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## Sorbitol hydrogenolysis to glycols by supported ruthenium catalysts

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### ABSTRACT

Supported Ru catalysts were prepared by wet impregnation to evaluate the role of different oxide supports ( $\text{Al}_2\text{O}_3$ ,  $\text{SiO}_2$ ,  $\text{TiO}_2$ ,  $\text{ZrO}_2$ ) in sorbitol hydrogenolysis to glycols. X-ray diffraction, transmission electron microscopy, hydrogen chemisorption, X-ray photoelectron spectroscopy, and  $\text{NH}_3$  temperature-programmed desorption were used to characterize the catalysts, which were active in the hydrogenolysis of sorbitol. The support affected both the physicochemical properties and catalytic behavior of the supported Ru particles. The characterization results revealed that the  $\text{Ru}/\text{Al}_2\text{O}_3$  catalyst has a high surface acidity, partially oxidized Ru species on the surface, and a higher surface Ru/Al atomic ratio, which gave it the highest selectivity and yield to glycols.

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### 1. Introduction

Lignocellulosic biomass is an important raw material due to its abundance, availability, and renewable nature [1–3]. The lignocellulosic feedstock is composed of structural carbohydrates, cellulose (38%–50%) and hemicelluloses (23%–32%), and aromatic polymer lignin (15%–25%) [4]. Cellulose is currently used in the paper, textile, and wood industries. Several catalytic processes are being developed to convert cellulose in a single step into high added value chemicals like sugars and alcohols like sorbitol or derived polyols with less carbon atoms [5–11]. Currently, sorbitol is industrially obtained by glucose hydrogenation with Raney Ni catalysts. Cellulose is hydrolyzed into glucose which in turn is reduced in the presence of a supported metal catalyst to sorbitol.

Sorbitol is one of the ten most relevant building blocks derived from biomass because many high added value products can be derived from it [12]. Among the possible reactions for sorbitol valorization, we focused here on the hydrogenolysis pathway to produce glycols, mainly 1,2-propylene (1,2-PG) and ethylene glycols (EG), which are both important commodities.

They are widely used as antifreeze, lubricants, hydraulic fluids, monomers for thermoplastics, and also in the pharmaceutical industry [13–16]. At the moment, 1,2-PG and EG are petrochemicals because they are produced by the hydrolysis of propylene oxide and ethylene oxide, respectively. Consequently, the hydrogenolysis of sorbitol is an interesting renewable alternative to produce these chemicals.

The hydrogenolysis of sorbitol starts with the dehydrogenation reaction to give aldose and ketoses followed by retro-aldol condensation, which is favored in basic medium, to yield carbonyl compounds like glyceraldehyde and glycolaldehyde. Hydrogenation of the latter results in the selective formation of glycols (1,2-PG and EG) [17]. Keenan et al. [18] reported that the retro-aldol mechanism was insufficient for explaining the product distribution, while the decarbonylation mechanism can explain the selectivity of the terminal C-C scission. Sorbitol hydrogenolysis requires the use of Ni or Ru-based catalysts under high  $\text{H}_2$  pressure and the use of basic promoters. The selectivity to glycols increases with the presence of a basic promoter, but the problems of accelerated degradation and glycol product separation occur [16].

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Much research work reported to date on sorbitol hydrogenolysis has focused on the effect of the type of metal catalyst and reaction conditions on the catalytic behavior. Sohounlouse et al. [19] described in their pioneering work sorbitol hydrogenolysis with Ru/SiO<sub>2</sub> as the catalyst, and they reported an overall glycol selectivity of 50% at 483 K, 8.0 MPa of H<sub>2</sub> and pH = 12.5. In a neutral medium, the lowering of the temperature leads to an increase in selectivity giving mainly glycerol and 1,2-PG. Zhao et al. [20–22] reported a sorbitol conversion of 86% and selectivity of 51% for glycols and 9% glycerol at 493 K, 8.0 MPa of H<sub>2</sub> and 800 r/min after 4 h of reaction using carbon nanofiber supported Ru catalysts in the presence of a basic promoter (CaO). These authors also suggested that glycerol was the primary product and propylene glycol was derived from glycerol. Banu et al. [14,23] studied the catalytic properties of Ru(1%) and Ni(6%) supported on a basic zeolite NaY in the presence of Ca(OH)<sub>2</sub> as a basic promoter. A nickel catalyst presented the highest selectivity to propylene glycol, 69% for a sorbitol conversion of 75% at 493 K, 6.0 MPa of H<sub>2</sub> 300 r/min after 6 h of reaction.

Sun et al. [13] studied xylitol hydrogenolysis reaction on supported Ru catalysts at 473 K and 4.0 MPa H<sub>2</sub>. These authors examined the effects of the support and basic promoter on the catalytic performance and obtained 20% xylitol conversion and a selectivity to glycols of 50% in the presence of a basic promoter Ca(OH)<sub>2</sub>. The activity and selectivity depended on the H<sub>2</sub> pressure, reaction temperatures, and pH. The addition of Ce into the Ni/Al<sub>2</sub>O<sub>3</sub> catalysts showed a remarkable promoting effect on the catalytic behavior of sorbitol hydrogenolysis to produce glycols [24]. A glycol selectivity higher than 40% for complete sorbitol conversion was reported at 493 K under 7.0 MPa of H<sub>2</sub> and after 8 h of reaction in basic medium.

Recently, Soták et al. [25] reported yields to glycols of 46 % and 71% for the hydrogenolysis of 20 ml of 5 wt% aqueous solution of sorbitol and xylitol, respectively, at 473 K and 4.0 MPa in 45 min of reaction. These authors used high loadings of nickel phosphides supported on active carbon as catalyst (0.2 g) and a basic promoter (0.25 g), Ba(OH)<sub>2</sub>·8H<sub>2</sub>O for adjusting the pH of the reaction. Chen et al. [16] have reported sorbitol hydrogenolysis without a basic promoter using coprecipitated Ni/MgO catalysts. After 4 h of reaction at 473 K and 4.0 MPa H<sub>2</sub>, the best catalyst exhibited 68% sorbitol conversion and 60% selectivity to glycols. Deactivation occurred because MgO was partly solubilized by water.

Despite these investigations, the effect of the support on the catalytic properties has received much less attention. Thus, the aim of this work was to investigate the effect of the oxide support (Al<sub>2</sub>O<sub>3</sub>, SiO<sub>2</sub>, TiO<sub>2</sub>, ZrO<sub>2</sub>) on the structure and physicochemical properties of supported Ru catalysts and their catalytic performance in sorbitol hydrogenolysis to glycols (1,2-PG and EG). The study was conducted in the absence of a basic promoter and under a low pressure of H<sub>2</sub> (4.0 MPa). It is well known that these parameters are important for a good yield to glycols, but under our reaction conditions, the effect of the support would not be overshadowed by the presence of a basic promoter and high H<sub>2</sub> pressure, and the effect of the support would be more visible and detectable.

## 2. Experimental

### 2.1. Preparation of the catalysts

A series of 5 wt% supported Ru catalysts was prepared by impregnation of an aqueous solution of Ru(NO)(NO<sub>3</sub>)<sub>3</sub> (Alfa Aesar) on Al<sub>2</sub>O<sub>3</sub> (209 m<sup>2</sup>/g), SiO<sub>2</sub> (208 m<sup>2</sup>/g), TiO<sub>2</sub> (53 m<sup>2</sup>/g), and ZrO<sub>2</sub> (39 m<sup>2</sup>/g) supports (Sigma-Aldrich). The solid obtained was dried at 383 K for 12 h. Prior to use as catalyst, the dried solid was subjected to the following treatment: (1) calcination under a 20 vol% O<sub>2</sub>/Ar flow (100 mL/min) at 623 K (heating rate of 10 K/min) for 1 h; (2) reduction in 5 vol% H<sub>2</sub>/Ar flow (100 mL/min) at 473 K (heating rate of 5 K/min) for 0.5 h. These temperatures were selected based on previous evolved gas analysis by mass spectrometry and temperature programmed reduction (TPR) experiments, respectively, that showed that these calcination and reduction procedures fully decomposed the precursor and reduced the Ru oxides formed in the calcination step. Metal oxides with an acidic or neutral nature were selected for this study. Basic oxides such as MgO would suffer leaching in the reaction [16].

### 2.2. Characterization of the catalysts

Evolved Gas Analysis by Mass Spectrometry (EGA-MS) was performed by loading the sample (0.05 g) in a U-shaped quartz reactor connected to a Balzer Prisma™ quadrupole mass spectrometer (QMS 200). The analysis was conducted while flowing a 20 vol% O<sub>2</sub>/Ar mixture (50 mL/min) from room temperature to 1000 K at a heating rate of 10 K/min. The fragments  $m/z = 18$  (H<sub>2</sub>O<sup>+</sup>),  $m/z = 30$  (NO<sup>+</sup>),  $m/z = 40$  (Ar<sup>+</sup>),  $m/z = 44$  (N<sub>2</sub>O<sup>+</sup>), and  $m/z = 46$  (NO<sub>2</sub><sup>+</sup>) were continuously monitored with the mass spectrometer. Gas lines from the reactor to the MS inlet were heated at 393 K to avoid H<sub>2</sub>O condensation. TPR experiments were conducted in the same experimental set-up. A 5 vol% H<sub>2</sub>/Ar mixture was flowed through the sample (ca. 0.1 g) while heating from room temperature to 1000 K at a rate of 5 K/min. In this case, the fragments  $m/z = 2$  (H<sub>2</sub><sup>+</sup>),  $m/z = 18$  (H<sub>2</sub>O<sup>+</sup>), and  $m/z = 40$  (Ar<sup>+</sup>) were registered to evaluate the reduction process.

Powder X-ray diffraction (XRD) patterns were recorded at  $2\theta = 10^\circ$ – $90^\circ$  in the scan mode (0.04°, 20 s) using an X'Pert Pro PANalytical diffractometer with Cu K<sub>α1,2</sub> ( $\lambda = 0.15418$  nm) radiation. Diffractograms were analyzed with the X'Pert HighScore Plus software. The crystallite size (D) was calculated by the Scherrer equation.

A JEOL JEM-2100F transmission electron microscope (TEM) operated at 200 kV (point resolution 0.19 nm) was employed to conduct high resolution TEM analysis of the catalysts. The TEM was equipped with a EDAX Genesis detector. The catalytic precursors were calcined and reduced under the conditions detailed in the activation procedure. The reduced samples were transferred to the TEM without exposure to air.

H<sub>2</sub> chemisorption was performed using a dynamic method. 0.1 g of reduced catalyst was loaded in a U-shaped quartz reactor connected to a Balzer Prisma™ quadrupole mass spectrometer (QMS 200). After an in situ activation procedure, the

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