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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 (Al_2O_3 , SiO_2 , TiO_2 , ZrO_2) in sorbitol hydrogenolysis to glycols. X-ray diffraction, transmission electron microscopy, hydrogen chemisorption, X-ray photoelectron spectroscopy, and 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 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/SiO₂ as the catalyst, and they reported an overall glycol selectivity of 50% at 483 K, 8.0 MPa of H₂ 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 H₂ 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)₂ 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 H₂ 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 H₂. 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)₂. The activity and selectivity depended on the H₂ pressure, reaction temperatures, and pH. The addition of Ce into the Ni/Al₂O₃ 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 H₂ 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)₂·8H₂O 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 H₂, 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 (Al₂O₃, SiO₂, TiO₂, ZrO₂) 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 H₂ (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 H₂ 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)(NO₃)₃ (Alfa Aesar) on Al₂O₃ (209 m²/g), SiO₂ (208 m²/g), TiO₂ (53 m²/g), and ZrO₂ (39 m²/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% O₂/Ar flow (100 mL/min) at 623 K (heating rate of 10 K/min) for 1 h; (2) reduction in 5 vol% H₂/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 PrismaTM quadrupole mass spectrometer (QMS 200). The analysis was conducted while flowing a 20 vol% O₂/Ar mixture (50 mL/min) from room temperature to 1000 K at a heating rate of 10 K/min. The fragments $m/z = 18$ (H₂O⁺), $m/z = 30$ (NO⁺), $m/z = 40$ (Ar⁺), $m/z = 44$ (N₂O⁺), and $m/z = 46$ (NO₂⁺) were continuously monitored with the mass spectrometer. Gas lines from the reactor to the MS inlet were heated at 393 K to avoid H₂O condensation. TPR experiments were conducted in the same experimental set-up. A 5 vol% H₂/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 $m/z = 2$ (H₂⁺), $m/z = 18$ (H₂O⁺), and $m/z = 40$ (Ar⁺) were registered to evaluate the reduction process.

Powder X-ray diffraction (XRD) patterns were recorded at $2\theta = 10^\circ$ – 90° in the scan mode (0.04°, 20 s) using an X'Pert Pro PANalytical diffractometer with Cu K _{α} 1,2 ($\lambda = 0.15418$ 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.

H₂ 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 PrismaTM quadrupole mass spectrometer (QMS 200). After an in situ activation procedure, the

reactor was flushed with an Ar flow (50 mL/min) for 1 h at the same temperature, then the temperature was decreased and the catalyst was kept at 373 K. Subsequently, a flow of 0.32 vol% H₂/He/Ar was passed through the sample bed. The $m/z = 40$ (Ar⁺) and $m/z = 4$ (He⁺) signals increased rapidly while the $m/z = 2$ (H₂⁺) signal was delayed as a result of both H₂ physisorption and chemisorption. Then, physisorbed H₂ was removed by flowing Ar for 30 min. Finally, a second H₂ adsorption experiment was performed to determine the amount of chemisorbed H₂, which was calculated by subtracting one curve from the other and integration of the area obtained. Dispersion and particle size (d_{VA}) data were calculated assuming a stoichiometry Ru/H of 2. The average particle size was determined by the expression, $d_{\text{VA}} = 6v_{\text{m}}/Da_{\text{m}}$, where D is metal dispersion (the ratio of the surface metal atoms to the total number of metal atoms), v_{m} is the volume occupied by a metal atom ($1.364 \times 10^{-2} \text{ nm}^3/\text{atom}$) in the bulk, and a_{m} is the surface area occupied by an surface metal atom ($9.09 \times 10^{-2} \text{ nm}^2/\text{atom}$) [26–28]. The supports were also used as blank for all samples.

X-ray photoelectron spectra (XPS) were acquired with a VG Escalab 200R spectrometer equipped with a hemispherical electron analyzer and a Mg K_{α} ($h\nu = 1253.6 \text{ eV}$) X-ray source. The reduced powder sample was rapidly placed into a flask containing isooctane to prevent sample oxidation by ambient air. Then, the solid was rapidly pressed into a copper holder mounted on a sample rod in the pretreatment chamber of the spectrometer to remove the protecting agent (isooctane). The solid was outgassed at room temperature for 1 h at 10^{-5} mbar to remove isooctane before the transfer to the analysis chamber. Ru 3d, Al 2p, Si 2p, Ti 2p, Zr 3d, C 1s, and O 1s regions were scanned sufficient times to obtain high signal-to-noise ratios. The areas of the peaks were computed by fitting the experimental spectra to Gaussian/Lorentzian curves after removing the background using the Shirley function. Surface atom ratios were calculated from peak area ratios normalized by the corresponding atomic sensitivity factor [29].

The acidic properties of the catalysts were determined by temperature programmed desorption of ammonia (NH₃-TPD). The reduced catalyst (0.2 g) was pretreated at 473 K for 0.5 h and then cooled to 373 K under Ar (50 mL/min). A flow of 5 vol% NH₃/He was passed through the sample bed for 0.5 h at 373 K, and a subsequent flushing with Ar at the same temperature to remove the physisorbed ammonia was applied. NH₃ desorption was carried out from room temperature to 1000 K with a heating rate of 10 K/min. TPD analysis was registered with a Balzer PrismaTM quadrupole mass spectrometer (QMS 200) by following the fragments $m/z = 16$ (NH₂⁺), $m/z = 17$ (NH₃⁺), $m/z = 18$ (H₂O⁺), $m/z = 28$ (N₂⁺), $m/z = 30$ (NO⁺), $m/z = 40$ (Ar⁺), $m/z = 44$ (N₂O⁺), and $m/z = 46$ (NO₂⁺) to record the desorption of NH₃ and to account for the oxidation of NH₃ to nitrogen oxides. Quantitative determination of desorbed ammonia was based on the $m/z = 16$ signal normalized to $m/z = 40$ signal (Ar) by integrating the area under this desorption curve. The calibration of this signal was carried out by using streams with different NH₃ concentration.

2.3. Activity measurement

Sorbitol hydrogenolysis was carried out in a stainless steel autoclave Parr reactor (100 mL). In a typical experiment, 30 g of aqueous sorbitol solution (20 wt% sorbitol) and 0.3 g of reduced catalyst (5 wt% relative to sorbitol) were loaded in the autoclave, which was then flushed several times with N₂ and H₂ to remove ambient air. Subsequently, the temperature was increased to 493 K and the H₂ pressure adjusted to 4.0 MPa, which was kept unchanged during the reaction. Finally, the mixture was stirred at 500 r/min to start the reaction, which was conducted for 4 h. The reactants and liquid products were analyzed by high performance liquid chromatography (HPLC) equipped with a Rezex RHM-Monosaccharide H⁺ (8%) (300 × 7.80 mm) column and refraction index (RI) and UV (DAD) detectors. Samples for the chromatographic analysis were prepared by adding a known amount of internal standard. A H₂SO₄ (5 mmol/L, 0.45 mL/min) mobile phase was employed as eluent at 313 K. Sorbitol conversion was defined as the ratio between the number of sorbitol moles consumed in the reaction and the number of sorbitol moles initially present in the mixture. The yield was defined as the ratio of the number of moles of product formed to the total moles of sorbitol initially present with taking into account the molar stoichiometry of the product. The selectivity was defined as the result of dividing the yield by the sorbitol conversion.

The total carbon balance in the liquid was measured with a total organic carbon analyzer TOC-V CSH of Shimadzu. This instrument measures the concentration of total carbon (TC) and inorganic carbon (IC). Total organic carbon (TOC) was calculated as the difference between these two values. To perform this analysis, 3 mL of solution was filtered with a Varian Captiva TM column with a pore diameter of 0.45 μm. 1 mL of the filtered sample was diluted in 100 mL of deionized water and an aliquot of this solution was injected into the analyzer.

3. Results and discussion

3.1. Catalytic activity of supported Ru catalysts

Table 1 summarizes the conversion and selectivity shown by the supported Ru catalysts, including a commercial Ru/Al₂O₃ catalyst (Ru/Al₂O₃-c) and a blank Al₂O₃ support. A reaction time of 4 h was selected based on kinetic experiments

Table 1
Catalytic activity of supported Ru catalysts in sorbitol hydrogenolysis.

Catalyst	X_{sorbitol} (%)	Selectivity (%)				
		Glycols ^a	GLY ^b	PA ^c	MA ^d	DP ^e
Al ₂ O ₃	15.7	0.0	0.0	100.0	0.0	0.0
Ru/Al ₂ O ₃	73.9	19.1	6.5	6.8	4.9	1.2
Ru/Al ₂ O ₃ -c	80.2	9.2	5.1	12.3	5.0	2.7
Ru/SiO ₂	96.1	4.9	2.1	14.6	3.2	1.9
Ru/TiO ₂	85.8	5.0	1.7	23.1	2.5	3.1
Ru/ZrO ₂	83.4	5.2	1.5	26.5	1.9	2.3

Reaction conditions: sorbitol 6 g, H₂O 24 g, catalyst 0.3 g, H₂ 4.0 MPa, 493 K, 4 h, 500 r/min.

^a 1,2-propanediol and ethylene glycol; ^b glycerol; ^c polyalcohols: xylitol, ribitol, and erythritol; ^d monoalcohols: ethanol; ^e dehydration products: sorbitan and acetol.

(results not shown) that observed the evolution of the reactants and products versus time. All the supported Ru catalysts gave higher than 70% sorbitol conversion. Ru supported on SiO₂ showed the highest sorbitol conversion, followed by the catalyst on TiO₂ and ZrO₂ supports, with the least active being the supported Al₂O₃ catalyst. However, the Ru/Al₂O₃ catalyst presented the best selectivity to glycols (19.1%). A pure Al₂O₃ support gave 15.7% sorbitol conversion, and was completely selective to polyalcohols of five carbon atoms. This means that Ru was the selective species in the sorbitol transformation to glycols.

With respect to selectivity, it should be first noted that the distribution of products was very broad, and to simplify this, we have grouped the reaction products into glycols (1,2-PG and EG), glycerol (GLY), polyalcohols (PA) including sugar alcohols with 4 or 5 carbon atoms as xylitol, ribitol, and erythritol, and monoalcohols (MA) such as ethanol and dehydration products (DP) such as sorbitan and acetol derived from sorbitol and glycerol. Table 1 shows that the Ru/Al₂O₃ catalysts, both the commercial one and that prepared in our laboratory, gave higher selectivities to glycols and glycerol, and consequently higher yields than the other supported Ru catalysts tested. In contrast, the Ru/SiO₂, Ru/TiO₂, and Ru/ZrO₂ samples exhibited higher selectivity to polyalcohols (around 14%–27%). Low selectivity to monoalcohols and dehydration products were obtained for all the catalysts.

The wide distribution of products can be explained by the competition between the C–C and C–O bond cleavage route to produce polyalcohols, glycols, glycerol and monoalcohols and the dehydration of sorbitol to sorbitan, which lead to the formation of isosorbide by a second dehydration reaction. Previous studies have reported the dehydration of sorbitol in water at a high temperature or in the presence of a solid acid catalyst under hydrogen pressure [30–32].

In general, these selectivity values were lower than those reported by other authors with supported Ru based catalyst [13,14,18,20–22]. However, it must be kept in mind that our reaction conditions were selected to highlight the effect of the support on sorbitol hydrogenolysis. The presence of other activity enhancing factors, in particular the pH of the medium and the H₂ pressure, would have overshadowed the smaller effect of the support. Also, since a fraction of the reaction products cannot be identified and quantified by liquid chromatography, the measurement of the total organic carbon (TOC) present in the liquid product was carried out. Around 20% of the carbon in the liquid product was not quantified in the HPLC analysis. Under our reaction conditions, some gas products were formed, which would be C₁ compounds like methanol, CH₄, and CO since polyalcohols C₅ (xylitol and ribitol) were identified in the liquid phase.

In summary, Ru/Al₂O₃ clearly gave a higher yield to glycols due to the significantly higher selectivity than the other catalysts tested.

3.2. Characterization of the Ru catalysts

The thermal decomposition of the ruthenium (III) nitrosyl

nitrate precursor salt in air was followed by temperature programmed EGA-MS (results not shown). The aim was to determine the temperature required to form the Ru oxide. Fragments with $m/z = 2, 18, 30, 32, 44$, and 46 were registered. Only signal $m/z = 30$ corresponding to the NO⁺ fragment was detected. All the samples exhibited a broad peak associated with the decomposition process in the range of 400–625 K. Therefore, all the catalytic precursors were treated in air at 623 K for 1 h, which guaranteed the complete decomposition of the precursor salt to the oxide.

The reducibility properties of these calcined catalysts were studied by H₂-TPR. This also allowed the determining of the required temperature to generate metallic Ru by the complete reduction of Ru oxide. Figure 1 depicts the H₂ signal normalized to the weight of catalyst loaded into the reactor for each experiment. All the catalysts gave a H₂ consumption peak with a maximum centered at 400–425 K. The Ru/SiO₂ and Ru/TiO₂ catalysts gave a reduction peak at a slightly higher temperatures than the Ru/Al₂O₃ and Ru/ZrO₂ catalysts. This peak was attributed to reduction of Ru ions in RuO_x to metallic Ru⁰ [33,34]. From these results, a reduction at 473 K for 0.5 h was selected (see dashed line in Fig. 1) to carry out the reduction of all samples.

The XRD patterns of the Ru catalysts are represented in Fig. 2. The Ru/SiO₂ and Ru/Al₂O₃-c catalyst diffractograms have peaks associated with the Ru⁰ phase (JCPDS 6-0663) with reflections at $2\theta = 44.0^\circ, 38.4^\circ$, and 42.2° . For the other catalysts, these peaks were not observed. Although they may not have been detected due to overlapping by the more intense diffraction peaks from the support, the absence of these diffraction lines in these samples suggested that Ru was well dispersed and consequently have a small particle size (less than 5 nm). Diffraction peaks associated with the RuO_x phase were not observed. The diffraction peaks in the Ru/Al₂O₃-c, Ru/ZrO₂, Ru/TiO₂, and Ru/Al₂O₃ diffractograms were due to the oxide support in the catalyst. Ru/Al₂O₃ showed peaks corresponding to the Al₂O₃ support (JCPDS 46-1131), Ru/TiO₂ presented mainly the peaks of TiO₂ anatase (JCPDS 21-1272) and some TiO₂ rutile phase (JCPDS 77-0442). The Ru/ZrO₂ diffractogram peaks corresponding to monoclinic (JCPDS 1-0750) and tetragonal ZrO₂ (JCPDS 81-1546) were visible. The Ru/Al₂O₃-c

Fig. 1. H₂-TPR profiles of calcined supported Ru catalysts.

Fig. 2. XRD patterns of the supported Ru catalysts with the attribution. 1, Ru⁰; 2, AlOOH; 3, ZrO₂ monoclinic; 4, ZrO₂ tetragonal; 5, TiO₂ anatase; 6, TiO₂ rutile; 7, Al₂O₃.

diffraction pattern exhibited narrower and more intense peaks which were attributed to the boehmite phase (JCPDS 5-0190) indicating a better crystallized structure compared to the more amorphous aluminum oxide structure observed for Ru/Al₂O₃. The Ru crystallite sizes for the Ru/SiO₂ and Ru/Al₂O₃-c samples were calculated by Scherrer equation to the diffraction line at $2\theta = 44^\circ$, and were 8.3 and 8.0 nm, respectively. The absence of diffraction lines from Ru prevented the estimate of the Ru particle size by XRD for the other catalysts.

TEM characterization was conducted to estimate the Ru particle size in all the catalysts. Representative TEM images of the supported Ru catalysts are shown in Fig 3, and the histograms of the Ru particle size distribution are also included. Around 200 particles were used to establish the distribution of particle sizes for each sample. The Ru/Al₂O₃ catalyst presented a narrow particle size distribution with an average size of 3.7 nm. Similar homogeneous distributions of Ru particles with an average particle size of 3.8 and 2.7 nm, respectively, were observed for the Ru/TiO₂ and Ru/ZrO₂ catalysts. In the case of the Ru/SiO₂ catalyst, the particle size was larger than 9 nm and had a wider distribution. These results confirmed the XRD data, that is, the Ru/SiO₂ catalyst had larger and less dispersed Ru particles than the other catalysts.

H₂ chemisorption measurements were also conducted. The irreversible H₂ uptake, amount of Ru atoms exposed at the surface, estimated particle size and derived Ru dispersion are

Fig. 3. TEM micrographs and histograms of the Ru particle size distribution for the supported Ru catalysts.

compiled in Table 2. In the case of the RuSi catalyst, the dispersion could not be determined due to the negligible amount of H₂ uptake at 373 K. The same behavior has been previously reported in the range of 303–523 K by other authors [35]. In general, the chemisorption was performed appropriately at 373 K. However for the Ru/TiO₂ catalyst, the chemisorption was carried out at 333 K to avoid the hydrogen spillover effect from Ru to the support because this effect is accentuated at

Table 2

Irreversible H₂ uptake determined by H₂ chemisorption and Ru average particle size by different techniques for the supported Ru catalysts.

Catalyst	H ₂ chemisorption					Size (nm)	
	<i>T</i> /K	Irrev. H ₂ uptake (μmol H ₂ /g _{cat})	Ru exposed (μmol Ru/g _{cat})	<i>D</i> _{Ru} (%)	Size (nm)	TEM	XRD
Ru/Al ₂ O ₃	373	71	141	29	3.2	3.7	— ^a
Ru/SiO ₂	373	≈ 0	n.d.	n.d.	n.d.	8.9	8.3
Ru/TiO ₂	333	62	125	25	3.7	3.8	— ^a
Ru/ZrO ₂	373	148	297	60	1.5	2.7	— ^a

^aNo diffraction peaks of Ru could be clearly identified.

n.d.: not determined.

high temperature. Ru/Al₂O₃ has a Ru dispersion of 29% which corresponded to a mean particle size of 3.2 nm. Ru/ZrO₂ showed a higher dispersion of 60% to give an average particle size of 1.5 nm.

Table 2 also compiled the particle size estimated by XRD, TEM, and H₂ chemisorption. It was possible to estimate the Ru particle size by TEM for all the catalysts. The mean particle size followed the order: Ru/ZrO₂ < Ru/Al₂O₃ ≈ Ru/TiO₂ << Ru/SiO₂. Except Ru/SiO₂ catalyst, the estimated particle sizes of other catalysts by TEM and H₂ chemisorption were within the same size range.

XPS studies were carried out for the supported Ru catalysts to identify the oxidation state of the Ru species present on the catalyst surface and their surface Ru/X atomic ratio. Figure 4 shows the XPS spectra of the Ru 3d region for the Ru/Al₂O₃, Ru/SiO₂, Ru/TiO₂, and Ru/ZrO₂ catalysts. In all of these, there was a component between 279–283 eV corresponding to the Ru 3d_{5/2} core level and a Ru 3d_{3/2} contribution at 4.1 eV higher BE which overlapped with the C 1s region. Due to this overlapping, the C peak was not used as reference and the metal of the catalyst support was used as reference. The Ru/Al₂O₃ catalyst presented two peaks in the Ru 3d_{5/2} region: one centered at 280.6 eV corresponding to the Ru⁰ species and a second contribution at 282.4 eV which was associated with the Ru^{δ+} species in RuO_x [33,36–38]. The intensity of the latter was slightly less. The presence of Ru^{δ+} species on the surface cannot be associated with reoxidation during the transfer to the XPS chamber because after the reduction the catalysts were protected from contact with the ambient atmosphere. As will be seen later, the presence of Ru^{δ+} in this catalyst can be associated with the interaction of Ru species with acid centers of moderate strength present on the surface of the Al₂O₃ support, which was not reduced in the activation process. The Ru/SiO₂ catalyst presented a single peak in the Ru 3d_{5/2} region, which was centered at 280.1 eV and assigned to Ru in the metallic state. For the Ru/TiO₂ catalyst, two less intense contributions were de-

Fig. 4. Ru 3d XPS spectra obtained for the supported Ru catalysts.

Table 3

Ru 3d_{5/2} binding energies and Ru/X atomic ratios derived from XPS data for the supported Ru catalysts.

Catalyst	BE ref (eV)	Ru 3d _{5/2} ^a (eV)	Ru/X ^b
Ru/Al ₂ O ₃	Al 2p (74.5)	280.6 (55), 282.4 (45)	0.15
Ru/SiO ₂	Si 2p (103.4)	280.1	0.01
Ru/TiO ₂	Ti 2p (458.5)	279.7 (70), 281.4 (30)	0.06
Ru/ZrO ₂	Zr 3d (182.1)	280.2	0.05

^a Values in brackets refer to the percentage.

^b X refers to the metallic atom on the support oxide.

tected at 279.7 and 281.4 eV, which were attributed to the Ru⁰ and Ru^{δ+} species, respectively. Ru/ZrO₂ displayed only a peak for Ru 3d_{5/2} at 280.2 eV corresponding to metallic Ru, and the contribution from Ru^{δ+} species was not observed as was also the case with the Ru/SiO₂ catalyst. The peak 277.4 eV could not be unambiguously assigned but it was not due to Ru species because the binding energy was very low.

Table 3 compiles the parameters deduced from the XPS study. Ru/Al₂O₃ clearly presented a high proportion of Ru^{δ+} species (45%) as compared with the Ru/TiO₂ catalyst (30%). For Ru/SiO₂ and Ru/ZrO₂, uniquely metallic Ru species were observed. The Ru/X atomic ratios (where X is the metal used in the support for each catalyst) were also collected in the Table 3. The Ru supported on Al₂O₃ presented the largest atomic ratio (Ru/Al = 0.15). The XPS atomic ratio was smaller for the Ru/TiO₂ and Ru/ZrO₂ catalysts (Ru/Ti = 0.06 and Ru/Zr = 0.05). The Ru/SiO₂ catalyst showed the lowest atomic ratio with a value of Ru/Si = 0.01. Two relevant conclusions regarding the Ru/Al₂O₃ catalyst can be drawn: first, a large fraction of the surface Ru atoms were partially oxidized, and second, the Ru surface concentration was higher than that found for the other catalysts.

To examine further the formation of partially oxidized Ru species on the surface of Ru/Al₂O₃, the surface acidity of the supported Ru catalysts was evaluated by NH₃-TPD. During TPD experiments the reduction of the catalysts by ammonia can be discarded since associated fragments to nitrogen oxide compounds have not been detected. Figure 5 displays the NH₃-TPD profiles of the supported Ru catalysts. The profile of the Al₂O₃ support is also displayed as a reference. It was clearly observed

Fig. 5. NH₃-TPD profiles of the supported Ru catalysts.

that the NH_3 desorption from the Al_2O_3 support gave the peaks at 560 and 607 K, which have been suppressed with the supported Ru catalyst. This suppression indicated that the strongest acid sites of the Al_2O_3 surface have disappeared. This behavior has been previously reported [35,39] and it was attributed to the strong interaction between the Ru particles and the acid centers with the strongest acidity of the Al_2O_3 support. This interaction generated the partially oxidized Ru species on the surface seen in the XPS analysis. For the Ru/ TiO_2 and Ru/ ZrO_2 catalysts, this phenomenon could also occur, but to a lesser extent.

The quantification of the weak acidity (400–550 K range) for the supported Ru catalysts showed that the number of acid sites was the highest for Ru/ Al_2O_3 (38 $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$), while the Ru/ SiO_2 catalyst showed a flat desorption profile, that is, its surface acidity was practically negligible. The Ru/ TiO_2 and Ru/ ZrO_2 catalysts presented desorption peaks with medium intensity at temperatures in the range of 400–550 K, representing the desorption of 19 and 7 $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$, respectively.

3.3. Role of surface species on the catalytic performance

The use of different supports changed the physicochemical properties of the Ru particles and allowed more Ru to be exposed to facilitate the interaction with adsorbed sorbitol. For the dispersion of Ru, it must be kept in mind that with H_2 chemisorption, only Ru in the metallic state can be titrated. A fraction of the Ru was partially oxidized ($\text{Ru}^{\delta+}$) that was present on the surface of Ru/ TiO_2 and especially the Ru/ Al_2O_3 catalyst. Thus the dispersion of Ru was underestimated for Ru/ TiO_2 and Ru/ Al_2O_3 . With taking this into account, it can be concluded that the Ru/ ZrO_2 catalyst has the highest metal dispersion and consequently the smallest particle size, closely followed by the Ru/ Al_2O_3 and Ru/ TiO_2 catalysts. If one assumes that sorbitol hydrogenolysis to produce glycerol, 1,2-PG and EG needs C-C and C-O scission sites [14,19,20,22,23], metallic sites are required and a larger amount of exposed Ru atoms is beneficial. However, according to the values obtained for the different catalysts in this work, there was no clear correlation between sorbitol conversion and the particle size of Ru, at least, in the range of particle size smaller than 9 nm.

Concerning the oxidation state of Ru on the surface, the Ru/ ZrO_2 and Ru/ SiO_2 catalysts only presented Ru in the metallic state while some $\text{Ru}^{\delta+}$ was detected in Ru/ Al_2O_3 and Ru/ TiO_2 . The presence of $\text{Ru}^{\delta+}$ was due to the interaction of small Ru particles with acid sites. Although both the Ru/ Al_2O_3 and Ru/ TiO_2 catalysts have $\text{Ru}^{\delta+}$ species on the surface, however, there were significant differences between the two catalysts, which may explain their different catalytic behavior. The binding energy of the $\text{Ru}^{\delta+}$ species on the surface of the Ru/ TiO_2 catalyst was 1 eV lower than for Ru/ Al_2O_3 , suggesting that the interaction of Ru particles with Al_2O_3 was stronger resulting in more transfer of charge from the Ru particles to the support and consequently a higher oxidation state for the Ru atoms. Besides the Ru/ TiO_2 catalyst has a lower proportion of $\text{Ru}^{\delta+}$ on the surface compared to the Ru/ Al_2O_3 sample: the XPS Ru/ TiO_2 ratio was smaller than the XPS Ru/ Al_2O_3 ratio and the

XPS spectrum was much less intense (spectrum was multiplied by 2, see Fig. 4). In summary the surface concentration of $\text{Ru}^{\delta+}$ on the Ru/ Al_2O_3 catalyst was larger than on the Ru/ TiO_2 sample, and therefore so was the effect of $\text{Ru}^{\delta+}$.

Another significant difference between the Ru/ Al_2O_3 and the other catalysts was the concentration of acid sites measured by NH_3 -TPD, being 38 $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$ for Ru/ Al_2O_3 while the Ru/ TiO_2 catalyst has 19 $\mu\text{mol NH}_3/\text{g}_{\text{cat}}$ and these were well above those of Ru/ ZrO_2 and Ru/ SiO_2 catalysts. Therefore, it would seem that the surface concentration of acid sites was also relevant for glycerol dehydration to produce glycols (1,2-PG and EG).

In summary, an explanation for the higher selectivity and yield to glycols with the Ru/ Al_2O_3 catalyst may be that the Al_2O_3 promoted the dehydrogenation rate of sorbitol due to the presence of acid sites as was recently proposed for Ni/ Al_2O_3 catalysts [17]. Once the retro-aldol condensation step occurred, the higher acidity of the Ru/ Al_2O_3 catalyst allowed glycerol dehydration and subsequent hydrogenation to give glycols selectively. More study is needed to understand the specific role of the presence of $\text{Ru}^{\delta+}$ on the dehydrogenation rate of sorbitol and the acidic surface in the reaction mechanism and its relevance to the yield and selectivity to glycols.

4. Conclusions

The support has an effect on the physicochemical properties of supported Ru catalysts and their catalytic activity. The Ru/ Al_2O_3 catalyst prepared by impregnation showed the highest selectivity and yield to glycols. Under the reaction conditions used (493 K, 4 MPa of H_2 and without basic promoter), the surface concentration of both acid sites and partially oxidized Ru species were relevant properties that gave a high selectivity to glycols. The Ru dispersion was less important for determining the catalytic performance.

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References

- [1] Wettstein S G, Alonso D M, Gürbüz E I, Dumesic J A. *Curr Opin Chem Eng*, 2012, 1: 218
- [2] Adsul M G, Singhvi M S, Gaikawai S A, Gokhale D V. *Bioresour Technol*, 2011, 102: 4304
- [3] Zhu J Y, Zhuang X S. *Prog Energ Combust*, 2012, 38: 583
- [4] Dautzenberg G, Gerhardt M, Kamm B. *Holzforchung*, 2011, 65: 439
- [5] Wang A, Zhang T. *Accounts Chem Res*, 2013, 46: 1377
- [6] Ji N, Zhang T, Zheng M, Wang A, Wang H, Wang X, Chen J G. *Angew Chem Int Ed*, 2008, 47: 8510
- [7] Baek I G, You S J, Park E D. *Bioresour Technol*, 2012, 114: 684
- [8] Liu M, Wang H, Han J, Niu Y. *Carbohydr Polym*, 2012, 89: 607
- [9] Han J W, Lee H. *Catal Commun*, 2012, 19: 115

Graphical Abstract

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Sorbitol hydrogenolysis to glycols by supported ruthenium catalysts

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A Ru/Al₂O₃ catalyst prepared by impregnation showed the highest selectivity and yield to glycols because it has the most acid sites and partially oxidized Ru species.

- [10] Fukuoka A, Dhepe P L. *Angew Chem Int Ed*, 2006, 45: 5161
- [11] Ji N, Zhang T, Zheng M, Wang A, Wang H, Wang X, Shu Y, Stottelmyer A L, Chen J G. *Catal Today*, 2009, 147: 77
- [12] Bozell J J, Petersen G R. *Green Chem*, 2010, 12: 539
- [13] Sun J, Liu H. *Green Chem*, 2011, 13: 135
- [14] Banu M, Venuvanalingam P, Shanmugam R, Viswanathan B, Sivasanker S. *Top Catal*, 2012, 55: 897
- [15] Li N, Huber G W. *J Catal*, 2010, 270: 48
- [16] Chen X, Wang X, Yao S, Mu X. *Catal Commun*, 2013, 39: 86
- [17] Liang G, He L, Cheng H, Li W, Li X, Zhang C, Yu Y, Zhao F. *J Catal*, 2014, 309: 468
- [18] Deutsch K L, Lahr D G, Shanks B H. *Green Chem*, 2012, 14: 1635
- [19] Sohounloue D K, Montassier C, Barbier J. *React Kinet Catal Lett*, 1983, 22: 391
- [20] Zhao L, Zhou J, Chen H, Zhang M, Sui Z, Zhou X. *Korean J Chem Eng*, 2010, 27: 1412
- [21] Zhou J H, Zhang M G, Zhao L, Li P, Zhou X G, Yuan W K. *Catal Today*, 2009, 147: S225
- [22] Zhao L, Zhou J H, Sui Z J, Zhou X G. *Chem Eng Sci*, 2010, 65: 30
- [23] Banu M, Sivasanker S, Sankaranarayanan T M, Venuvanalingam P. *Catal Commun*, 2011, 12: 673
- [24] Ye L, Duan X, Lin H, Yuan Y. *Catal Today*, 2012, 183: 65
- [25] Soták T, Schmidt T, Hronec M. *Appl Catal A*, 2013, 459: 26
- [26] Lin H Y, Chen Y W. *Thermochim Acta*, 2004, 419: 283
- [27] Shen X, Garces L J, Ding Y, Laubernds K, Zerger R P, Aindow M, Neth E J, Suib S L. *Appl Catal A*, 2008, 335: 187
- [28] Okal J, Zawadzki M, Kepinski L, Krajczyk L, Tylus W. *Appl Catal A*, 2007, 319: 202
- [29] Wagner C D, Davis L E, Zeller M V, Taylor J A, Raymond R H, Gale L H. *Surf Interface Anal*, 1981, 3: 211
- [30] Yamaguchi A, Hiyoshi N, Sato O, Shirai M. *Green Chem*, 2011, 13: 873
- [31] Vilcocq L, Cabiac A, Especel C, Lacombe S, Duprez D. *Catal Today*, 2012, 189: 117
- [32] Xia J, Yu D, Hu Y, Zou B, Sun P, Li H, Huang H. *Catal Commun*, 2011, 12: 544
- [33] Mazzieri V, Coloma-Pascual F, Arcoya A, L'Argentièrre P C, Fígoli N S. *Appl Surf Sci*, 2003, 210: 222
- [34] Choque V, de la Piscina P R, Molyneux D, Homs N. *Catal Today*, 2010, 149: 248
- [35] Vasiliadou E S, Heracleous E, Vasalos I A, Lemonidou A A. *Appl Catal B*, 2009, 92: 90
- [36] Cattania M G, Parmigiani F, Ragaini V. *Surf Sci*, 1989, 211-212: 1097
- [37] Chan H Y H, Takoudis C G, Weaver M J. *J Catal*, 1997, 172: 336
- [38] Hengne A M, Biradar N S, Rode C V. *Catal Lett*, 2012, 142: 779
- [39] Liao X, Li K, Xiang X, Wang S G, She X, Zhu Y, Li Y. *J Ind Eng Chem*, 2012, 18: 818