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ScienceDirect
Mendeleev Commun., 2020, **30**, 119–120

Mendeleev
Communications

Hydrodeoxygenation of glycerol into propanols over a Ni/WO_3–TiO_2 catalyst

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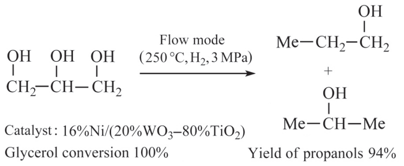
DOI: 10.1016/j.mencom.2020.01.040

Hydrodeoxygenation of glycerol in a flow reactor over a bifunctional Ni/WO_3–TiO_2 catalyst at 240–255 °C and hydrogen pressure of 3 MPa affords propan-1-ol and propan-2-ol in total yield of 94%.



Keywords: bifunctional catalysis, hydrogenolysis, glycerol, propanols, titania, tungsten oxide.

Propan-1-ol (1-Pr) and propan-2-ol (2-Pr) are the products that can be produced by hydrodeoxygenation of glycerol.[1–4] The values for the Gibbs free energy $\Delta G°$ for the glycerol conversion into 1-Pr and 2-Pr are significantly negative (–206 and –166 kJ mol^{-1}, respectively),[5] so the reactions can proceed irreversibly. Obviously, the process comprises consecutive dehydration and hydrogenation steps. Dehydration requires strong Brønsted acid centers on the catalyst surface, whereas hydrogenation needs metal centers.[6,7]

The yield of intermediate propane-1,3-diol correlated with the concentration of the acidic Brønsted centers.[1,8–14] Some active catalysts for glycerol hydrogenolysis contain tungsten oxides,[8,5–17] in particular Pt/WO_3/TiO_2[12] or 4%Pt/WO_3–ZrO_2[15] (the yields of 1-Pr and 2-Pr were 56.2 and 5.3%, respectively, and the glycerol conversion was 84.5% at 130 °C and 4 MPa of H_2). The 1-Pr formation in yields up to 24% was observed[18,19] on the Ir/SiO_2 catalyst modified with Re and small additive of sulfuric acid at 120 °C and 8 MPa of hydrogen. A 33% yield of 1-Pr was obtained in the glycerol hydrogenolysis over the Pt–HSiW/SiO_2 catalyst with a heteropolyacid at 200 °C and 5 MPa of hydrogen.[8] Bimetallic Pd–Fe nanoparticles provided a high yield of alcohols.[20]

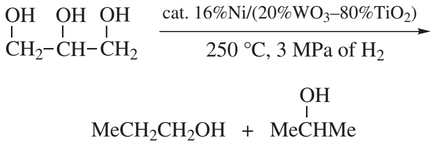
Nickel catalysts are rarely employed in glycerol conversion, because the yield of alcohols remains low even under severe conditions. Nickel nanoparticles on oxide carriers (Ni/SiO_2 or Ni/Al_2O_3) with a Ni content of 45–55 wt% catalyze hydrogenation of glycerol into alcohols at 230–320 °C, a hydrogen pressure of 40–75 atm and liquid hourly space velocity (LHSV) of 3 h^{-1}, the selectivity to 1-Pr at 275 °C and 60 atm on Ni/SiO_2 was close to 14%.[4]

The present work was focused on the development of an active catalyst for glycerol hydrogenolysis into propanols, as well as the search for the appropriate conditions in order to improve the selectivity towards propanols. Thus, a bifunctional catalyst based on a co-precipitated mixture of WO_3 with TiO_2 with a molar WO_3/TiO_2 ratio of 1:4 exhibiting strong Brønsted acidity was used as a carrier.[21,22] Metallic nickel (16 wt%) served as a hydrogenating component of the catalyst, which is important because nickel is significantly cheaper than any of noble metals.

The 20%WO_3–80%TiO_2 carrier was prepared by co-precipitation with an ammonia solution of titanium and tungsten hydroxides from an aqueous solution containing ammonium tungstate $(NH_4)_{10}[H_2W_{12}O_{41}]$ and titanium tetrachloride $TiCl_4$. The resulting precipitate was washed with distilled water to a neutral reaction, dried in air at 150 °C for 2 h and calcined in an air flow at 520 °C for 3 h. The 16%Ni/WO_3–TiO_2 catalyst was prepared by impregnating the 20%WO_3–80%TiO_2 carrier with an aqueous solution of nickel nitrate $Ni(NO_3)_2 \cdot 6H_2O$, followed by drying the catalyst at 120 °C for 2 h and calcination at 350 °C for 2 h. Before the catalytic tests, the catalyst loaded into the reactor was reduced in a hydrogen flow at 350 °C for 3.5 h. The phase and elemental compositions of the catalyst were characterized by XRD and EDX data (see Online Supplementary Materials).

Experiments on glycerol hydrogenolysis (Scheme 1) were carried out in a stainless steel flow reactor with an inner diameter of 7 mm. The catalyst (2 g) with a particle size of 0.25–0.5 mm was loaded into the central part of the reactor. The free volume of the reactor was filled with ground quartz with particle size of 0.5–1.0 mm. A 30% aqueous solution of glycerol was fed to the reactor by a syringe pump, the LHSV of the glycerol solution was varied in the range of 0.46–1.66 h^{-1}. The process was carried out at 240–270 °C. The hydrogen pressure was varied in the range of 2.0–3.6 MPa. The feed rate of hydrogen was 40 cm^3 min^{-1}. Liquid samples for the GC analysis were taken every 30 min.

It should be noted that the yield and selectivity to propanols are affected not only by the composition and properties of the



Scheme 1

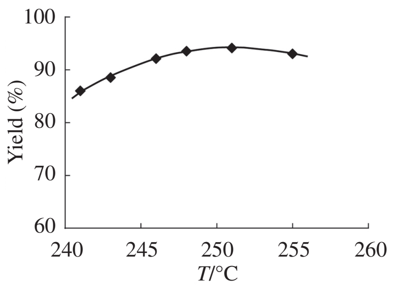


Figure 1 The dependence of the yields of propanols on the reaction temperature ($V_{\text{cat.}}$ = 2 ml, 30% glycerol solution, P_{H_2} = 3.0 MPa, LHSV = 0.46 h^{-1}, U_{H_2} = 15 ml min^{-1}).

catalyst, but also by the conditions of the process, in particular, such parameters as the concentration of glycerol in the initial solution, the reaction temperature, pressure, the volume rate of hydrogen supply and the contact time. The optimal conditions for glycerol hydrogenolysis imply higher yield of propanols with minimized yield of by-products, including propanediols. It was necessary to carry out the reaction under conditions ensuring glycerol being in a liquid state. Indeed, in this case highly viscous glycerol does not penetrate into the pores of the catalyst, and the reaction occurs exclusively on its outer surface. Then the main factor affecting the reaction rate is the value of the external catalyst surface, which directly depends on the size of the catalyst granules. In our experiments, the catalysts with grain sizes of 0.25–0.50 mm were used.

According to experimental data obtained, the specified conditions have a complex effect on the reaction outcome. In particular, propanols have a lower boiling point than glycerol, as a result they can be removed from the catalyst by a hydrogen flow. At the same time, the increase in the hydrogen pressure in the reactor not only enhances the rate of hydrogenation of unsaturated bonds, but simultaneously reduces evaporation of intermediate propanediols, thereby ensuring their conversion into propanols. It must be noted that the reaction temperature and the LHSV value (or contact time) have a crucial impact on the yield of propanols.

Figures 1 and 2 show the dependence of the yields of propanols on these parameters in the reaction catalyzed by 16%Ni/WO_3–TiO_2. According to these data, the optimum temperature is 250 °C and the LHSV parameter should be not higher than 0.46 h^{-1}. Noteworthy, only a certain combination of the reaction parameters provides rather high yield of propanols with the conversion of glycerol close to 100%. In our case, the maximum yield of propanols reaches 94.1%. Importantly, the higher total propanol yield, the higher the 1-Pr/2-Pr ratio, *e.g.*, when the total propanol yield grows from 80 to 94%, the 1-Pr/2-Pr ratio increases from 9 to 14. This means that the selectivity towards 1-Pr increases approaching 93% in the mixture of 1-Pr and 2-Pr. Thus, the catalyst 16%Ni/WO_3–TiO_2 is characterized by a high selectivity towards primary propan-1-ol.

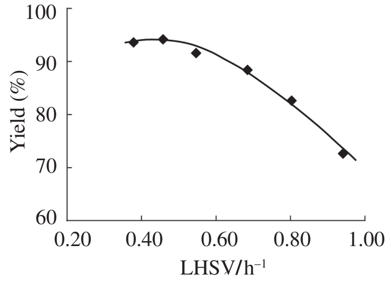


Figure 2 The dependence of the yield of propanols on LHSV ($V_{\text{cat.}}$ = 2 ml, 30% glycerol solution, T = 250 °C, P_{H_2} = 3.0 MPa, U_{H_2} = 15 ml min^{-1}).

In summary, the present study demonstrates that the catalyst 16%Ni/20%WO_3–80%TiO_2 is capable of providing the total yield of propanols as high as 94%. Such an extraordinary result can be explained by the optimal ratio of the two different functions in the catalyst prepared using co-precipitated oxides WO_3–TiO_2. On the one hand, the catalyst possesses a rather strong Brønsted acidity, providing high dehydration activity, and on the other hand, the presence of a large amount of Ni nanoparticles supported on the catalyst surface creates the conditions favorable for efficient hydrogenation.

This work was supported by the Ministry of High Education and Science of the Russian Federation (project RFMEFI57617X0089).

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2020.01.040.

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Received: 17th July 2019; Com. 19/5988