Hydrolysis-Hydrogenolysis of Cellulose to Ethylene and 1,2-Propylene Glycols in the Presence of Catalysts Based on Tungsten Carbide

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Ethylene and 1,2-propylene glycols (EG and 1,2-PG) are important chemicals, which are widely used in industry. The main source of EG and 1,2-PG production are fossil sources. It's gradual depletion makes it necessary to search for alternative methods of glycol production. A promising field of research in the production of glycols is the one-pot hydrolysis-hydrogenolysis of cellulose which is the major part of plant biomass. The production of EG and 1,2-PG from cellulose consists of two successive stages: 1) hydrolysis of the polysaccharide into glucose and 2) hydrogenolysis of glucose to EG and 1,2-PG. Bifunctional catalysts are required for one-pot cellulose hydrolysis-hydrogenation to be carried out. Catalytic systems based on tungsten carbides and nickel nanoparticles supported on tungsten carbides appear to be promising bifunctional catalysts for the process under investigation.

The aim of this work was to produce bifunctional catalysts based on tungsten carbide and to investigate the catalytic activity in the hydrolysis-hydrogenolysis of cellulose to EG and 1,2-PG.

Tungsten carbide catalysts (WC) were obtained by self-propagating high-temperature synthesis. The deposition of Ni nanoparticles on WC surface was carried out by the of impregnation method.

The obtained WC and Ni/WC catalysts were characterized by the number of physicochemical methods (XRD, TEM, nitrogen adsorption, pH_{ZPC}).

The study of the specific surface area by low-temperature nitrogen adsorption showed that the developed WC systems have a quite low specific surface area (27-46 m^2/g). The deposition of Ni onto the WC samples leads to a slight increase in the specific surface area. According to XRD, the materials are a mixture of metallic W and W_2C with small impurities of WC. The phase composition of the materials depends on the ration of the reagents in the synthesis of catlysts. The deposition of Ni does not cause phase changes in the tungsten carbide supports. The surface acidity of the catalyst samples was estimated by pH of zero charge point. pH_{ZPC} values of WC catalysts without Ni in the range 4.1–4.9 and increased with Ni deposition to 9.3–9.7.

The catalytic properties of all the catalysts were studied in the hydrolysis-hydrogenolysis of cellulose in a high pressure autoclave at 245 °C and under H_2 atmosphere. Microcrystalline cellulose mechanically activated in a planetary mill was used as a substrate in the work. The main reaction products were EG and 1,2-PG, and the by-product was glycerol. Among the tested systems based on CW-n carbides, in the process of hydrolysis-hydrogenolysis, CW-2 has the highest activity. In the presence of CW-2, The yields of EG and 1,2-PG reached 11.5 and 18.5 mol%, respectively, in the presence of WC catalysts without Ni nanoparticles. The deposition of Ni on WC led to an increase of the yields of both EG and 1,2-PG to 16.8% EG and 28.3% 1,2-PG, respectivelly.

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