

Catalytic Performance of Ru/polymer Catalyst in the Hydrogenation of Furfural to Furfuryl Alcohol

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Furfural (FF) is one of the main components of bio-oil obtained by the treatment of lignocellulose biomass. Furfural alcohol (FA) as the main product of the selective FF hydrogenation is a source of value-added chemicals. In this paper, the results of the study of ruthenium catalysts based on hyper-crosslinked polystyrene (PS) in the selective hydrogenation of FF to FA are presented. Two types of ruthenium catalysts: nanoparticles of RuO₂ and Ru⁰ stabilized in the PS pores were synthesized and compared. The novelty of this work is in the comparison of the PS stabilized Ru⁰ and RuO₂ nanoparticles were performed and differences in their catalytic properties were shown. The BET, TEM, and SAXS data showed the formation of Ru-containing nanoparticles similar in size and structure for both catalysts. The comparison of the catalytic properties of the Ru catalysts showed that the catalyst with Ru⁰ (Ru-PS) exhibits higher values of FF conversion (99 %) and selectivity to FA (96 %). It can be assumed that Ru⁰ nanoparticles are responsible for the formation of catalytically active sites of selective hydrogenation of FF to FA.

1. Introduction

Reduced availability of oil sources and different environmental problems increase the interest in developing cost-effective and environmentally friendly technologies for the treatment of biomass into the fuels and chemicals. Furfural obtained from biomass is considered to be a potential platform for the production of biofuels and chemicals, and its modernization has recently gained interest (Figure 1) (Lange et al., 2012).

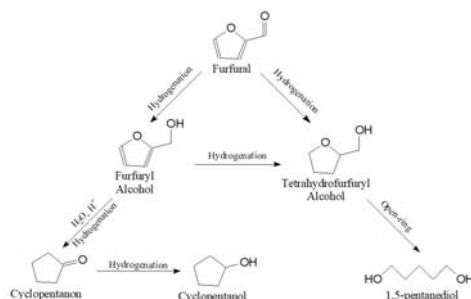


Figure 1: The scheme of catalytic hydrogenation of furfural

The selective hydrogenation of furfural (FF) to furfuryl alcohol (FA) (Durdell et al., 2019) provides new highly effective pathways for the synthesis of high-value products, including methyl furan, levulinic acid, γ -valerolactone (GVL), various resins (O'Driscoll et al., 2017) and lubricants (Taylor et al., 2016).

Heterogeneous transition and noble metal-based catalysts (Pt, Pd, Ru, Ni, Cu, and others) are used in the hydrogenation of furfural, both in the liquid and gas phase (Lange et al., 2012). The selective hydrogenation of furfural to furfuryl alcohol in the liquid phase was systematically studied over Ru nanoparticles based on silica to elucidate the structure-reactivity relationships and obtain a mechanistic understanding (Durndell et al., 2019). It was shown that the hydrogenation of furfural to furfuryl alcohol is weakly sensitive to the structure of Ru nanoparticles (Ru/SiO₂ and Ru/SBA-15) with size from 2 to 25 nm, and the dominant reaction pathway reaches 95 % selectivity under mild conditions (<2.5 MPa H₂ and 100-165 °C). Many authors have studied ruthenium catalysts on carbon supports. In the work Mironenko et al. (2015), weak activity was observed for the aqueous-phase furfural hydrogenation over Ru nanoparticles on carbon nanotubes and carbon black. The catalysts exhibited high activity under milder reaction conditions (50 °C, 0.5 MPa H₂), but strong water adsorption was found to be attributed to the catalyst action. The effect of alcohol as a reaction solvent on the hydrogenation of furfural over a Ru/RuO₂/C catalyst was studied by Panagiotopoulou et al. (2015). It was shown that both species of Ru and RuO₂ are catalytically active. The modifying effect of Fe₃O₄ on the Ru/Carbon nanotubes catalysts has been studied by Li et al. (2015). This catalyst showed 99.4 % FF conversion and 100 % FA selectivity using *i*-propanol under 120 °C and 0.1 MPa for 4 h. The addition, iron oxide promotes the formation of catalytically active species Ru⁰. At the same time, mixed active centers of RuOx-Fe₃O₄ - Lewis acid is formed, which is necessary for the intermolecular hydride transfer. The review of Wang et al. (2019) shows the results of a study of Ru-based catalysts in the hydrogenation of FF to FA but does not compare catalysts containing Ru and/or RuO₂.

Various polymers including solid porous polymer matrices (Shifrina et al., 2020) can be used as carbon-containing supports. Effective hydrogenation catalysts of the C=O group were created based on nanoparticles of noble metals (Ru (Manaenkov et al., 2014), Pd (Matveeva et al., 2017) and other metals (Sulman et al., 2016)) immobilized in a matrix of hyper-crosslinked polystyrene (Manaenkov et al., 2019). The properties of ruthenium catalysts based on hyper-crosslinked polystyrene (PS) for the liquid phase hydrogenation of FF to FA were reported in this work. The novelty of the work is that the structure, morphology, and catalytic properties of PS stabilized Ru⁰ and RuO₂ nanoparticles are compared. The conversion of furfural and selectivity to furfuryl alcohol was found to depend on Ru species in the catalyst. This study is aimed at providing the high efficiency of bioderived compound conversion into valuable chemicals.

2. Experimental

2.1 Materials

The hyper-crosslinked polystyrene of Macronet MN 270/3860 type 2/100 (designation PS) was purchased from Purolite Inc., (U.K.) and purified by rinsing with water and drying in vacuum. Ruthenium (IV) hydroxychloride (Ru(OH)Cl₃, 99 %), furfuryl alcohol (98 %), furfural (99 %) and *i*-propanol (≥99.5 %) were purchased from Sigma-Aldrich, USA.

2.2 Synthesis of catalysts

The ruthenium catalysts were prepared by the impregnation method according to moisture capacity of support, it was described in the work Manaenkov et al. (2016). Hypercrosslinked polystyrene of the MN-270 type was used as a support. Mesoporous support (PS) impregnated with the solutions of the amount of Ru-precursor calculated based on the metal loading was prepared. The following catalysts were prepared: RuOx-PS (initial catalyst) and Ru-PS (RuOx-PS catalyst after reduction in hydrogen flow). The loading of ruthenium was 3 % for all samples.

2.3 Method for hydrogenation of furfural

Hydrogenation of furfural was carried out in a batch steel reactor Series 5000 Multiple Reactor System (Parr Instruments, USA). Catalyst, furfural, and *i*-propanol were introduced into the reactor. The reactor was purged with nitrogen. After, the reactor was heated to operating temperature, and hydrogen was supplied. The hydrogenation process was carried out under continuous stirring (mixing rate 1000 rpm). During the reaction, samples of the reaction medium were taken for analysis. The time of one experiment was 180 minutes (Salnikova et al., 2018).

2.4 Gas chromatography method

Analysis of the reaction mixture was carried out by gas chromatography (gas chromatograph "Crystallux-4000M", OOO NPF "Meta-Chrom", Yoshkar-Ola, Russia) in the temperature programming mode according to the program: column temperature 50 °C, detector 200 °C, the evaporator 120 °C. Chromatograms were processed in the "NetChrom" program. Furfural (starting material) - and products of the main and intermediate reactions - tetrahydrofuran, furfuryl alcohol, and tetrahydrofurfuryl alcohol were identified.

The conversion of furfural and furfuryl alcohol selectivity was calculated using Eq(1) and (2).

$$\text{Conversion, \%} = \frac{n_{FF}^0 - n_{FF}^S}{n_{FF}^0} \cdot 100\% \quad (1)$$

$$\text{Selectivity, \%} = \frac{n_{FA}}{n_{FF}^0 - n_{FF}^S} \cdot 100\% \quad (2)$$

where n_{FF}^0 - initial moles of furfural, n_{FF}^S - moles of furfural in the reaction mixture, n_{FA} - moles of furfuryl alcohol in the reaction mixture.

2.5 The method of low-temperature adsorption of nitrogen

The specific surface area, the pore size distribution of the supports and the Ru-containing catalysts were investigated by the low-temperature nitrogen adsorption using BECKMAN COULTER™ SA 3100™ (Coulter Corporation, USA), BECKMAN COULTER™ SA-PREP™ (Coulter Corporation, USA), and electronic balance GX-200 (A&D Company, Limited, Japan). The following analysis conditions were used: $t = -196$ °C, relative pressure 0.9814 (for the pores less than 100 nm), PSD (ADS) profile.

2.6 Transmission electron microscopy

Electron-transparent specimens for transmission electron microscopy (TEM) were prepared by placing a drop of a sample suspension onto a carbon-coated Cu grid. Images were acquired at an accelerating voltage of 80 kV on a JEOL JEM1010 transmission electron microscope (JEOL, USA).

2.7 Small-angle X-ray scattering

The small-angle X-ray scattering (SAXS) was performed with the S3 MICRO (HECUS, USA) small-angle diffractometer (Cu K α , 50W) with point collimation of the primary beam. It was used for measuring scattering patterns of all samples. The scattering vector magnitude $q = 4\pi \cdot \sin(\theta)/\lambda$ (where 2θ is the scattering angle, and $\lambda = 1.541$ Å is the radiation wavelength) was used as the scattering coordinate. The scattering intensity was measured in the range of the scattering vector magnitudes $0.01 < q < 0.6$ Å⁻¹.

3. Results and discussion

To determine the influence of the ruthenium nature (oxidized and reduced forms) in catalytically active nanoparticles, corresponding samples of catalysts were synthesized. Ruthenium containing catalysts were synthesized based on porous support - hyper-crosslinked polystyrene. The first type of catalyst (RuOx-PS) contained ruthenium in the form of RuO₂·H₂O was formed after precipitation of ruthenium (IV) hydroxychloride with alkali. The second type of catalyst (Ru-PS) was obtained by reducing ruthenium oxide with hydrogen in the gas phase (reduced with hydrogen at 400 °C and atmospheric pressure for 2 h) to Ru (0). The oxidized (Sapunov et al., 2013) and reduced form of ruthenium in these samples were confirmed by XPS data in the work Protsenko et al. (2020). According to the data of XPS analysis, in the initial catalyst RuOx-PS for the band Ru 3d_{5/2} the values of binding energy corresponded RuO₂ and RuO₂ × nH₂O. For the reduced catalyst Ru-PS, most of the ruthenium on the surface corresponded to Ru⁰.

The results of the low-temperature nitrogen adsorption (see Table 1) showed that the initial support PS has a hierarchical structure and there are micro-, meso- and macropores. The introduction of Ru(OH)Cl₃ and the formation of ruthenium-containing nanoparticles (catalysts RuOx-PS and Ru-PS) into the porous matrix of PS leads to a decrease in the surface area of about 200 m²/g (Table 1). The obtained data show that when the ruthenium precursor is introduced, the surface of both the micro- and mesopores of the support decreases. The formation of ruthenium-containing particles occurs precisely in micro- and mesopores can be assumed.

Table 1: The porosity data of the support and ruthenium catalysts (according to BET)

Sample	Specific surface, m ² /g	Specific surface of micropores, m ² /g	Specific surface of mesoporous, m ² /g	Total pore volume, mL/g
PS	1,360	929	330	0.9875
RuOx-PS	1,168	846	218	0.7091
Ru-PS	1,163	801	214	0.6477

The Ru-containing catalysts have also been studied by SAXS. Figure 2 shows the SAXS curves for RuOx-PS and Ru-PS catalysts. The bimodal distributions of Ru particles for Ru-PS catalysts with the average size of 7.4 nm and besides the fraction of particles with a size of 10-20 nm were observed. In the case of RuOx-PS SAXS data indicate also the presence of two particle fractions: the major small particles 6.6 nm and a minor amount of larger particles (10–20 nm). According to TEM data, ruthenium particles are very unevenly distributed across the polymer support for the Ru-PS. The particles are observed both as very large sintered agglomerates (200-500 nm or more) (Figure 3a) and as small nanoparticles (1-20 nm) (Figure 3b). The size distributions of

ruthenium particles were calculated from the TEM images (Figure 4a). The results of SAXS and TEM (Figure 4b) were compared and good data convergence was found.

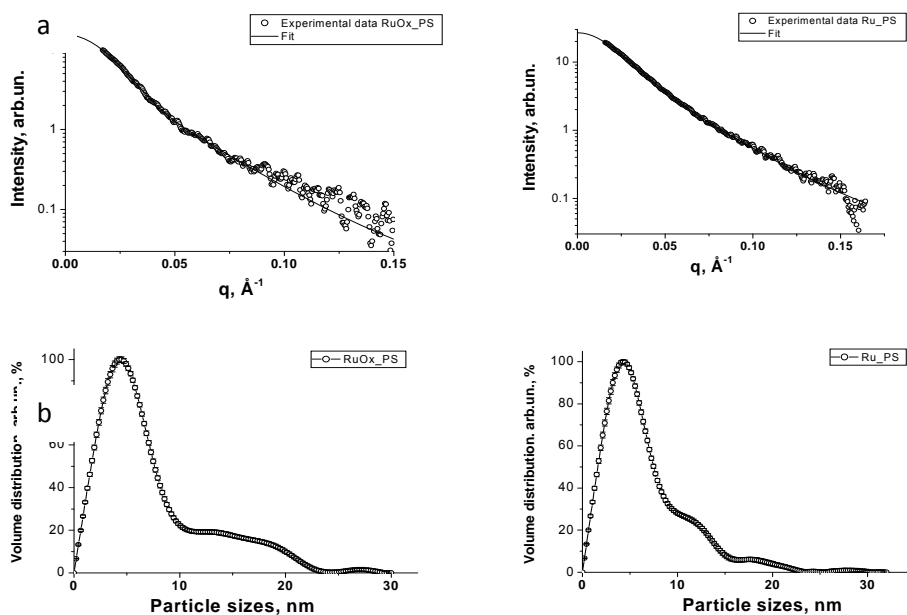


Figure 2: (a) SAXS data for RuOx-PS and Ru-PS symbols show experimental data, while solid curves represent fits. (b) Volume particle size distributions of Ru-containing particles in the catalysts.

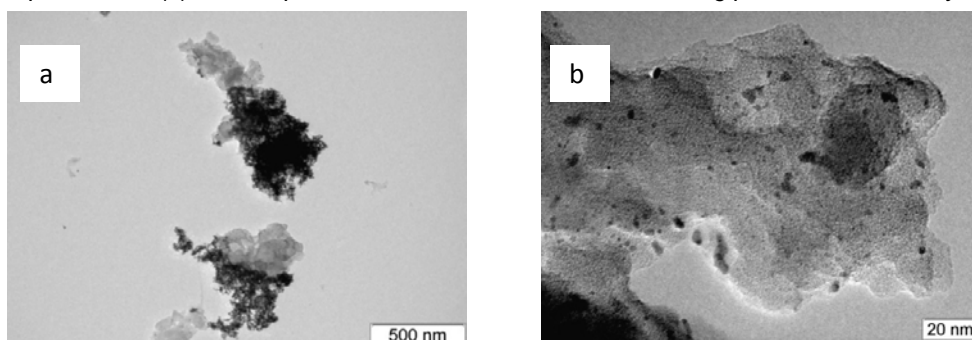


Figure 3: TEM image of Ru-PS catalyst

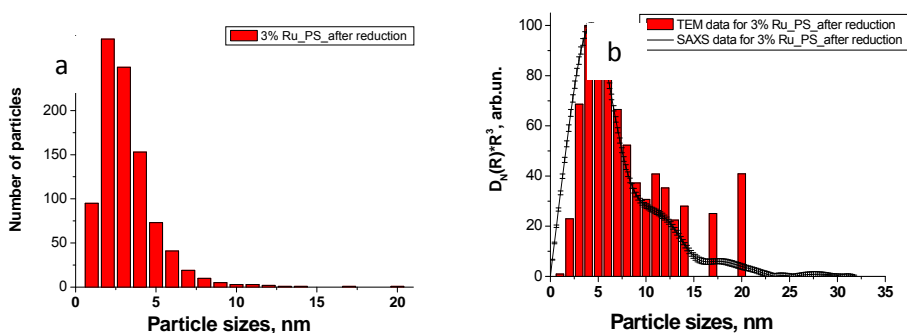


Figure 4: Histograms of Ru particle-size distribution on (a) TEM data (out of 938 particles), (b) TEM and SAXS data

The catalytic properties of the RuOx-PS and Ru-PS catalysts were studied in the selective hydrogenation of FF to FA. Optimal conditions of furfural hydrogenation have been determined in the previous work (Salnikova et al., 2018): a temperature of 120 °C and a hydrogen pressure of 6.0 MPa. Propanol-2 was used as a solvent. The results of the catalytic testing of both Ru catalysts are presented in Figure 5. The dependence of

the conversion of furfural on time for the prepared ruthenium catalysts is shown in Figure 5a. The high conversion of FF (99.0 %) over the observed reaction period was achieved in the presence of the Ru-PS catalyst, a lower value (86.2 %) was obtained on the RuOx-PS catalyst. It should be noted that the selectivity to FA for the catalyst with Ru⁰ was high 87.0 % (3 min) and 96.0 % (180 min) (Figure 5b). While for a catalyst RuOx-PS with an oxidized form of ruthenium, selectivity on FA increases gradually during the reaction: 17 % (3 min) and 94.5 % (180 min) (Figure 5b). The obtained data show that the catalytic properties of ruthenium catalysts during selective hydrogenation of FF to FA depend on the form of ruthenium.

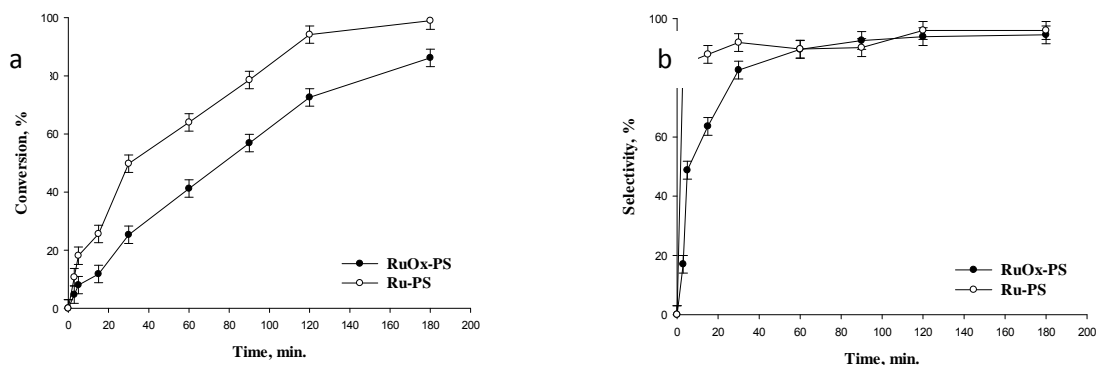


Figure 5: Dependence of the conversion of furfural (a) and the selectivity of furfuryl alcohol (b) on the reaction time in the presence of ruthenium catalysts.

To evaluate the stability of ruthenium catalysts in repeated use, 30 h (ten consecutive experiments) of FF hydrogenation under optimal conditions were performed. Figure 6 shows that the Ru-PS catalyst is more stable in comparison with RuOx-PS. From the presented data, it can be seen that for 30 h the relative rate (mol FF/mol Ru · h) decreases by 2 % and 14 % for Ru-PS and RuOx-PS catalysts accordingly.

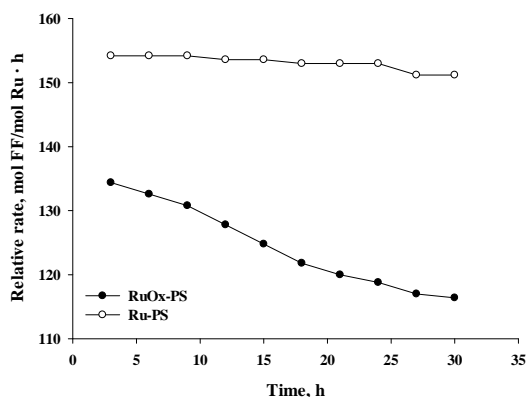


Figure 6: The ruthenium catalyst stability in ten cycles (30 h)

4. Conclusions

Ru-containing nanoparticles stabilized by hyper-cross-linked polystyrene have been synthesized and studied as catalysts in a complex multistage process of furfural hydrogenation involving the main reaction for the formation of the target product - furfuryl alcohol. The synthesized catalysts differed in the composition and structure of ruthenium-containing nanoparticles. In one sample, RuO₂ particles were formed in the hyper-crosslinked polystyrene pores, and in the other, Ru⁰ nanoparticles were formed. The detailed comparison of PS stabilized Ru⁰ and RuO₂ nanoparticles was performed. BET data indicated the same specific surface value of micro- and mesopores for both catalysts. The data of TEM and SAXS showed the formation of similar-sized Ru-containing nanoparticles with practically the same distribution. Two particle fractions were formed: the major small particles fraction (7.4 and 6.6 nm for Ru-PS and RuOx-PS accordingly) and the minor amount of larger particles (~10-20 nm). The comparison of the catalytic properties of the Ru-containing catalysts showed

that the catalyst with Ru⁰ (Ru-PS) showed higher values of FF conversion and selectivity to FA. Ru⁰ nanoparticles are likely responsible for the formation of catalytically active sites of selective hydrogenation of FF to FA. The combination of high performance and increased stability makes this catalyst promising for further applications in fuel and energy-related fields.

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