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The Liquid Phase Catalytic Hydrogenation of the Furfural to Furfuryl Alcohol

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The results of the study of palladium catalysts in the selective hydrogenation of furfural to furfural alcohol are presented. A comparison of the properties of palladium catalytic systems prepared on different supports (aluminium oxide, hypercrosslinked polystyrene and magnetite/hypercrosslinked polystyrene) is carried out. It is shown that the nature of the support has a significant impact on both the morphology of the catalyst and its activity in the selective hydrogenation of furfural. The most effective catalyst was magnetically recoverable 3 % Pd/Fe_3O_4/HPS, in the presence of which the conversion of furfural was> 95% with selectivity for furfuryl alcohol> 94 %.

1. Introduction

Increasing interest to biomass as a source of chemicals and energy has recently arisen due to the limited fossil fuel resources and the demand for new clean chemical processes (Halilu et al., 2016). The research to develop alternative liquid transport fuels has increased considerably in recent years influenced by the implementation of legislation and directives on alternative energy. To achieve these aims in an ethical, environmentally sustainable and economical manner the use of lignocellulosic biomass or agri-waste for the production of second generation biofuels is proposed (Taylor et al., 2016). Chemicals derived from biomass have attracted a considerable interest in the recent years (Climent et al., 2014). The production of biofuels from hemicellulose requires acid hydrolysis to open the biomass structure giving large quantities of xylose (Paulsen et al., 2013). The synthesis of furfural as a by-product of this biofuel production process has developed an additional important research area (O'Driscoll et al., 2017). Furfural is one of the key derivatives which can be obtained from renewable biomass for the production of different important fine chemicals (Hu et al., 2012).

Selective hydrogenation of furfural has attracted much attention for the production of furfuryl alcohol, methyl furan, tetrahydrofurfuryl alcohol and others (Figure 1). Furfuryl alcohol is widely used in chemical industry, mainly for the production of special resins, polymers and coatings on their basis, which are resistant to acids, alkalies and various solvents. In addition, furfuryl alcohol is employed as diluents for epoxy resins and as a solvent for phenol formaldehyde resins and poorly soluble pigments. In the organic synthesis, furfuryl alcohol is a feedstock for the production of tetrahydrofurfuryl alcohol and 2,3-dihydropyranand an intermediate for the synthesis of lysine, vitamin C, various lubricants and plasticizers. There are two ways of producing furfuryl alcohol through hydrogenation of furfural, gas phase hydrogenation and liquid phase hydrogenation (Nagaraja et al., 2007). In industry, furfuryl alcohol is obtained by catalytic hydrogenation of furfural in a liquid or vapor phase (Zeisch, 2000). The liquid-phase process is carried out with copper chromite systems as the catalysts. The main disadvantage of copper-chromite catalysts is their toxicity caused by the presence of chromium oxides, which allows considering such catalysts as environmental pollutants (Taylor et al., 2016).

In the case of liquid-phase hydrogenation, the reaction conditions are milder and it is possible to use both homogeneous and heterogeneous catalysts based on mono- (Pd (Aldosari et al., 2016), Pt (Chen et al., 2016), Ru (Huang et al., 2007), Ni (Li et al., 2016), Cu (Maligal-Ganesh et al., 2016)) and bimetals (Pd-Ni (Merlo et al., 2011), Pd-Ir, Pd-Ru (Nagaraja et al., 2003), Pt- Sn (Wu et al., 2005)). Depending on the process conditions,

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namely the type of catalyst and the nature of the solvent, furfural hydrogenation proceeds in various directions and with the formation of a large number of products. Thus, for example, Yu et al. (2011) in the case of hydrogenation of furfural in the aqueous phase in the presence of Co/TiO_2 noted the formation of such by-products as pentadioles, pentanols, hydroxycyclopentanone, etc. When using alcohols (methanol, ethanol, isopropanol), esterification products and aldol condensation: isopropyl-furfuryl ether, 2-furaldehyde diisopropyl acetal (Taylor et al., 2016), 2-furaldehyde dimethyl acetal (Fulajtárova et al., 2015), 2-furaldehyde diethyl acetal (Lee et al., 2015) are noted as the reaction medium.

By varying the conditions for hydrogenation of furfural (pressure, temperature, etc.), it is possible to regulate the selectivity for one or another product. This study is devoted to the selection of the catalytic system and process conditions for achieving maximum selectivity for furfuryl alcohol.

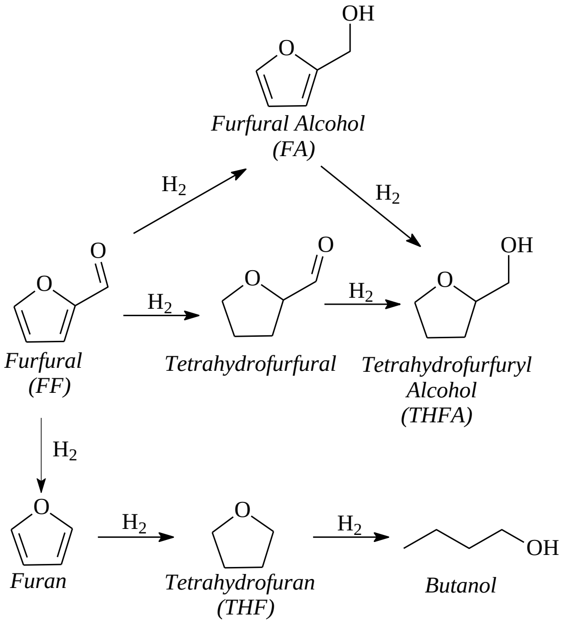

Figure 1: The scheme of catalytic hydrogenation of the furfural

2. Experimental

2.1 Materials

As the support of the palladium catalyst, the hypercrosslinked polystyrene (HPS) of Macronet MN 270/3860 type 2/100 (designation MN-270) was purchased from Purolite Int., (U.K.) and purified by rinsing with water and drying in vacuum. Palladium (II) chloride ($PdCl_2$, 99%), Iron (III) chloride hexahydrate ($FeCl_3$ $6H_2O$, 98 %), aluminium oxide (Al_2O_3, mesoporous, 60 micrometers, for chromatography) were purchased at Sigma-Aldrich. Furfural (99 %), furfuryl alcohol (98 %), and *i*-propanol (≥ 99.5 %) were purchased from Sigma-Aldrich and used without purification.

2.2 Synthesis of catalysts

The investigated palladium catalysts (Nemygina et al., 2016) were prepared by the method of impregnation according to the moisture capacity were described in previous works (Sulman et al., 2016). Aluminium oxide and hypercrosslinked polystyrene of the MN-270 type were used as a carrier. Based on the calculated quantities of $PdCl_2$ solutions of precursors were prepared, which were impregnated with mesoporous carriers. Magnetically recoverable support (Fe_3O_4/HPS) was synthesized by impregnation of $FeCl_3$ solution, followed by alkali treatment. The following catalysts were prepared: 3% Pd/Al_2O_3, 3 % Pd/HPS and 3 % Pd/Fe_3O_4/HPS (here 3 % is the calculated palladium content, in parentheses precursor).

2.3 Method for hydrogenation of furfural

Hydrogenation of furfural was carried out in a batch steel batch reactor of the Series 5000 Multiple Reactor System (Parr Instruments). Catalyst, furfural and propanol-2 were introduced into the reactor. The reactor was purged with nitrogen. After the reactor was heated to operating temperature, hydrogen was supplied. The hydrogenation process was carried out with continuous stirring (mixing rate 1000 rpm). During the reaction, samples of the reaction medium were taken for analysis. The time of one experiment was 240 minutes.

2.4 Gas chromatography method

Analysis of the reaction mass was carried out by gas chromatography (gas chromatograph "Crystallux-4000M", OOO NPF "Meta-Chrom", Yoshkar-Ola, Republic of Mari El) 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 were identified; tetrahydrofurfuryl alcohol.
The conversion of furfural and furfuryl alcohol selectivity were calculated using the Eq (1) and Eq(2):

$$\text{Conversion, \%} = \frac{\mathrm{n}_{FF}^{0}-n_{FF}^{s}}{n_{FF}^{0}} * 100 \quad (1)$$

$$\text{Selectivity, \%} = \frac{\mathrm{n}_{FA}}{n_{FF}^{0}-\mathrm{n}_{FF}^{s}} * 100 \quad (2)$$

n_{FF}^{0} - initial moles of furfural
n_{FF}^{s} - moles of furfural in sample
n_{FA} - moles of furfuryl alcohol

2.5 The method of low-temperature adsorption of nitrogen

The specific surface area, pore size distribution of the supports and the Pd-containing catalysts were investigated by low-temperature nitrogen adsorption using BECMAN COULTERTM SA 3100TM (Coulter Corporation, Miami, Flor-ida), BECMAN COULTERTM SA-PREPTM (Coulter Corporation, Miami, Florida), and electronic balance GX-200 (A&D Company, Limited, Tokyo, Japan). The following analysis conditions were used: t = -196 °C, relative pres-sure 0.9814 (for the pores less than 100 nm), PSD (ADS) profile.

2.6 X-ray fluorescence analysis

X-ray fluorescence analysis (XRF) was performed to determine the palladium content of the catalysts under study. A VRA-30 spectrometer from “Zeiss Jena” with a molybdenum anode was used, the crystal analyzer was a LiF and SZ detector. Samples (for analysis and comparison) were prepared by mixing 1 g of polystyrene with 10-20 mg of the substance. The measurement time (analysis) is 10 s.

2.7 Atomic-absorption spectrometry

To study the catalyst for heterogeneity (stability), an analysis was carried out for the content of palladium in the liquid phase using an atomic absorption spectrometer MGA-915 (NPF AP “Lumeks”, Russia).

2.8 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.

3. Results and discussion

The results of the elemental analysis (see Table 1) showed that the palladium content in the catalysts under study is practically the same as calculated. According to the data of atomic absorption spectrometry, the synthesized heterogeneous palladium systems are stable against leaching, and the active phase does not wash out. From this it follows that hydrogenation of furfural proceeds on the surface of a heterogeneous catalyst.

Table 1: The main characteristics of palladium catalysts (according to BET, RFA and TEM)

Sample	Specific surface, m^2/g	Specific surface of micropores, m^2/g	The size of palladium particles, nm	Content of palladium, %
3 % Pd/Al_2O_3	59	0	-	2.87
3 % Pd/HPS	816	94	25 - 30	2.93
3 % Pd/Fe_3O_4/HPS	450	290	25 - 30	2.78

In early studies (Stepacheva et al., 2016), it was shown that the palladium particle size synthesized in the HPS matrix is 25-30 nm. TEM result for 3 % Pd/Fe_3O_4/HPS showed that the average diameter of palladium particles is 27.8 nm (Figure 2). The introduction of Fe_3O_4 magnetic particles into the HPS matrix did not affect the formation and size of palladium particles.

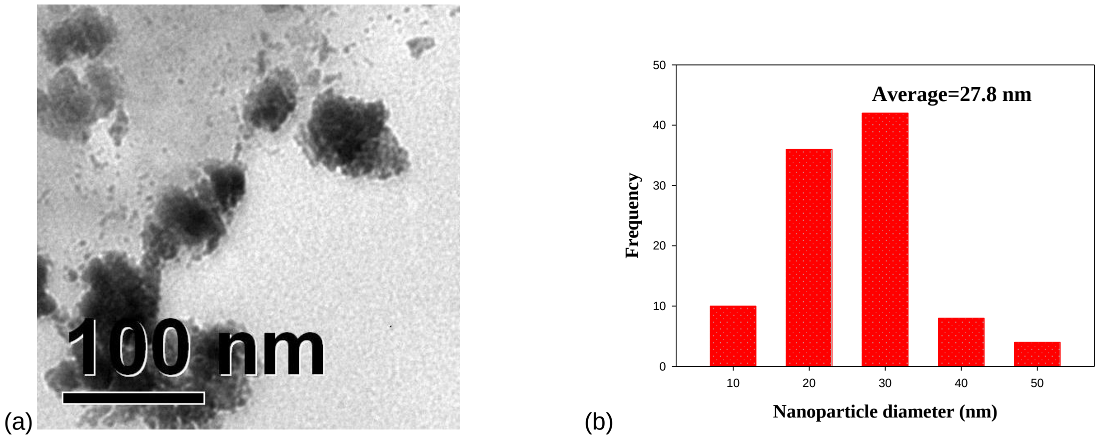

Figure 2: a) TEM image of 3% Pd/Fe_3O_4/HPS catalyst. b) Pd particle-size distribution for 3% Pd/Fe_3O_4/HPS.

Studies of the texture of palladium catalysts by low-temperature adsorption of nitrogen have shown that the surface areas of the samples vary significantly (Table 1). The minimum surface area was found in a sample of 3 % Pd/Al_2O_3) (59 m^2/g) in comparison with catalysts on the basis of the HPS. The catalyst surface area of 3% Pd/ HPS was 816 m^2/g with an insignificant microporous surface area (94 m^2/g) (Table 1). The introduction of magnetite Fe_3O_4 (catalyst 3 % Pd/Fe_3O_4/HPS) into the porous matrix of HPS leads to decrease in the surface area almost twice (450 m^2/g) (Table 1). For a sample 3% Pd/Fe_3O_4/HPS, the specific surface of micropores increases to 290 m^2/g (which is about 60 % of the total specific surface). It is likely that this is due to the formation of magnetite particles in the HPS pores.

The catalytic properties of the samples of 3 % Pd/Al_2O_3, 3 % Pd/HPS, 3 % Pd/Fe_3O_4/HPS were studied in the selective hydrogenation of furfural to furfuryl alcohol. Optimal conditions of the furfural hydrogenation have been determined: a temperature of 120 °C and a hydrogen pressure of 6.0 MPa. Propanol-2 was used as the solvent. The dependence of the conversion of furfural on time for the prepared palladium catalysts is shown in Figure 3 (a). The highest conversion of furfural (95.6 % and 95.3 %) over the observed reaction period was achieved in the presence of an HPS catalysts (3 % Pd/Fe_3O_4/HPS and 3% Pd/HPS accordingly), a lower value (87.0 %) was obtained on a 3 % Pd/Al_2O_3 catalyst. The specific surface of the classical carrier Al_2O_3 is small in comparison with that of the HPS, which, apparently, determines the smaller number of active sites and, accordingly, the lower activity of the catalyst on Al_2O_3.

It should be noted that the selectivity of the process for furfural alcohol for catalyst on the Al_2O_3 support is not very high (73.5 %). At the same time, selectivity of the process for furfural alcohol was significantly higher for samples based on HPS: 91.4% for the catalyst 3% Pd/HPS and 94.3 % for 3 % Pd/Fe_3O_4/HPS accordingly (Figure 3 (b)).

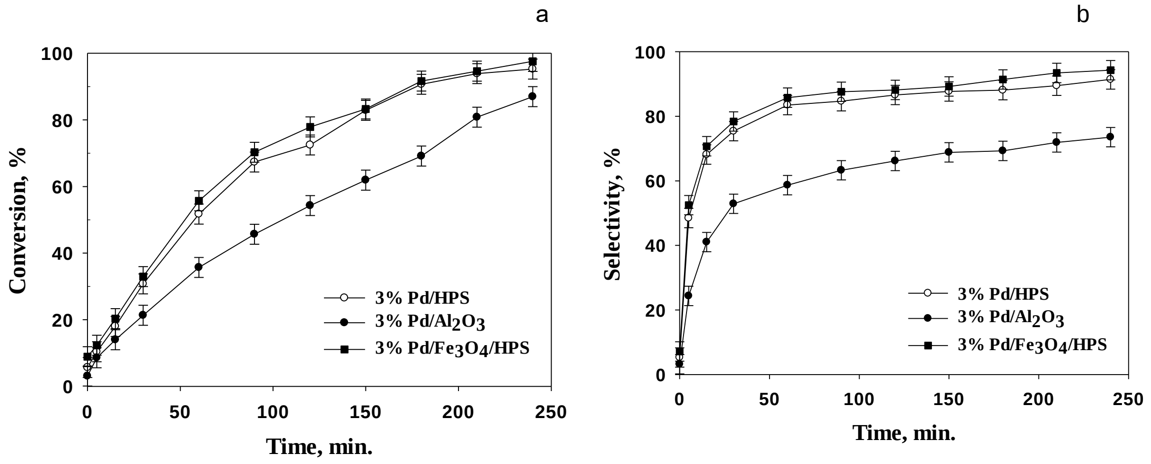

Figure 3: Dependences of the conversion of furfural (a) and the selectivity of furfuryl alcohol (b) on the reaction time in the presence of palladium catalysts

In this case, it may indicate that the active centers are formed differently for Al_2O_3 and HPS. As by-products, hydrogenation products of furfuryl alcohol, 2-methylfuran and tetrahydrofuran, have been identified. The obtained results testify to the influence of the nature of the support on its catalytic properties.

In order to evaluate the catalyst stability in the repeated use, ten successive experiments of the furfural hydrogenation were carried out in the optimal conditions discussed above.

Figure 4a shows that catalysts based on HPS are more stable in comparison Al_2O_3 support. Catalysts based on HPS lose only 1-3 % of its activity after ten catalytic cycles, while 3 % Pd/Al_2O_3 loses 14 %. Palladium catalysts based on magnetite and HPS (3 % Pd/Fe_3O_4/HPS) showed higher activity and selectivity in the process for the hydrogenation of furfural to furfuryl alcohol. Moreover, it is necessary to note the advantage of this catalyst in-easy separation from the reaction mixture by magnet (Figure 4b).

Such a high activity and selectivity showed Pd-containing magnetite nanoparticles stabilized by polyphenylquinoxaline, as presented in the work of the Alibegovic and co-workers (Alibegovic et al., 2017).

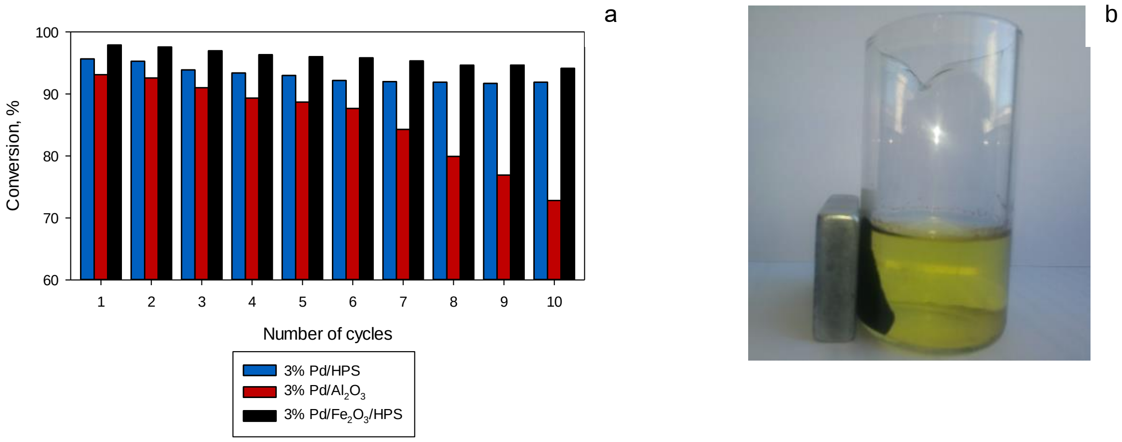

Figure 4: (a) the Pd catalyst stability in ten cycles, (b) separation of the 3% Pd/Fe3O4/HPS catalyst from the reaction mixture by a magnet

4. Conclusions

Studies and catalytic tests of palladium catalysts in a complex multistage process of furfural hydrogenation involving the main reaction for the formation of the desired product - furfuryl alcohol and side reactions of hydrogenation were carried out. Samples of palladium catalysts were prepared on different supports. The supports were aluminium oxide, hypercrosslinked polystyrene and magnetite/hypercrosslinked polystyrene. Studies have shown that the nature of the support has a significant effect on the conversion of furfural and the selectivity for furfuryl alcohol. The most effective catalyst was magnetically recoverable 3 % Pd/Fe_3O_4/HPS, in the presence of which the conversion of furfural was> 95% with selectivity for furfuryl alcohol> 94 %.

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References

Aldosari O. F., Iqbal S., Miedziak P. J., Brett G. L., Jones D. R., Liu X., Edwards J. K., Morgan D. J., Knight D. K., Hutchings G. J., 2016, Pd-Ru/TiO2 catalyst – an active and selective catalyst for furfural hydrogenation, Catal. Sci. Technol, 6, 234-242.

Alibegovic K., Gene Morgan D., Losovyj Ya., Pink M., Stein B.D., Kuchkina N.V., Serkova E.S., Salnikova K.E., Shifrina Z.B., Matveeva V.G., Sulman E.M., Bronstein Lyudmila M., 2017, Efficient furfuryl alcohol synthesis from furfural over magnetically recoverable catalysts: does the catalyst stabilizing medium matter? ChemistrySelect, 2, 5485 – 5491.

Chen X., Zhang L., Zhang B., Guo X., Mu X., 2016, Highly selective hydrogenation of furfural to furfuryl alcohol over Pt nanoparticles supported on g-C3N4 nanosheets catalysts in water, Sci. Rep., 6, 28558.

Climent M. J.; Corma A.; Iborra S., 2014, Conversion of biomass platform molecules into fuel additives and liquid hydrocarbon fuels, Green Chem., 16, 516−547.

Fulajtárova K., Soták T., Hronec M., Vávra I., Dobroˇcka E., Omastová M., 2015, Aqueous phase hydrogenation of furfural to furfuryl alcohol over Pd–Cu catalysts, Appl. Catal. A., 502, 78-85.

Halilu A.; Ali T.H.; Atta A.Y.; Sudarsanam P.; Bhargava S.K.; Abd Hamid S.B., 2016, Highly selective hydrogenation of biomass-derived furfural into furfuryl alcohol using a novel magnetic nanoparticles catalyst, Energy Fuels, 30, 2216−2226.

Hu L.; Zhao G.; Hao W., Tang X.; Sun Y.; Lin L.; Liu S.**,** 2012**,** Catalytic conversion of biomass-derived carbohydrates into fuels and chemicals *via* furanic aldehydes**,** RSC Adv.**,** 2**,** 11184−11206**.**

Huang W., Li H., Zhu B., Feng Y., Wang S., Zhang S., 2007, Selective hydrogenation of furfural to furfuryl alcohol over catalysts prepared via sonochemistry, Ultrason. Sonochem., 14, 67–74.

Lee J., Burt S. P., Carrero C. A., Alba-Rubio A. C., Ro I., O'Neill B. J., Kim H. J., Jackson D., Kuech T. F., Hermans I., Dumesic J. A., Huber G. W., 2015, Stabilizing cobalt catalysts for aqueous-phase reactions by strong metal-support interaction, J. Catal., 330, 19–27.

Maligal-Ganesh R. V., Xiao C., Goh T. W., Wang L.-L., Gustafson J., Pei Y. Q., Zhiyuan, Johnson D. D., Zhang S., Tao F., Huang W., 2016, A ship-in-a-bottle strategy to synthesize encapsulated intermetallic nanoparticle catalysts: Exemplified for furfural hydrogenation, ACS Catal., 6, 1754-1763.

Merlo A.B., Vetere V., Ramallo-Lopez J.M., Requejo F.G., Casella M.L., 2011, Liquid-phase furfural hydrogenation employing silica-supported PtSn and PtGe catalysts prepared using surface organometallic chemistry on metals techniques, React. Kinet. Mech. Catal., 104, 467-482.

Nagaraja B. M., Kumar V. S., Shasikala V., Padmasri A. H., Sreedhar B., Raju B. D., Rao K. R., 2003, A highly efficient Cu/MgO catalyst for vapour phase hydrogenation of furfural to furfuryl alcohol, Catal. Commun., 4, 287–293.

Nagaraja B. M., Padmasri A. H., Raju B. D., Rama Rao K. S., 2007, Vapor phase selective hydrogenation of furfural to furfuryl alcohol over Cu–MgO coprecipitated catalysts, J. Mol. Catal. A., 265, 90–97.

Nemygina N.A., Nikoshvili L.Zh., Sulman M.G., Matveeva V.G., Sulman E.M., 2016, Suzuki cross-coupling in environmentally friendly solvents in a batch mode using hypercrosslinked polystyrene-supported Pd catalysts, Chem. Eng. Trans., 52, 691-696.

O'Driscoll, Á., Leahy, J. J. and Curtin, T., 2017, The influence of metal selection on catalyst activity for the liquid phase hydrogenation of furfural to furfuryl alcohol, Catalysis Today, 279, Part 2, 194-201.

Paulsen A. D., Mettler M. S.; Dauenhauer P. J., 2013, The role of. sample dimension and temperature in cellulose pyrolysis, Energy Fuels, 27, 2126−2134.

Sulman E. M., Doluda V. Y., Matveeva V. G., Grigorev M. E., Sulman M. G., Bykov A. V. (2016) Ru-containing catalysts in hydrogenation of d-glucose in flow-type microreactor. Chemical Engineering Transactions 52: 673-678.

Stepacheva A.A., Matveeva V.G., Sulman E.M., Sapunov V.N., 2016, Fatty Acid Hydrotreatment Using Hypercrosslinked Polystyrene-supported Pd Catalysts to Produce Biofuels, Chemical Engineering Transactions, 52, 625-630.

Taylor M. J.; Durndell L. J.; Isaacs M. A.; Parlett C. M., Wilson A. K., Lee A. F., Kyriakou G., 2016, Highly selective hydrogenation of furfural over supported Pt nanoparticles under mild conditions, Appl. Catal. B, 180, 580−585.

Wu J., Shen Y., Liu C., Wang H., Geng C., Zhang Z., 2005, Vapor phase hydrogenation of furfural to furfuryl alcohol over environmentally friendly Cu–Ca/SiO2 catalyst, Catal. Commun., 6, 633–637.

Yu, W., Tang, Y., Mo, L., Chen, P., Lou, H., Zheng, X., 2011, Bifunctional Pd/Al-SBA-15 catalyzed one-step hydrogenation–esterification of furfural and acetic acid: A model reaction for catalytic upgrading of bio-oil, Catal. Commun., 13 (1), 35–39.

Zeitsch K.J. 2000, The Chemistry and Technology of Furfural and Its Many Co-Products, Elsevier, Amsterdam, Netherlands.