



Liquid-phase glycerol hydrogenolysis to 1,2-propanediol under nitrogen pressure using 2-propanol as hydrogen source

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ABSTRACT

2-Propanol was studied as a hydrogen donor molecule in the transfer hydrogenation process to selectively convert glycerol into 1,2-propanediol under N₂ pressure and using Ni or/and Cu supported on Al₂O₃ catalysts. The results were compared to those obtained under the same operating conditions but under H₂ pressure. The results of the activity tests and catalyst characterization techniques (N₂-physiosorption, H₂-chemisorption, TPD of NH₃, TPR, TPO and XPS) suggest that glycerol hydrogenolysis to yield 1,2-propanediol occurred through a different mechanism regarding the origin of the hydrogen species. When atomic hydrogen came from dissolved molecular hydrogen dissociation, glycerol was first dehydrated to acetol and then hydrogenated to 1,2-propanediol. On the other hand, when the hydrogen atoms were produced from 2-propanol dehydrogenation, glycerol was directly converted to 1,2-propanediol through intermediate alkoxide formation.

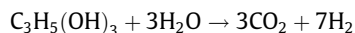
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1. Introduction

Nowadays, there is a tendency to reduce the use of fossil hydrocarbon sources in the production of commodity chemicals. The main reasons are increasing and fluctuating oil prices, the drive to renewable resources and a global concern to reduce CO₂ emissions. Glycerol, obtained as a by-product in biodiesel manufacture, is a versatile feedstock for the production of a whole range of chemicals, polymers and fuels [1]. The glycerol hydrogenolysis process for obtaining propanediols (PDOs) has aroused considerable interest due to the attractive applications of 1,2-PDO, an important commodity chemical traditionally derived from propylene oxide, and 1,3-PDO, a monomer that can be used to produce polyester fibres. In the reaction pathway, glycerol is first dehydrated to 1-hydroxypropan-2-one (acetol) or 3-hydroxypropanal (3-HPA), which are subsequently hydrogenated to 1,2 and 1,3-PDO, respectively [2]. Several reaction systems have been studied to maximize glycerol conversion and PDO selectivity. Dasari et al. developed a two-step reaction process using a copper chromite catalyst. In the first step, acetol was produced through glycerol reactive distillation at 473 K and 0.65 bar, while in the second step the acetol was further hydrogenated to 1,2 PDO at 473 K and 13.8 bar hydrogen pressure [3]. Interesting results have been reported using Cu/Al₂O₃ in single-step vapour-phase glycerol

hydrogenolysis at near ambient hydrogen pressure [4,5]. Liquid-phase glycerol hydrogenolysis has also been studied [6–10], as it has both energy- and plant-scale reduction benefits. Nevertheless, reported results are not as promising as the ones from vapour phase and two-step processes. In liquid-phase reactions, high hydrogen pressures are needed due to the low solubility of hydrogen in glycerol/water solutions, and limited H₂ availability may cause undesired side reactions such as cracking and coking.

Hydrogen accessibility problems could be avoided if the hydrogen required for glycerol hydrogenolysis was to be generated directly in the active sites of the catalyst, allowing a process with inert atmosphere and lower working pressure. Among others, two different processes can be considered to generate hydrogen: aqueous-phase reforming (APR) and catalytic transfer hydrogenation (CTH). Hydrogen production from glycerol APR is a well-reported process [11,12].



The production of PDOs by APR of glycerol has already been studied [13]. The process initially involves hydrogen and CO₂ formation. The hydrogen produced in the reforming step is then consumed in the hydrogenolysis of glycerol, leading to an overall conversion of glycerol to 1,2-PDO, CO₂ and water [14].

CTH, in which hydrogen is transferred from a hydrogen donor molecule to an acceptor, is an interesting process for reducing organic compounds, as it has real advantages compared to processes with molecular hydrogen. Molecular hydrogen has high diffusibility, being easily ignited and presents considerable hazards on a large

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scale; the use of hydrogen donors obviates these difficulties [15]. Alcohols have been widely used in CTH processes [16], and 2-propanol is a suitable hydrogen donor for glycerol hydrogenolysis [17].

This paper studies aqueous-phase reforming and catalytic transfer hydrogenation processes as sources of hydrogen for glycerol hydrogenolysis to PDOs.

2. Experimental

2.1. Catalysts

Amorphous silica-alumina loaded with 1 wt.% Pt (Pt/ASA) was kindly supplied by Shell, while Ni–Cu/Al₂O₃^(A) was kindly supplied by the Boreskov Institute of Catalysis. CuCr₂O₃ was purchased from Süd-Chemie. Ni/Al₂O₃^(S), Cu/Al₂O₃^(S) and Ni–Cu/Al₂O₃^(S) were prepared by the sol–gel method. Aluminium isopropoxide (Aldrich) was dissolved in deionised water (9 mL of H₂O per gram of aluminium isopropoxide) by vigorous stirring of the solution at 313 K. The pH was measured and kept between 3.8 and 4.2 adding the required amounts of HNO₃ (0.5 M). Simultaneously, nickel(II) nitrate hexahydrate (Aldrich) and/or Copper(II) nitrate hemi pentahydrate (Alfa Aesar) were dissolved in ethanol. The precursor solution was slowly added to an aluminium isopropoxide solution. The mixture was stirred for 30 min at 313 K and then introduced into the ultrasonic apparatus for another 30 min. The mixture was then rested for 24 h at 313 K and subsequently for another 12 h at 375 K. The product obtained was crushed and calcined from room temperature to 723 K at a heating rate of 2 K/min. The temperature was maintained for 4 h. Catalyst samples for activity tests were used in powdered form with a granule size between 320 and 500 µm.

2.2. Activity test

The hydrogenolysis of glycerol was carried out in a 50 mL stainless steel autoclave with a magnetic stirrer. The catalyst powder (166 mg catalyst/g of glycerol) was introduced into the autoclave and the reactor was then purged with H₂ or N₂. After purging, some of the catalysts (Ni–Cu/Al₂O₃^(A), Ni–Cu/Al₂O₃^(S), Ni/Al₂O₃^(S) and Cu/Al₂O₃^(S)) were pre-treated, reducing them under a 50 vol.% H₂/N₂ flow for 4 h at 593 or 723 K, while the others (Pt/ASA and CuCr₂O₃) were used as received. Next, the reactor temperature was set to 493 K and the N₂ or H₂ pressure was increased to 45 bar. The aqueous solution (41 mL) with the reactants was placed on a feed cylinder and heated to the reaction temperature. The reaction starting time was established when the line connecting the feed cylinder and the reactor was opened. During the reaction, changes in the system pressure were observed: a decrease in the experiments under H₂ pressure (due to H₂ consumption), and an increase in the experiments under N₂ pressure when a hydrogen donor molecule was added (due to the formation of H₂ and other gaseous species). Nevertheless, as diluted glycerol and donor feeds were used, the pressure variations were negligible.

Five liquid samples were taken throughout the reaction in order to obtain the time evolution of reactant and product concentrations. These compounds were analysed using a gas chromatograph (Agilent Technologies, 7890 A) equipped with a flame ionization detector (FID) and a thermal conductivity detector (TCD). A Meta-Wax capillary column (diameter 0.53 mm, length 30 m) was used for product separation. After reaction, the gas phase was collected in a gas bag and analysed with another GC-TCD-FID (Agilent Technologies, 7890 A) equipped with a molecular sieve column (HP-MOLESIEVE, diameter 0.535 mm, length 30 m) and a capillary column (HP-PLOT/Q, diameter 0.320 mm, length 30 m). The conversion of the reactants was calculated according to following equation:

Conversion of glycerol. %

$$= \frac{\text{sum of C-based mol of all liquid prod. } t = t}{\text{C-based mol of glycerol. } t = 0}$$

The selectivity of the products was calculated on a carbon basis.

Selectivity of liquid products %

$$= \frac{\text{C-based mol of the product}}{\text{Sum of C-based mol of all liquid products}}$$

Initial Turnover Number (TON₀) was calculated as the ratio between the converted amount of glycerol in the first 2 h per gram of catalyst and per hour.

2.3. Catalyst characterization

The catalysts were chemically analysed by Inductively Coupled Plasma Atomic Emission (ICP-AES) using a Perkin–Elmer Optima 2000 instrument. The solid samples were first digested with a mixture of HF, HCl and HNO₃ at 453 K in a microwave oven. Surface area, pore volume and pore size distributions were determined with N₂ physisorption at 77 K on a Quantachrome AUTOSORB-1C instrument. Prior to the analysis, all samples were dried at 393 K overnight under high vacuum. The surface area was calculated using the Brunauer, Emmett and Teller (BET) method, while pore size distributions were calculated using the Barrett–Joyner–Halenda (BJH) method applied to the desorption leg of the isotherms.

The reducibility of catalysts was studied by hydrogen temperature-programmed reduction (TPR) on a Quantachrome AUTOSORB-1C apparatus with TPR capability. The catalyst sample was reduced in flowing gas containing 5 vol.% H₂ in Ar at a total flow rate of 50 mL/min, using a heating rate of 10 K/min up to a final temperature of 1223 K. A TCD detector downstream of the sample monitored changes in the concentration of H₂. Hydrogen chemisorption was performed at 313 K with the Quantachrome AUTOSORB-1C volumetric system. All the catalysts were reduced at 873 K in pure H₂ flow for 4 h prior to the measurements. The quantity of H₂ adsorbed at monolayer coverage was estimated by extrapolating the linear portion of the isotherms to zero pressure.

Temperature-programmed oxidation analyses of fresh and used catalysts were carried out using a thermo-gravimetric analyser (Mettler Toledo TGA/SDTA 851e). The standard protocol involved the pre-treatment of the sample (45–50 mg) in 125 mL/min of N₂ flow from 297 K to 673 K at a heating rate of 10 K/min. The sample was then cooled to 323 K and the weight change of the sample was continuously monitored during its heating in 125 mL/min of N₂ as purge gas and 75 mL/min of 10 vol.% O₂ in He as reactive gas from 323 to 1173 K at a heating rate of 5 K/min.

The acidity of the freshly reduced samples was determined by ammonia temperature-programmed desorption (TPD) measurements. The sample was pre-treated in a He stream at 673 K for 0.5 h and then cooled to 373 K and ammonia-saturated using a stream of 5 vol.% NH₃/He flow (50 mL/min) for 0.5 h. Following catalyst equilibration in a helium flow, the ammonia was desorbed using a linear heating rate of 10 K/min to 723 K. The area under the curve was integrated to determine the total acidity of the sample from its NH₃ desorption profile.

X-ray photoelectron spectroscopy (XPS) studies were performed with a Physical Electronics PHI 5700 spectrometer equipped with a hemispherical electron analyser (model 80-365B) and a Mg Kα (1253.6 eV) X-ray source. High-resolution spectra were recorded at a 45° take-off-angle by a concentric hemispherical analyser operating in the constant pass energy mode at 29.35 eV, using a 720 mm diameter analysis area. Charge referencing was done against adventitious carbon (C 1s 284.8 eV). The pressure in the analysis chamber was kept below 5 × 10^{−6} Pa. The PHI

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