EDN: GKNMLS

УДК 544.478.02+544.478.1

Ruthenium Catalysts on Zr-SBA-15 and Nb/Zr-SBA-15 Supports for Xylose Hydrogenation

Viktor A. Golubkov^{*a, b}, Yulia N. Zaitseva^a, Valentin V. Sychev^{a, b}, Anna O. Eremina^a, Sergei D. Kirik^{a, b}, Svetlana A. Novikova^a, Kseniva A. Litvintseva^c and Oxana P. Taran^{a, b, c}

^aInstitute of Chemistry and Chemical Technology SB RAS Federal Research Center "Krasnoyarsk Scientific Center SB RAS" Krasnoyarsk, Russian Federation ^bSiberian Federal University Krasnoyarsk, Russian Federation ^cFederal Research Center "Boreskov Institute of Catalysis" SB RAS Novosibirsk, Russian Federation

Received 18.10.2024, received in revised form 12.11.2024, accepted 15.11.2024

Abstract. A novel Ru-catalysts based on niobia modified Zr-SBA-15 were developed for xylose to xylitol hydrogenation. The catalysts showed excellent activity and selectivity in the process at temperature as low as 70 °C providing 93 % conversion and >98 % selectivity within 90 min. As shown by the catalysts characterization: spectroscopy (XPS, UV–Vis DRS), microscopy (TEM), temperature-programmed reduction (TPR-H2) and low angle X-ray diffraction, niobium oxide has a strong interaction with the deposited ruthenium. This causes a slight decrease of the initial reaction rate of xylose hydrogenation. However, modification of Zr-SBA-15 with niobia drastically improves the acidic properties required for a potential use of the developed catalyst in one-pot hydrolysis-hydrogenation processing of plant polysaccharides into polyols, which will be the focus of a future research.

Keywords: SBA-15 silica, mesoporous, mesostructure, ruthenium, niobium oxide, xylose, hydrogenation.

Acknowledgements. The work was carried out with the support of the Russian Science Foundation (project No. 21–73–20269) on the equipment of the Center for Collective Use "National Center for Research of Catalysts" and the Krasnoyarsk Regional Center for Collective Use of the KSC SB RAS.

[©] Siberian Federal University. All rights reserved

This work is licensed under a Creative Commons Attribution-NonCommercial 4.0 International License (CC BY-NC 4.0).

^{*} Corresponding author E-mail address: golubkov.va@icct.krasn.ru

Citation: Golubkov V. A., Zaitseva Yu. N., Sychev V. V., Eremina A. O., Kirik S. D., Novikova S. A., Litvintseva K. A., Taran O. P. Ruthenium catalysts on Zr-SBA-15 and Nb/Zr-SBA-15 supports for xylose hydrogenation. J. Sib. Fed. Univ. Chem., 2024, 17(4), 528–538. EDN: GKNMLS



Рутениевые катализаторы гидрирования ксилозы на носителях Zr-SBA-15 и Nb/Zr-SBA-15

В. А. Голубков^{а, б}, Ю. Н. Зайцева^а, В. В. Сычев^{а, б}, А. О. Еремина^а, С. Д. Кирик^{а, б}, С. А. Новикова^а, К. А. Литвинцева^в, О. П. Таран^{а, б, в} ^аИнститут химии и химической технологии СО РАН ФИЦ «Красноярский научный центр СО РАН» Российская Федерация, Красноярск ⁶Сибирский федеральный университет Российская Федерация, Красноярск ⁶Федеральный исследовательский центр "Институт катализа им. Борескова" СО РАН

Аннотация. Разработаны новые рутениевые катализаторы на основе Zr-SBA-15 и модифицированного оксидом ниобия Zr-SBA-15 для гидрирования ксилозы в ксилит. Катализаторы показали отличную активность и селективность в процессе гидрирования при температуре до 70 °C, обеспечивая 93 % конверсии и >98 % селективности за 90 минут. Как показало комплексное исследование, включающее спектральный анализ (РФЭС, спектроскопию диффузного отражения), просвечивающую электронную микроскопию, температурно-программируемое восстановление (TПВ-H₂), порошковую рентгеновскую дифракцию в малоугловой области, наблюдается сильное взаимодействие оксида ниобия с нанесенным рутением. Это вызывает некоторое снижение начальной скорости реакции гидрирования ксилозы. Однако модификация Zr-SBA-15 оксидом ниобия существенно улучшает кислотные свойства носителя, необходимые для использования разработанных катализаторов в одностадийных процессах гидролиза-гидрирования растительных полисахаридов до многоатомных спиртов, что является целью дальнейших исследований.

Ключевые слова: SBA-15, мезопористые материалы, мезоструктурированные материалы, рутений, оксид ниобия, ксилоза, гидрирование.

Благодарности. Работа выполнена при поддержке Российского научного фонда (проект № 21–73–20269) на оборудовании Центра коллективного пользования «Национальный центр исследования катализаторов» и Красноярского краевого центра коллективного пользования КНЦ СО РАН.

Цитирование: Голубков В. А., Зайцева Ю. Н., Сычев В. В., Еремина А. О., Кирик С. Д., Новикова С. А., Литвинцева К. А., Таран О. П. Рутениевые катализаторы гидрирования ксилозы на носителях Zr-SBA-15 и Nb/Zr-SBA-15. Журн. Сиб. федер. ун-та. Химия, 2024, 17(4). С. 528–538. EDN: GKNMLS

Introduction

Xylitol is largely produced in the world due to its wide range of applications, such as low-calorie sweetener, anti-caries agent and an excipient in pharmaceutical products. The industrial production of xylitol is based on the reduction of xylose obtained by hydrolysis of xylan [1]. Typically hydrogenation is carried out in an autoclave at 120–150 °C and 3–7 MPa of H₂ for 2–4 hours [2, 3]. The commercial catalyst for the process is Raney nickel, but its pyrophoric nature and susceptibility to leaching have adverse effects on its handling and durability [4]. Ruthenium has the highest catalytic activity in reactions of hydrogenation of carbohydrates in aqueous medium [5, 6]. Supported Ru catalysts are not subjected to leaching [7], making them reasonable to use. The right choice of support may provide high metal dispersion and stability preventing leaching and sintering of nanoparticles. The medium to large pore size should minimize diffusion limitation in aqueous media making mesoporous silicas such as MCF, MCM-41 and SBA-15 highly attractive.

Previously, we have developed acid catalysts for the hydrolysis of hemicelluloses based on SBA-15 doped with ZrO_2 [8, 9] and Ru catalysts for hydrogenation of carbohydrates based on this support [10]. The catalysts demonstrated high activity in xylose hydrogenation even under very mild conditions (70 °C in water with 5.5 H₂ MPa) with xylitol selectivity 96–99 %.

In this work we develop nanocomposite of Zr-SBA-15 and niobia via impregnation method, such doping may result in improved support acidity leading to a different Ru distribution and better overall catalyst stability. The catalysts are characterized (XPS, UV–Vis DRS, TEM, TPR-H₂, XRD) to establish the fine interconnections tuning the catalyst activity.

Material and methods

Synthesis of supports and catalysts

The detailed synthesis of supports and catalysts is provided in the Supporting Information.

Synthesis of 5Zr-SBA-15 support with ZrO_2 content 5 wt.% was carried out by co-precipitation according to the modified methodology [11]. For the synthesis of composites with niobia, the method of impregnation by moisture capacity was carried out [12] using niobium oxalate in 0.1 M oxalic acid. Ruthenium deposition was carried out by the incipient wetness impregnation method using aqueous solution of Ru(NO)(NO₃)₃ with further reduction and passivation. The nominal loading of Ru 2 wt.% was used.

Study of supports and catalysts

The detailed methods used in the study are provided in the Supporting Information.

The acidic properties were studied by IR spectroscopy using pyridine as a probe molecule. The spectra were recorded on an IRTracer-100 FTIR spectrometer (Shimadzu, Japan). The morphology was studied on a Hitachi Regulus SU 8230 FE-SEM scanning electron microscope. The microstructure was studied by high-resolution transmission electron microscopy (HRTEM) using a ThemisZ microscope (Thermo Fisher Scientific, USA). XPS studies were carried out on a SPECS X-ray photoelectron spectrometer (Germany) using MgK radiation (1253.6 eV). Diffuse reflectance spectra (UV–Vis

DRS) were recorded using a Shimadzu 3600 scanning spectrometer and an ISR-603 Integrating Sphere Attachment. Studies by the temperature-programmed reduction method were carried out on a ChemBET Pulsar TPR/TPD (Quantachrome Inst., USA). Textural properties of samples were studied by low-temperature nitrogen adsorption-desorption method on the analyzer ASAP 2420 (Micromeritics). Specific surface area (S_{BET}) was calculated by BET method with correction by Ruckerol plot [13]. The pore volume was determined by the SinglePoint method at P/P₀ = 0.995. Pore size distribution was determined by the BJH-KJS method, mesopore diameter (D) by the maximum of the distribution. The wall thickness was determined as the difference between the cell parameter and the pore diameter. Powder diffraction data were obtained on an X'Pert PRO diffractometer with a PIXcel detector (PANalytical) with a graphite monochromator and CuK α radiation. Patterns were taken in the low-angle range from 0.5 to 5° on the 2 θ scale, step 0.026°, $\Delta t - 1$ s. In the high-angle region from 3 to 80° 2 θ , step 0.026°, $\Delta t - 0.1$ s. The cell parameter was calculated from the interplanar distance of the reflex (100) $a = (2/\sqrt{3} * d_{100})$.

Catalytic tests in the hydrogenation of xylose were carried out in a 100 mL AutoclaveEngineers (USA) autoclave reactor made of Hastelloy C 276. 0.3 g of xylose (Panreac, Pharm.), 0.1 g of catalyst, and 0.03 L of water were loaded. The reaction was carried out at 70 °C, 5.5 MPa H₂, 1200 rpm. Quantitative analysis was performed on an Agilent 1260 Infinity II HPLC, Rezex RPM–Monosaccharide Pb column²⁺ 300 × 7.8 mm, refractometric detection, eluent was deionized water, 70 °C, 0.6 mL/min. Qualitative analysis was performed on an Agilent 7890A with an Agilent 7000A quadrupole mass detector, HP-5ms 30 m × 0.25 mm × 0.25 mm capillary column; silanization.

Results and Discussion

Acidic species are required for potential use of supported catalyst in one-pot hydrolysishydrogenation processing of plant polysaccharides to polyols. Doping of SBA-15 silica with zirconium and modification with niobia improve the acidic properties [8, 9] (Table 1) with retaining its structure with a large number of transport mesopores. Ruthenium deposition decreases the content of weak (150 °C) acid species, but increases the content of stronger (350 °C) ones.

The 5Zr-SBA-15 particles inherently are patterned plates of $0.3-0.5 \times 2-4 \mu m$ (Fig. 1a). The addition of niobia does not change the characteristic morphology of the particles. Zr and Nb are uniformly distributed on grain of SBA-15 (Fig. 1b). The channel pore structure characteristic of SBA-15 is present (Fig. 1c, d). Upon deposition of niobia, nanocomposite is formed in the SBA-15 matrix. Thickenings consisting of niobia are formed on the pore walls (Fig. 1e, f). It was not possible to estimate the depth of niobium penetration using microscopy data. Such altered pores with thickened walls are arranged chaotically in the mesostructure. There are no large areas significantly filled with them.

Sample	5Zr-SBA-15		2Ru/Zr-SBA-15		10Nb/Zr-SBA-15		2Ru/10Nb/Zr-SBA-15	
T _{desorption} , °C	150	350	150	350	150	350	150	350
C _{BAS} , µmol/g	105	0	90	15	97	20	92	52
$C_{LAS}, \mu mol/g$	353	57	230	70	281	52	205	84

Table 1. Content of acid centers of supports and catalysts according to FTIR data with adsorbed pyridine



Fig. 1. SEM images: (a) images of 5Zr-SBA-15 support grains; (b) distribution of elements in 10Nb/5Zr-SBA-15 grains. TEM images: (c) 5Zr-SBA-15 channels, view perpendicular to the channels and (d) along the channels; (e) 10Nb/5Zr-SBA-15 channels partially occupied by niobia, with EDX mapping superimposed on (f)

Ruthenium is highly dispersed over the grain of the catalysts, but there are areas with high ruthenium content in the form of films (Fig. 2a). The average ruthenium particles size on the 5Zr-SBA-15 support was about 1 nm or less (Fig. 2b). On the outer surface of 2Ru/10Nb/5Zr-SBA-15, Ru nanoparticles with sizes of 1.5–4 nm (Fig. 2c), with an average size of 2.2 nm, are present. However, it is impossible to make a conclusion about the distribution, morphology and particle size of the deposited ruthenium inside the pores.

The catalysts were tested in the hydrogenation of xylose with molecular hydrogen. Although usually temperatures of 80–140 °C are required to achieve acceptable process duration (2–4 hours) and high yield of the target product [2, 3]. The developed catalysts allow the reaction to be carried out even at a low temperature of 70 °C. Within 90 min, a substrate conversion of ~93–94 % with xylitol selectivity of 98–99 % was observed. No by-products were detected by HPLC. Ribose, arabitol, ribitol, erythritol, ethylene glycol, 1,2-propylene glycol, glycerol were detected in trace amounts by GC–MS. This is consistent with the best known results: in the study of Dmitry Yu. Murzin et al [14] ruthenium



Fig. 2. TEM images of the catalysts. a) Ruthenium-rich region on 2Ru/5Zr-SBA-15; b) ruthenium nanoparticles on 2Ru/5Zr-SBA-15; c) nanoparticles on 2Ru/10Nb/5Zr-SBA-15



Fig. 3. Kinetic curves of xylose and xylitol (70 °C, 5.5 MPa H₂, 1200 rpm)

catalysts deposited on mesoporous molecular sieves such as SBA-15, MCM-41 and MCF including aluminum doped, also showed similar activity and selectivity at 70 °C.

The kinetics of the initial period (30 min) for the catalysts on 2Ru/5Zr-SBA-15 and 2Ru/10Nb/5Zr-SBA-15 are different (Fig. 3). To explain a drop of the initial reaction rate of xylose hydrogenation on 2Ru/10Nb/5Zr-SBA-15, the catalysts were investigated by thermo-programmed reduction, the ruthenium state was determined by XPS and UV-vis DRS.

The XPS data regarding the supports are presented in Supporting Information. The Ru3*d* spectrum is a doublet Ru3*d*_{5/2}-Ru3*d*_{3/2}, the magnitude of spin-orbit splitting is 4.17 eV. Accordingly, in the spectra of the studied samples we observe doublets with Ru3*d*_{5/2} binding energies of 279.9; 280.8 and 282.2±0.1 eV (Fig. 4). According to literature data, the doublet with Ru3*d*_{5/2} binding energy of 279.9 eV belongs to Ru⁰, 280.8 eV belongs to RuO₂, and 282.2 eV to RuO₃ [15–17]. In 2Ru/Zr-SBA-15 Ru⁰ 20 at.%; RuO₂–56; and RuO₃–24. All Ru in 2Ru/10Nb/Zr-SBA-15 is present as RuO₂.

Diffuse reflectance Uv-vis spectroscopy shows a fundamentally different pattern in the distribution of ruthenium states in the catalysts (Fig. 4). The data regarding the supports are presented in Supporting Information. The introduction of ruthenium leads to the bathochromic effect and the appearance of new absorption bands in the range of 350–430 nm. The spectrum of 2Ru/5Zr-SBA-15



Fig. 4. The spectral data regarding ruthenium state a) X-ray photoelectron spectra Ru3d of catalysts. b) Diffuse reflectance spectra of supports and catalysts

has maxima at 373 and 402 nm, while 2Ru/10Nb/5Zr-SBA-15 has maxima at 367, 378, and 411 nm. The 373–378 nm bands probably refer to the charge transfer of $4d^4 Ru^{4+} \leftarrow O^{2-}$, OH⁻ and OH₂ in RuO₂ for both samples. Similarly, ruthenium deposited on the zeolite (RuO₂/Y) has an absorption band at 375 nm [18]. Differences in the spectra of 2Ru/Zr-SBA-15 and 2Ru/10Nb/Zr-SBA-15 indicate different environment and state of Ru in the samples, we can assume a strong interaction of deposited RuO₂ with niobia.

On the profiles of temperature-programmed reduction by hydrogen of deposited ruthenium catalysts, complete reduction to Ru^0 is observed at temperatures below 400 °C. Ruthenium on 5Zr-SBA-15 support has 2 peaks of Ru reduction with temperatures of ~90 and 140 °C. When niobia is introduced into the support, additional peaks with higher reduction temperature appear, and H₂ absorption is two times higher than that of 2Ru/5Zr-SBA-15–1.3 mmol H₂ per g of catalyst and 0.5, respectively.

The reduction of Ru^{2+} and Ru^{3+} occurs without formation of intermediate valence states [14]. Two reduction peaks may be related to the effect particle size – smaller particles interact more strongly with the support and are reduced at a higher temperature [19]. According to literature data, the reduction temperature of ruthenium deposited on zirconia is noticeably lower than for SBA-15 silica – 80–110 °C [20]. This explains the relatively low reduction temperatures observed in this study. The reduction of 2Ru/10Nb/5Zr-SBA-15 proceeds differently, the coating of the silica surface with niobia shifts the complete reduction of the deposited Ru towards higher temperatures. Although according to the XPS data only Ru₂O is present, the 3 temperature regions can be distinguished. The high-temperature region (>300 °C) is related to the reduction of the support itself: the H₂ intake by the 10Nb/Zr-SBA-15 support is 0.3 mmol/g, the reduction occurs from 300 °C with a maximum at 525 °C. However, the middle temperature region (140–300 °C) can be explained only in the framework of consideration of Ruthenium-support interaction, which requires further study; oxygen transfer from the support to the metal can be realized as well [21].

Thus, the addition of niobium to 5Zr-SBA-15 improves acidic properties, which is favorable for the development of a one-pot process of hydrolysis-hydrogenation of plant polysaccharides into polyols. However, we found that ruthenium-support interaction can lead to a drop of the initial reaction rate.

 N_2 adsorption-desorption isotherms (type IV) and hysteresis (type H1) confirms the homogeneous packing of close in size pores, which are isolated and open at both ends cylindrical capillaries (Fig. 6).



Fig. 5. Profiles of H₂ temperature-programmed reduction of ruthenium catalysts



Fig. 6. N_2 adsorption-desorption isotherms of supports and catalysts (a) and pore size distribution calculated from adsorption (b) and desorption (c) branches

Sample	Specific surface area, m ² /g	Pore volume, cm ³ /g	Diameter of mesopores ^{ads} , Å	Diameter of mesopores ^{des} , Å	Cell parameter, Å	Wall thickness, Å
5Zr-SBA-15	634	0.60	74.0	58.1 (46.9)	103.7	29.7
2Ru/5Zr-SBA-15	580	0.52	73.5	57.6 (47.6)	104.7	31.2
10Nb/5Zr-SBA15	443	0.46	70.2 (57.1)	53.4 (46.3)	101.9	31.7 (44.8)
2Ru/10Nb/5Zr-SBA-15	425	0.41	71.9 (52.7)	54.2 (46.5)	102.2	30.3 (49.5)

Table 2. Textural and structural characteristics of supports and catalysts

in parentheses data on the second mode in the distribution of mesopore diameter and wall thickness; ^{ads} data calculated from the isotherm adsorption branch; ^{des} data calculated from the isotherm desorption branch.

Niobia is deposited on the pore walls, which leads to the pore diameter decrease, which is consistent with the microscopy data. The pore diameter insignificantly shifts towards smaller sizes, and a second mode with a smaller value appears (Fig. 6, Table 2). Ruthenium deposition reduces the total surface area and pore volume without affecting the mesopore diameter.

Thus, according to HRTEM and N₂ adsorption- desorption data, niobia is distributed in the form of films partially covering the pore walls. The thickness of the deposited niobium oxide is 7–10 Å. The diameters of the pore mouths according to HRTEM data and the pore diameters according to the adsorption branch for the 2Ru/10Nb/5Zr-SBA-15 catalyst have two modes, with the distribution maximum at 70–72 Å coinciding, and the position of the second, smaller maximum at ~47 Å, later corresponds to the pores coated with niobia. However, this pore diameter corresponds to the distribution maximum calculated from the desorption branch (Fig. S3).

In the high-angle region, all samples are X-ray amorphous (Fig. S4), ruthenium nanoparticles, zirconium embedded in the walls of SBA-15, and niobium deposited as a structured coating do not provide reflexes. In X-ray pattern of the samples, the presence of reflexes in the low-angle region indicates the formation of a characteristic hexagonal-type mesostructure. The modified samples have a more compressed structure, smaller cell parameter than unmodified SBA-15 silicate (110 Å) [8, 9] (Table 2). Ruthenium deposition on 5Zr-SBA-15 has almost no effect on the reflexes position, but changes their relative intensities. When ruthenium is supported to 10Nb/5Zr-SBA-15, a new reflex appears at the ~1.28° 2 θ , which is uncharacteristic of the SBA-15 mesostructure. It was not possible to detect such an effect in the literature.



Fig. 7. Diffractograms in low-angle region, insets - magnification of fragments in 5 or 3 times

Obviously, the appearance of a new reflex is associated with the appearance of a mesostructure with an appropriate size. Thus, the interplanar distance d_{100} of the ordered structure 5Zr-SBA-15 is 8.75 nm (Fig. 8). 2Ru/5Zr-SBA-15 contains small-sized ruthenium particles, less than 1 nm, on the outer surface, according to TEM. It is assumed that due to the curvature of the silicate wall in the interior of the pores, the ruthenium particles are even smaller. Therefore, at the interference of X-ray waves reflected from two walls or a wall and a deposited ruthenium cluster, the position of the diffraction maximum does not change ($d_{100} \approx d_a$), but there is a drop in the intensity of the reflex 100.

The situation with the 2Ru/10Nb/5Zr-SBA-15 is different. The reflex at $1.28^{\circ} 2\theta$ corresponds to $d_b = 6.90$ nm. This interplanar distance can be attributed to diffraction at narrower pores. But in the structure of catalysts and supports, a decrease in the interplanar distances (d_{100} , d_a and d_b , not to be confused with the pore diameter) by almost 2 nm is not detected. The only explanation is the appearance of ruthenium particles in the mesostructure, which have a size of about 2 nm on the outer surface, but inside can be smaller. Diffraction occurs on the pore walls and ruthenium nanoparticles distributed in the mesostructure, and a new reflex appears as a result of interference. Considering that the thickness of niobium oxide deposited on the wall is 0.7–1 nm. Then we can estimate the size of ruthenium particles inside the mesostructure of the 2Ru/10Nb/5Zr-SBA-15 catalyst:

 $d_{100} - d_b - thickness of Nb_xO_y = 0.8-1 nm$



Fig. 8. Schematic representation of 2Ru/10Nb/5Zr-SBA-15 structure

Conclusion

New ruthenium catalysts deposited on mesoporous mesostructured silica SBA-15 doped with Zr, as well as with deposited niobium oxide films, have been developed. The catalysts showed excellent activity and selectivity in the process of hydrogenation of xylose to xylitol already at a low temperature of 70 °C: within 90 min conversion >, 93 % and selectivity >98 %. As shown by the catalysts characterization: spectroscopy (XPS, UV–Vis DRS), microscopy (TEM), temperature-programmed reduction (TPR-H₂) and low angle X-ray diffraction, niobium oxide has a strong interaction on the deposited ruthenium. This causes a slight decrease in the initial reaction rate of xylose hydrogenation. However, modification of Zr-SBA-15 with niobia improves the acidic properties required for potential use of the developed catalyst in a one-pot hydrolysis-hydrogenation processing of plant polysaccharides into polyols, which will be the focus of future research.

Supplementary Information



References

[1] Schiweck H. B., Albert & Vogel, Roland & Schwarz, Eugen & K, MARKWART & Lüssem, Bernd & Moser, Matthias & Peters, Siegfried & C, DUSAUTOIS & Lefranc-Millot, Catherine & A, CLEMENT. Sugar Alcohols. *Ullmann's Encyclopedia of Industrial ChemistryEdition: 7th EditionChapter: Sugar Alcohols 2011.*

[2] Delgado Arcaño Y., Valmaña García O.D., Mandelli D., Carvalho W.A., Magalhães Pontes L.A. Xylitol: A review on the progress and challenges of its production by chemical route. *Catalysis Today 2020.* 344, 2–14.

[3] Chen B., Dingerdissen U., Krauter J., Rotgerink H.L., Möbus K., Ostgard D., Panster P., Riermeier T., Seebald S., Tacke T. New developments in hydrogenation catalysis particularly in synthesis of fine and intermediate chemicals. *Applied Catalysis A: General 2005.* 280(1), 17–46.

[4] García B., Orozco-Saumell A., López Granados M., Moreno J., Iglesias J. Catalytic Transfer Hydrogenation of Glucose to Sorbitol with Raney Ni Catalysts Using Biomass-Derived Diols as Hydrogen Donors. *ACS Sustainable Chemistry & Engineering 2021.* 9(44), 14857–14867.

[5] Michel C., Gallezot P. Why Is Ruthenium an Efficient Catalyst for the Aqueous-Phase Hydrogenation of Biosourced Carbonyl Compounds? *ACS Catalysis 2015*. 5(7), 4130–4132.

[6] Ahmed M. J., Hameed B. H. Hydrogenation of glucose and fructose into hexitols over heterogeneous catalysts: A review. *Journal of the Taiwan Institute of Chemical Engineers 2019*, 96, 341–352.

[7] Kusserow B., Schimpf S., Claus P. Hydrogenation of Glucose to Sorbitol over Nickel and Ruthenium Catalysts. *Advanced Synthesis & Catalysis 2003*. 345(1–2), 289–299.

[8] Skripnikov A. M., Eremina A. O., Novikova S. A., Zaitseva Y. N., Sychev V. V., Trotsky Y. A., Parfenov V. A., Kirik S. D., Glazneva T. S., Taran O. P. ZrO₂-containing Catalysts Based on SBA-15 for the Hydrolysis of Siberian Larch Arabinogalactan. The Influence of Synthesis Method and Zirconia Content. *Journal of Siberian Federal University. Chemistry 2023.* 16(4), 631–642. [9] Novikova S., Shaer Y.R., Eremina A., Sychev V., Baryshnikov S., Taran O. Synthesis of Heterogeneous Nanocomposite Catalyst ZrO₂@SBA-15 for Formic Acid Production from Hemicelluloses. *Russian Journal of Inorganic Chemistry 2024*, 1–9.

[10] Golubkov V. A., Zaitseva Y. N., Kirik S. D., Eremina A. O., Sychev V. V., Taran O. P. Xylitol Production from Xylose over Zirconia-Doped Silica SBA-15 Supported Ruthenium Catalysts. *Chemistry of Plant Raw Material 2023*(4), 397–405.

[11] Thunyaratchatanon C., Luengnaruemitchai A., Chaisuwan T., Chollacoop N., Chen S.-Y., Yoshimura Y. Synthesis and characterization of Zr incorporation into highly ordered mesostructured SBA-15 material and its performance for CO₂ adsorption. *Microporous and Mesoporous Materials* 2017. 253, 18–28.

[12] García-Sancho C., Saboya R.M. A., Cecilia J.A., Sales A.V., Luna F.M. T., Rodríguez-Castellón E., Cavalcante C.L. Influence of pore size and loading for Nb₂O₅/SBA-15 catalysts on synthetic ester production from free fatty acids of castor oil. *Molecular Catalysis 2017*. 436, 267–275.

[13] Rouquerol J., Llewellyn P., Rouquerol F. Is the BET equation applicable to microporous adsorbents. *Stud. Surf. Sci. Catal 2007.* 160(07), 49–56.

[14] Araujo-Barahona G., Shcherban N., Eränen K., Kopa I., Bezverkhyy I., Martínez-Klimov M., Vajglová Z., Aho A., García-Serna J., Salmi T., Murzin D. Y. Ruthenium supported on silicate and aluminosilicate mesoporous materials applied to selective sugar hydrogenation: Xylose to xylitol. *Chemical Engineering Journal 2024*. 485, 150019.

[15] Testova N., Shalygin A., Kaichev V., Glazneva T., Paukshtis E., Parmon V. Oxidative dehydrogenation of propane by molecular chlorine. *Applied Catalysis A: General 2015*. 505, 441–446.

[16] Morgan D. J. Resolving ruthenium: XPS studies of common ruthenium materials. *Surface and Interface Analysis 2015*. 47(11), 1072–1079.

[17] Shen J. Y., Adnot A., Kaliaguine S. An ESCA study of the interaction of oxygen with the surface of ruthenium. *Applied Surface Science 1991*. 51(1), 47–60.

[18] Dutta P. K., Vaidyalingam A. S. Zeolite-supported ruthenium oxide catalysts for photochemical reduction of water to hydrogen. *Microporous and Mesoporous Materials 2003*. 62(1), 107–120.

[19] Yang J., Hu Y., Yang Q., Guan Y. Mesoporous SBA-15 supported Ru nanoparticles for effective hydrogenation of ethyl levulinate at room temperature. *Journal of Porous Materials 2024*. 31(2), 727–736.

[20] Chen L., Zhu Y., Zheng H., Zhang C., Li Y. Aqueous-phase hydrodeoxygenation of propanoic acid over the Ru/ZrO₂ and Ru–Mo/ZrO₂ catalysts. *Applied Catalysis A: General 2012*. 411–412, 95–104.

[21] Jing Y., Wang Y., Furukawa S., Xia J., Sun C., Hülsey M.J., Wang H., Guo Y., Liu X., Yan N. Towards the Circular Economy: Converting Aromatic Plastic Waste Back to Arenes over a Ru/ Nb₂O₅ Catalyst. *Angewandte Chemie International Edition 2021*. 60(10), 5527–5535.