated kinetic curves of glucose (■), fructose (▲) and 5-HMF (○) transformations in the presence (solid curves) and the absence (dotted curves) of the additional ways for monosaccharide processing. Substrate: A - glucose, B - fructose. Cellulose and the catalyst 10 g·L⁻¹, 45 mL, 180 °C, Ar pressure 10 bar, 1500 rpm, reaction time 7 h.

The simulated kinetic curves described the experimental data at an appropriate accuracy, but considerable deviations were observed for some compounds. For example, the calculated yields of fructose were higher than the respected experimental data for all the runs except those with fructose as substrate. In the experiments with cellulose, the theoretical curve showed much higher yield of cellobiose than the experimentally observed yield. The reason is thought to be the presence of undetectable oligomers (cellotriose, cellotetrose etc.). Both kinetic modeling of hydrolysis-dehydration of cellulose, as well as calculations on the other sugars gave higher yields of 5-HMF against the

experimental data (Figure 38). In the experiments with mannose, modeling showed higher yields of not only 5-HMF, but also glucose and fructose. The said discrepancy may result from inaccurate determination of kinetic constants due to the low number of experimental points (7 for cellulose and 9 for the others), first order approximations of all the rate constants, as well as the presence of additional routes of the product and intermediate consumption. Hence, the calculated kinetic constants needed corrections for more adequate description of the observed kinetic results.

We assumed additional routes for consumption of glucose, mannose and fructose (rate constants k_{30} , k_{40} and k_{50} , respectively) with the constants included in the observed constants of sugar consumption. There are available literature data on these routes. Some researchers observed a side process of fructose transformation to glyceraldehydes and then to pyruvaldehyde and lactic acid [100, 104, 192, 205, 273] but the other were doubtful of the occurrence of this route in the presence of an acid catalyst at temperatures below 270 °C [271]. The reaction of glucose dehydration to 1,6-anhydroglucose with splitting of one water molecule is known [100, 192]. There may occur retroaldol cleavage of glucose and fructose to erythrose C₄ saccharide [100, 191, 273]. We failed to detect the said side products, and the constants of sugar consumption k_{30} , k_{40} and k_{50} were determined from the available experimental data by trial-and-error procedure.

Corrective factors were chosen for some constants. For example, constants k_3 and k_{31} determined from kinetics of glucose were $8.0 \cdot 10^{-3}$ and $7.6 \cdot 10^{-2} \text{ min}^{-1}$, respectively; they relate through the equilibrium constant $K_3 = \frac{k_{31}}{k_3} = 9.62$. However, in fructose kinetic simulation, $k_{31} = 1.1 \cdot 10^{-2} \text{ min}^{-1}$; therefore, by analogy to ref. [197], we introduced a reduction factor ($\alpha=0.145$) for this constant.

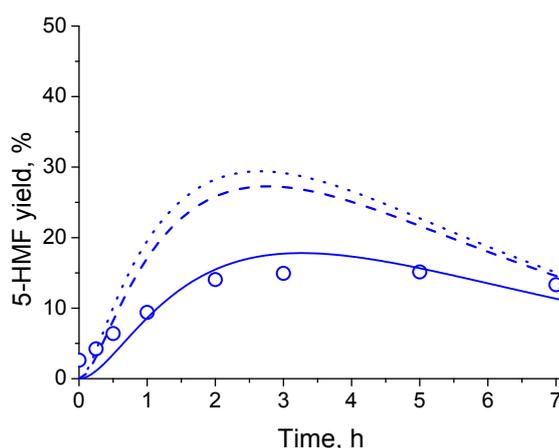


Figure 39. Simulated kinetic curves of 5-HMF formation with k_5 $9.6 \cdot 10^{-2} \text{ min}^{-1}$ (pointed curve), $6.0 \cdot 10^{-2} \text{ min}^{-1}$ (dotted curve) and $1.94 \cdot 10^{-2} \text{ min}^{-1}$ (solid curve) in compared to the experimental data (o). Cellulose and the catalyst $10 \text{ g} \cdot \text{L}^{-1}$, 45 mL, 180 °C, 10 bar (Ar), 1500 rpm, reaction time 7 h.

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From experimental data on transformations of sugars, the rate constant of 5-HMF formation from fructose (k_5) varied between 6.0 and $9.6 \cdot 10^{-2} \text{ min}^{-1}$. However, application of these constants led to the model kinetic curve of the formation of 5-HMF with a noticeable maximum at 2–3 h and the yields far above experimental data (Figure 39). Again, the experimentally observed total constant of fructose consumption $k_{\text{fru}} = k_{31} + k_4 + k_5 + k_{50} + k_6 = 4.23 \cdot 10^{-2} \text{ min}^{-1}$ does not fall into the range of constant (k_5) calculated this way. The constant k_5 revealed from equation of k_{fru} was $1.94 \cdot 10^{-2} \text{ min}^{-1}$ (the ratio of β coefficient was 0.204 - 0.322). The calculated value of k_5 well describes the experimental kinetics of 5-HMF (Figure 39).

The constant k_0 of cellulose dissolution was chosen by simulation; the constant appeared low enough to indicate that this is a limiting stage in the cellulose transformation. Hydrolysis constant k_2 was determined experimentally from cellobiose transformation; it equaled 0.11 min^{-1} that was more than k_0 by an order of magnitude and more than the rate constants of the other stages by several orders of magnitude. Hence, hydrolysis proceeded at a high rate. The calculated constant k_3 of isomerization of glucose to fructose was low enough (factor of 2.5 lower than the observed constant βk_5 of fructose dehydration to 5-HMF), i.e. the process of glucose conversion to fructose is limited by isomerization to result in a decrease in the yield of 5-HMF.

The determined constants k_2 (0.11 min^{-1}) of cellobiose hydrolysis to glucose and the total constant of glucose consumption through various routes $k_{\text{glu}} = k_3 + k_{30} + k_{34}$ ($1.1 \cdot 10^{-2} \text{ min}^{-1}$) were close to the literature data. In hydrolysis of cellobiose in the presence of 0.02 M H_2SO_3 at 180 °C, the constant was reported to be equal to 0.356 min^{-1} [272] (that is 3.2 times as high as the constant obtained by us). The literature constants for glucose consumption ($4.427 \cdot 10^{-3}$ [272], $8 \cdot 10^{-3}$ [270], $3.0 \cdot 10^{-3} \text{ min}^{-1}$ [194]) are factors of 2.4, 1.3 and 3.5 lower than the constants obtained by us. The calculated constant of mannose consumption $k_{\text{man}} = k_{43} + k_{40} + k_{41}$ is close to literature data ($6.2 \cdot 10^{-3} \text{ min}^{-1}$ against $9.8 \cdot 10^{-3} \text{ min}^{-1}$ at 180 °, pH 2.0 [270]). It is important that the cited data on the constants were obtained in the presence of sulfuric acid as the catalyst but under conditions close to our experiments (180 °C and pH 2.5-2.7).

At the same time, the constant of 5-HMF formation determined by us ($\beta k_5 = 1.9 \cdot 10^{-2} \text{ min}^{-1}$) was much higher than the literature data ($1.6\text{-}8.2 \cdot 10^{-3} \text{ min}^{-1}$ [270], observed at 170-190 °C and pH 2.0-4.0). This agrees with the unusually high yields of 5-HMF observed in the presence of solid catalysts. The reaction constant k_7 of decomposition of LA and FA was 10 orders of magnitude lower than the constant of 5-HMF transformation to humic substances ($k_8 = 5.1 \cdot 10^{-3} \text{ min}^{-1}$) that is close to literature data [270].

Note in conclusion that the developed kinetic model provides not only qualitative but also accurate enough quantitative description of the process of hydrolysis-dehydration of cellulose, as well as transformations of intermediates of the process under study (Figure 40).

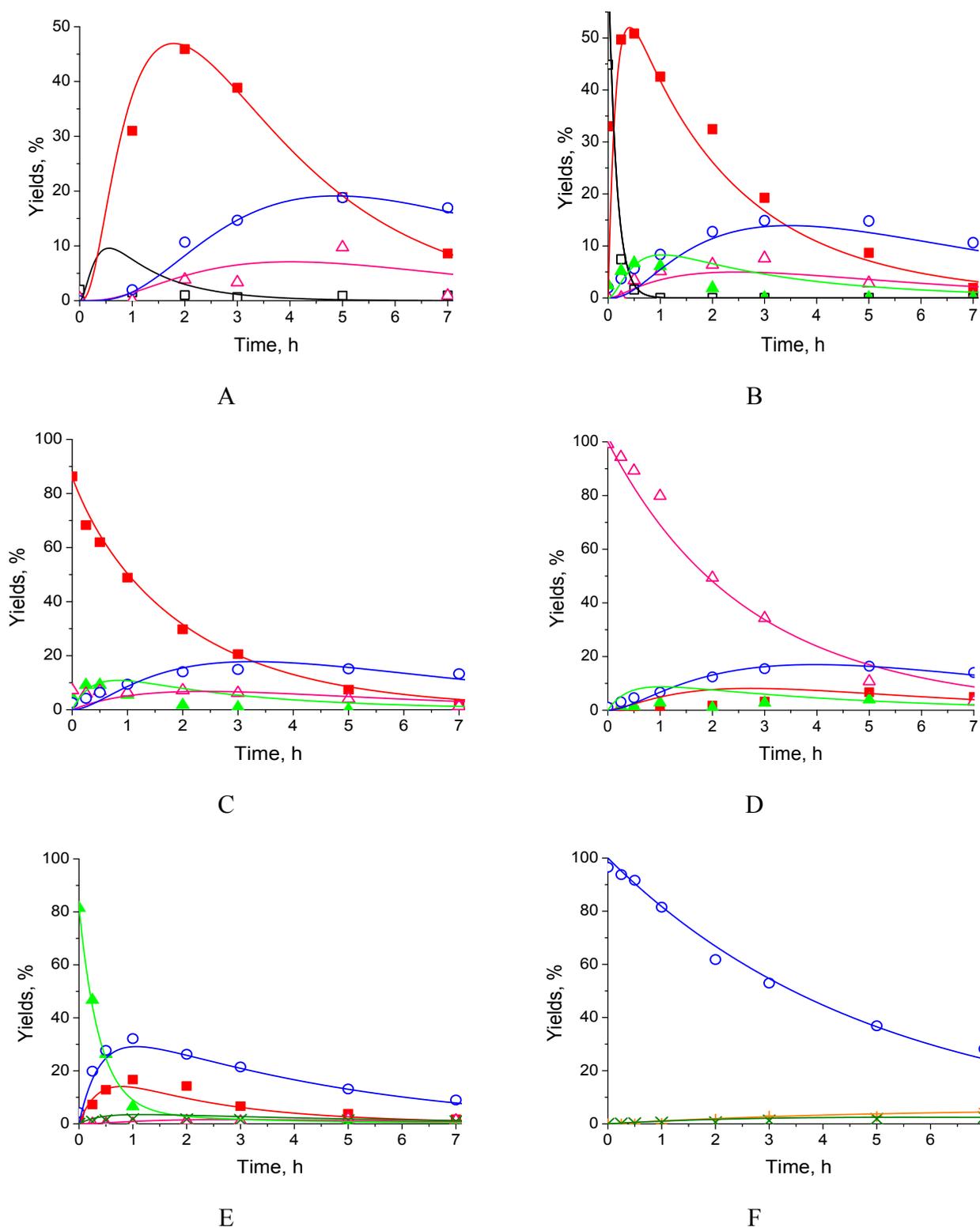


Figure 40. Simulated kinetic curves (solid curves) in comparison with the experimental data of the transformation of the main intermediates (\square - cellobiose, \blacksquare - glucose, \circ - 5-HMF, \triangle - mannose, \blacktriangle - fructose, \bullet - furfural, $+$ - levulinic acid, \times - formic acid). Substrate: A - cellulose, B - cellobiose, C - glucose, D - mannose, E - fructose, F - 5-HMF. Cellulose and the catalyst $10 \text{ g}\cdot\text{L}^{-1}$, 45 mL, 180°C , 10 bar (Ar), 1500 rpm, reaction time 7 h.

4.4 Chapter conclusions

The following conclusions devoted to cellulose hydrolysis-dehydration could be formulated from the experimental data.

The series of new Nb-containing zirconia catalysts have been prepared, characterized (with XRD, N₂ adsorption, ICP-OES, UV-vis DRS) and tested in pure hot water without any additives in one-pot hydrolysis-dehydration of activated microcrystal cellulose to produce glucose and 5-hydroxymethylfurfural. ICP-OES analysis of the spent catalysts and reaction solutions shows the excellent stability of the catalysts under hydrothermal conditions. The activity of the catalysts increases as follows: 0.5%Nb/ZrO₂ < ZrO₂ << 1.1%Nb/ZrO₂ ~ 2.8%Nb/ZrO₂. The maximum yields of glucose and HMF are 22 mol% and 16 mol%, respectively. All the catalysts are shown to be non-macroporous bulk zirconia containing mainly the monoclinic phase of ZrO₂ (97-99%). The formation of Nb₂O₅ crystal phase is not observed. The state of NbO_x species has been studied by UV-vis DRS spectroscopy. 0.5%Nb/ZrO₂ contains niobium as inactive isolated NbO₄ species, while polymerized niobia NbO_x (NbO₆) resides on the surface of 1.1%Nb/ZrO₂ and 2.8%Nb/ZrO₂. Isolated NbO₄ structures separate acid and base sites of ZrO₂ decreasing its own catalyst activity. Polymeric niobia brings Brønsted acid sites, thus increasing essentially the acid properties and the catalytic activity.

The studies have been carried out aimed at developing solid acid catalysts for synthesis of a valuable compound, 5-HMF, from cellulose via “one-pot” hydrolysis-dehydration. The catalysts have been prepared using a mesoporous graphite-like material Sibunit[®]. To choose the optimal method for generation of surface acid groups, the following procedures for Sibunit treatment have been used: sulfonation with fuming sulfuric acid, oxidation with nitric acid or wet air, as well as additional sulfonation of oxidized carbon samples. Carbon catalysts and untreated Sibunit sample have been characterized by low temperature N₂ adsorption, acid-base titration with NaOH, XPS, XRF. Catalytic properties have been investigated in cellulose hydrolysis-dehydration in the batch and flow reactors.

Sulfonation of Sibunit at a temperature above 200 °C leads to extremal destroying the material's structure. When the temperature is lower than 200 °C texture changes are not so strong. The content of acid groups on the carbon surface increases with the rise of the sulfonation temperature. It is 0.4 mmol·g⁻¹ in the most promising Sibunit sample sulfonated at 200 °C (C-S200).

All the oxidation techniques cause carbon material destruction. Additional sulfonation of the oxidized carbons strengthen this effect. The total amount of acid groups is comparable to C-S150 and C-S200 in the oxidized samples and 1.5–2 times higher in the oxidized-sulfonated samples.

The carbon catalysts are active in the process investigated. Glucose and 5-HMF are the main products.

Flow conditions and oxidized-sulfonated catalysts are most suitable for glucose production from cellulose. On the other hand, the batch reactor and sulfonated carbons are suited for 5-HMF

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synthesis from the polysaccharide. The highest yields of glucose and 5-HMF reached are 74 and 21%, respectively.

In conclusion, the requests to an effective cellulose hydrolysis-dehydration catalyst are the following ones. A catalyst should have high acidity (high amount of surface acid groups) and high amount of sulpho groups. A catalyst should possess a stable and significant specific surface area. Sibunit sulfonated at 150 and 200 °C (samples C-S150 and C-S200), oxydized by wet air mixture (C-O) and oxydized-sulfonated (C-O-S200) are the most perspective carbon catalysts investigated in the present work.

CONCLUSIONS

1. The pioneering systematic investigations of the one-stage catalytic process of cellulose hydrolysis-oxidation in the presence of P-Mo-V heteropolyacids as bifunctional catalysts in the aqueous medium led to the following.

- The possibility of the production of formic acid from cellulose at high yields (up to 66 %) was discovered.
- The optimal reaction conditions were determined: 150-160 °C, oxidative atmosphere (20% O₂ and 80% N₂). Pressure does not influence the initial reaction rate.
- The activation energy of the cellulose hydrolysis-oxidation was determined: 83 kJ·mol⁻¹.
- It was established that the maximal reaction rate is provided by the most acidic HPA solutions; a linear dependence of the reaction rate on the concentration of H⁺ and more complex dependence on the vanadium content was observed.
- The mechanism suggested for the sugar hydrolysis-oxidation in the presence of V-containing HPA catalysts involves bonding of VO₂⁺ to the neighboring hydroxyl groups in the carbohydrate molecule followed by cleavage of the C-C bond.

2. A high catalytic activity of solid NbO_x/ZrO₂ catalysts for hydrolysis-dehydration of cellulose to glucose and 5-HMF in pure water was discovered. Physicochemical characterization and catalytic testing of the catalysts led to the following.

- The maximal yields of glucose and 5-HMF (22 and 15 %, respectively) were obtained in the presence of the 2.8%Nb/ZrO₂ catalyst.
- The exceptional stability of the catalysts under hydrothermal conditions up to 300 °C was shown.
- The activity series of the catalysts was determined: 0.5%Nb/ZrO₂ < ZrO₂ < 1.1%Nb/ZrO₂ ~ 2.8%Nb/ZrO₂.
- The catalyst activity was established to increase due to the appearance of the Brønsted acidity upon formation of polymer structures NbO_x.

3. Solid acid catalysts were developed based on carbon material Sibunit-4 for hydrolysis-dehydration of cellulose to glucose and 5-HMF in an aqueous medium. Systematic investigations of the influence of the catalyst activation method (sulfation, oxidation, oxidation-sulfation) on the morphology and surface chemistry led to the following.

- It was discovered that glucose and 5-hydroxymethylfurfural are the main reaction products over the solid acid catalysts. High yields of the products were demonstrated: up to 74 % of glucose in a flow reactor and up to 21 % of 5-HMF in a static reactor.

- Sulfation of the carbon catalyst was established to result in the formation of oxygen-containing and sulfogroups on the surface. The total number of acid groups increases with the rise of sulfation temperature (from 80 to 250 °C). The temperature elevation above 200 ° results in the destruction of the Sibunit structure and in shrinkage of the specific surface area.
- Comparable contents of oxygen-containing acidic groups are produced upon Sibunit oxidation (with wet air and HNO₃) and sulfation at 150 °C. Sulfation of oxidized catalysts does not result in reliable anchoring of sulfogroups but in an increase in the content of catalytically active oxygen-containing acid centers and in destruction of the structure of the carbon catalyst.
- The catalyst activity increases with an increase in the total acidity but decreases upon destroying the Sibunit structure. Optimal catalytic systems were found: oxidized sulfated Sibunit for production of glucose; Sibunit sulfated at 150–200 °C and Sibunit oxidized with wet air for production of 5-HMF.
- A possibility of effective isolation of 5-HMF from the hydrolysate using extraction by methylisobutylketone or isobutanol was demonstrated.

4. Kinetics of cellulose hydrolysis-dehydration in the presence of a solid acidic carbon catalyst in static and flow reactors was studied for the first time. The results are as follows.

- Kinetic regularities of individual stages were studied. The observed first order for all the stages and rate constants of individual stages were determined.
- It was established that the limiting stages are cellulose dissolution and rearrangement of glucose to fructose.
- The heterogeneous catalytic mechanism was established for the overall process.
- The general process scheme was suggested to include cellulose dissolution, hydrolysis of oligosaccharides, isomerization of glucose to fructose, dehydration of fructose to 5-HMF, a number of stages of destruction of intermediates and products, polymerization of 5-HMF.
- A kinetic 17-stage model of the process was developed to provide accurate qualitative and quantitative description of experimental data on the static reactor.

This work will be continued and it will include the collaboration between the Boreskov Institute of Catalysis (BIC) and the Institute of Solid Matter Chemistry of Bordeaux (ICMCB) in the framework of the French-Russian scientific collaboration via Joint Catalytic valorization of biomass.

The work will be developed in the following areas:

1. The development of a new Sub- and/or Supercritical Water procedure for the separation of lignocellulosic polysaccharide components to produce soluble oligosaccharides (from hemicellulose and amorphous cellulose) and crystalline cellulose. Hollocellulose (mixture of hemicellulose and

cellulose obtained after isolation of organosolv lignin from biomass) and amorphous-crystalline cellulose will be tested as the substrates for this procedure.

2. The design of new techniques for the preparation of Nb/ZrO₂ catalysts for polysaccharides hydrolysis and one-pot hydrolytic-dehydration. The techniques will be developed using sub- and supercritical approaches developed at ICMCB for the production of nano-sized ceramic materials with unique properties. Characterization of catalysts will be carried out by a complex of physical-chemical methods in BIC and ICMCB.

3. The development of in situ characterization tools for investigating cellulose hydrolysis.

APPENDIX

Appendix 1. Summary of investigating the solid and heterogeneous catalysts in the depolymerization of different polysaccharides, disaccharides and monosaccharides. S : W : C – the ratio of substrate (g) – water (mL) – catalyst (g, mmol for CsHPA only). AC – activated carbon, MCM – mesopore carbon material [163], PC – pyrolytic carbon [144], CC – corn-cob, Sugar – sucrose.

№	Catalyst				Substrate	Main product			Reaction parameters			Ref.
	Name	S _{BET} , m ² /g	d _{PORE} , nm	C _{acid gr.} mmol/g		Name	Y, %	S, %	Ratio S : W : C	T, °C	τ, h	
1	CsH ₂ PW ₁₂ O ₄₀	-	-	0.67	Cell	Glucose	~27	~50	1.6 : 83 : 1	160	6	[118]
2	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	-	-	0.05	Cell	Glucose	~9	~80	1.6 : 83 : 1	160	6	[118]
3	Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀	-	-	0.45	Cell	Glucose	21.3	89.9	1.4 : 100 : 1	170	8	[137]
4	Cs ₂ HPW ₁₂ O ₄₀	72	-	0.23	Cell	Glucose + 5-HMF	~6	19/3	25 : 1 : 10	190	24	[138]
5	[C ₁₆ H ₃₃ N(CH ₃) ₃] H ₂ PW ₁₂ O ₄₀	-	-	1.8	Cell	Glucose	39.3	89.1	1.4 : 100 : 1	170	8	[137]
6	Cr[(DS)H ₂ PW ₁₂ O ₄₀] ₃	-	-	-	Cell	5-HMF	52.7	68.3	3.3 : 67 : 1	150	2	[189]
7	C	5	1.2	0	Cell	Glucose	~0	0	1 : 50 : 1	100	6	[144]
8	AC	703	-	0.05	Cell	Glucose	0	0	1 : 100 : 1.1	150	24	[32]
9	MCM-3	1120	3.8	-	Cell	Glucose 5-HMF	20.3 4.3	37.9 8.0	8.1 : 1 : 1.2	230	~0	[163, 164]
10	AC-OH-SO ₃ H	762	-	0.50	Cell	Glucose	62.6	84.2	1 : 100 : 1.1	150	24	[32]
11	AC-OH-SO ₃ H	695	-	0.89	Cell	Glucose	10	26	1 : 100 : 1.1	150	24	[31]
12	AC-SO ₃ H	945	-	0.47	Cell	Glucose	61.0	86.6	1 : 100 : 1.1	150	24	[32]
13	AC-SO ₃ H	595	-	0.56	Cell	Glucose	8	25	1 : 100 : 1.1	150	24	[31]
14	AC-SO ₃ H	806	< 2	1.63	Cell	Glucose	40	-	1 : 111 : 1.1	150	24	[90, 140]

№	Catalyst				Substrate	Main product			Reaction parameters			Ref.
	Name	S _{BET} , m ² /g	d _{PORE} , nm	C _{acid gr.} mmol/g		Name	Y, %	S, %	Ratio S : W : C	T, °C	τ, h	
15	PC-SO ₃ H	5	1.2	1.8	Celb	Glucose	35	-	1 : 50 : 1	100	6	[144]
16	PC-SO ₃ H	2	-	1.9	Cell	Olig Glucose	64 4	67 4	1 : 28 : 12	100	3	[139]
17	PC-SO ₃ H	-	-	0.8	Cell	Olig + Glucose	39	-	1 : 100 : 2	150	6	[143, 155]
18	PC-SO ₃ H + Cl ⁻	-	-	0.8	Cell	Olig + Glucose	55	-	1 : 100 : 2	150	6	[143, 155]
19	PC-SO ₃ H	-	-	0.8	Cell	Olig + Glucose	39	-	1 : 100 : 2	120	6	[143, 155]
20	Cl-PC-SO ₃ H	-	-	0.8	Cell	Olig + Glucose	90	-	1 : 100 : 2	120	6	[143, 155]
21	PC-SO ₃ H	-	-	0.8	Celb	Glucose	45	-	1 : 100 : 2	120	6	[143, 155]
22	Cl-PC-SO ₃ H	-	-	0.8	Celb	Glucose	45	-	1 : 100 : 2	120	6	[143, 155]
23	AC-OH oxydized by H ₂ O ₂	634	-	0.77	Cell	Glucose	2	7.7	1 : 100 : 1.1	150	24	[31]
24	AC-OH oxydized by HNO ₃	762	-	0.36	Cell	Glucose	9.7	30.8	1 : 100 : 1.1	150	24	[32]
25	2%Ru/MYM	1100	3.8	-	Cell	Glucose 5-HMF	27.6 3.0	47,0 5.1	8.1 : 1 : 1.2	230	~0	[163, 164]

№	Catalyst				Substrate	Main product			Reaction parameters			Ref.
	Name	S _{BET} , m ² /g	d _{PORE} , nm	C _{acid gr.} mmol/g		Name	Y, %	S, %	Ratio S : W : C	T, °C	τ, h	
26	2%Ru/AY	-	-	-	Cell	Glucose 5-HMF	11.3 1.4	29.3 3.6	8.1 : 1 : 1.2	230	~0	[163]
27	10%Ru/MCM	1100	3.8	-	Cell	Glucose 5-HMF	34.2 1.9	50.6 2.8	8.1 : 1 : 1.2	230	~0	[163]
28	2%Pd/MCM	1100	3.8	-	Cell	Glucose 5-HMF	13.3 1.3	30.1 3.0	8.1 : 1 : 1.2	230	~0	[163]
29	2%Pt/MCM	1100	3.8	-	Cell	Glucose 5-HMF	13.1 1.5	34.1 3.9	8.1 : 1 : 1.2	230	~0	[163]
30	Polystyrene resin-SO ₃ H	-	-	-	Cell	Glucose	93	90	30 : 300 : 1	120	10	[167]
31	Amberlist [®] -15	50	-	4.8	Cell	Glucose	6.2	21.1	1 : 10 : 1	150	3	[169, 186]
32	Amberlist [®] -15	50	-	4.8	Sugar	Glucose	22	-	1 : 10 : 1	100	0.3	[186]
33	Amberlist [®] -15	50	-	4.8	Starch	Glucose	11	-	1 : 10 : 1	100	0.3	[169, 186]
34	Nifion [®]	< 1	-	0.9	Cell	Glucose	0	0	1 : 28 : 12	100	3	[139]
35	Bimodal zeolite H-Z-5	427.6	-	0.73	Cell	5-HMF	49	74	1 : 40 : 2	190	4	[171]
36	Zeolite H-ZSM-5 (Si/Al - 25)	317	0.4	0.38	Cell	Glucose	1.6	12.5	3 : 200 : 1	160	12	[180]
37	Zeolite H-ZSM-5 (Si/Al -45)	124	< 2	0.3	Cell	Glucose	10	~80	9 : 1 : 1	150	24	[90]
38	Zeolite H-ZSM-5	300.8	-	0.51	Cell	5-HMF	9	75	1 : 40 : 2	190	4	[171]

№	Catalyst				Substrate	Main product			Reaction parameters			Ref.
	Name	S _{BET} , m ² /g	d _{PORE} , nm	C _{acid gr.} mmol/g		Name	Y, %	S, %	Ratio S : W : C	T, °C	τ, h	
39	Zeolite Hβ (Si/Al - 5)	-	-	0.98	Cell	Glucose	5	-	10 : 1 : 10	150	5	[146]
40	Zeolite Hβ (Si/Al -75)	315	-	0.18	Cell	Glucose	5	21.7	9 : 1 : 1	150	24	[90]
41	SO ₄ ²⁻ /Ti-MCM-41	606	2.9	-	Cell	5-HMF	7.5	-	10 : 300 : 1	230	2	[172]
42	γ-Al ₂ O ₃	140	-	0.05	Cell	Glucose	3	-	10 : 1 : 10	150	5	[146, 148]
43	Al ₂ O ₃	140	-	0.05	Cell	Glucose	1	~15	9 : 1 : 1	150	24	[90, 180]
44	CaP ₂ O ₆	0.5	0	-	Cell	Glucose + 5-HMF	22 18	-	10 : 100 : 1	230	0.1	[108]
45	CoFe ₂ O ₄ @SiO ₂ -SO ₃ H	-	-	0.5	Cell	Glucose	7.0	23.1	1 : 10 : 1	150	3	[186]
46	CoFe ₂ O ₄ @SiO ₂ -SO ₃ H	-	-	0.5	Celb	Glucose	88	-	1 : 10 : 1	100	0.3	[186]
47	CoFe ₂ O ₄ @SiO ₂ -SO ₃ H	-	-	0.5	Sugar	Glucose	93	-	1 : 10 : 1	100	0.3	[186]
48	CoFe ₂ O ₄ @SiO ₂ -SO ₃ H	-	-	0.5	Starch	Glucose	48	-	1 : 10 : 1	100	0.3	[186]
49	Fe ₃ O ₄ @SiO ₂ -SO ₃ H	464	4.8	1.1	Cell	Glucose	50	-	1 : 10 : 1	150	3	[148, 184]
50	Fe ₃ O ₄ @SiO ₂ -SO ₃ H	464	4.8	1.1	Cell	LA	42	-	1 : 10 : 1	150	3	[148, 184]
51	Fe ₃ O ₄ @SiO ₂ -SO ₃ H	464	4.8	1.09	Celb	Glucose	96	-	1 : 10 : 1	150	3	[148, 184]
52	Fe ₃ O ₄ @C-SO ₃ H	-	-	1.56	Cell	Glucose	52	-	10 : 1 : 10	150	5	[146]
53	Fe ₃ O ₄ @C-SO ₃ H	-	-	1.56	Cell	LA	44	-	10 : 1 : 10	150	5	[146]
54	Fe ₃ O ₄ @C-SO ₃ H	-	-	1.56	Celb	Glucose	94	-	10 : 1 : 10	150	5	[146]
55	NbHMoO ₆	153	-	0.4	Cell	Glucose	1	11.1	5 : 100 : 1	130	12	[169]
56	NbHMoO ₆	153	-	0.4	Starch	Glucose	21	-	5 : 100 : 1	100	15	[169]

№	Catalyst				Substrate	Main product			Reaction parameters			Ref.
	Name	S _{BET} , m ² /g	d _{PORE} , nm	C _{acid gr.} mmol/g		Name	Y, %	S, %	Ratio S : W : C	T, °C	τ, h	
57	Nb ₂ O ₅ ·nH ₂ O	90	-	0/4	Cell	Glucose	0	0	1 : 28 : 12	100	3	[139]
58	SiO ₂	671	3.5	1.96	Cell	Glucose	50	68.4	9 : 1 : 1	150	24	[180]
59	SiO ₂	603	4.7	0	Cell	Glucose	0	-	1 : 10 : 1	150	3	[148]
60	SiO ₂	773	-	-	Celb	Glucose	12	-	5 : 100 : 1	160	1.5	[185]
61	SiO ₂ -SO ₃ H	603	4/7	1.5	Cell	Glucose	52	-	1 : 10 : 1	150	3	[148]
66	Sr(PO ₃) ₂	0.5	0	-	Cell	Glucose + 5-HMF	35	-	10 : 100 : 1	230	0.1	[108]
67	TiO ₂	48.2	4.6	0.16	Cell	5-HMF	13	37	1 : 10 : 1	250	0.08	[176, 181]
68	TiO ₂	48.2	4.6	0.16	CC	5-HMF Furfural	~7 ~9	~34 ~39	1 : 10 : 1	250	0.08	[176]
69	TiO ₂ -ZrO ₂	187	2.5	0.64	Cell	5-HMF	14	50	1 : 10 : 1	300	0.08	[176]
70	TiO ₂ -ZrO ₂	187	2.5	0.64	CC	5-HMF Furfural	8.6 10.3	34.4 41.2	1 : 10 : 1	300	0.08	[176]
71	ZrO ₂	135	2.8	0.08	Cell	Glucose	9	57.0	9 : 1 : 1	150	24	[180]
72	ZrO ₂	103	4.5	0.23	Cell	5-HMF	8.3	33	1 : 10 : 1	250	0.08	[176, 181]
73	ZrO ₂	103	4.5	0.23	CC	5-HMF Furfural	6 8	31 42	1 : 10 : 1	300	0.08	[176]
74	ZrO ₂	407	-	0.09	Cell	Glucose	1	~10	9 : 1 : 1	150	24	[90, 140]
75	ZrO ₂ -SiO ₂	506	-	-	Celb	Glucose	14	-	5 : 100 : 1	160	1.5	[185]

№	Catalyst				Substrate	Main product			Reaction parameters			Ref.
	Name	S _{BET} , m ² /g	d _{PORE} , nm	C _{acid gr.} mmol/g		Name	Y, %	S, %	Ratio S : W : C	T, °C	τ, h	
76	ZrO ₂ -SiO ₂ -SO ₃ H	284	-	3.4	Celb	Glucose	53	-	5 : 100 : 1	160	1.5	[185]
77	ZrO ₂ -SO ₃ H	52	-.	1.6	Cell	Glucose	14.2	40	9 : 1 : 1	150	24	[90, 140]
78	ZrO ₂ -SO ₃ H 1.8%	243	3.6	0.73	Cell	5-HMF	11	42	1 : 10 : 1	250	0.1	[181]

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Titre: TRANSFORMATION CATALYTIQUE DE LA CELLULOSE EN MILIEU AQUEUX POUR LA PRODUCTION DE MOLECULES PLATEFORMES

Résumé:

Ce projet de thèse a concerné la recherche et le développement de catalyseurs multifonctionnels efficaces et de procédés catalytiques en une étape (hydrolyse-déshydratation, hydrolyse-oxydation) pour la transformation de la cellulose en produits chimiques à valeur ajoutée (glucose, 5-HMF, acide formique). Ces produits sont également connus sous le nom de molécules plateformes et ils présentent un intérêt dans une large gamme d'applications, par exemple, pour les industries alimentaires et chimiques et pour la production de carburants. Dans ce projet, des recherches systématiques sur la synthèse de l'acide formique en présence de catalyseurs HPA contenant du vanadium ont d'abord été conduites. En particulier, l'influence de la composition du catalyseur et des paramètres du procédé sur le rendement en produit cible a été étudiée. Le rendement en AF obtenu (66%) est supérieur à tous les résultats rapportés dans la littérature à ce jour. Les catalyseurs NbO_x / ZrO₂ ont été évalués pour la première fois sur la réaction d'hydrolyse-déshydratation de la cellulose microcristalline activée en milieu aqueux. Des rendements élevés en glucose et en 5-HMF (22 et 16%, respectivement) ont été observés. Des catalyseurs carbonés à base du matériau Sibunit modifié ont été utilisés pour la première fois pour l'hydrolyse-déshydratation de la cellulose. Les rendements en glucose (jusqu'à 74% dans un réacteur en continu) et en 5-HMF (jusqu'à 21% dans un réacteur statique) ont été obtenus en présence de Sibunit modifié par sulfonation et / ou oxydation. Ces résultats sont également supérieurs à ceux reportés à ce jour sur les systèmes catalytiques carbonés. La relation entre l'activité sur les réactions d'hydrolyse-déshydratation et la méthode d'activation du carbone a été étudiée en profondeur. L'étude du mécanisme et de la cinétique de la réaction d'hydrolyse-déshydratation de la cellulose en présence de catalyseurs acides solides a également été réalisée.

Mots clés: cellulose, hydrolyse-déshydratation, hydrolyse-oxydation, catalyse, carbone, Sibunit, zircone, niobium, hétéropolyanion, molécules plateformes, glucose, 5-hydroxyméthylfurfural, acide formique.

Title: CATALYTIC METHODS OF CELLULOSE TRANSFORMATION IN PURE WATER INTO VALUABLE CHEMICAL SUBSTANCES

Abstract:

The PhD project was devoted to search for and to develop effective multifunctional catalysts and catalytic one-stage processes (hydrolysis-dehydration, hydrolysis-oxidation) for transformation of cellulose to valuable chemicals (glucose, 5-HMF, formic acid). These products are also known as platform molecules and they seem to be promising for a wide range of application in food and chemical industries and for fuel production. In this project, systematic investigations of the formic acid synthesis in the presence of vanadium-containing HPA catalysts was first conducted; the influence of the catalyst composition and process parameters on the yield of the target product was studied. The obtained FA yield (66 %) was superior to all the results reported in literature. The NbO_x/ZrO₂ catalysts were applied for the first time for hydrolysis-dehydration of activated microcrystalline cellulose in pure water. High yields of glucose and 5-HMF (22 and 16 %, respectively) were observed. Carbon catalysts based on modified Sibunit material was used for the first time for cellulose hydrolysis-dehydration. The yields of glucose (up to 74 % in a flow reactor) and 5-HMF (up to 21 % in a static reactor) were obtained in the presence of Sibunit modified by sulfation and/or oxidation; these are much superior to the results on carbon catalytic systems reported in literature. The relation between the activity to hydrolysis-dehydration and the method of the carbon activation was thoroughly studied. Investigations of the mechanism and kinetics of cellulose hydrolysis-dehydration in the presence of solid acid catalysts were also carried out.

Keywords: cellulose, hydrolysis-dehydration, hydrolysis-oxidation, catalysis, carbon, Sibunit, zirconia, niobium, heteropolyacid, platform molecules, glucose, 5-hydroxymethylfurfural, formic acid.