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Parameters Affecting the Formation of 1,2-Propanediol from Glycerol over Ru/SiO_2 Catalyst

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ABSTRACT: The production of 1,2-propanediol from renewable glycerol in hydrogen atmosphere is of high interest. In this study the reaction was performed in the presence of 5 wt %Ru/SiO_2 catalyst and the effects of reaction temperature, hydrogen pressure and glycerol concentration were investigated. The catalytic results indicate that increased temperature and pressure favor glycerol conversion and propylene glycol selectivity. Glycerol conversion remains almost constant with water dilution, but 1,2-propanediol selectivity increases due to the function of water as a solvent and the suppression of side reactions, such as degradation and polymerization. At the optimum reaction conditions ($T = 240$ °C, $P = 8$ MPa H_2, pure glycerol feedstock, catalyst/glycerol ratio = 0.006, reaction time = 5 h) glycerol conversion reaches the value of 21.7% along with 60.5% 1,2-propanediol selectivity. The activity of the catalyst does not change in two consecutive runs, while propylene glycol selectivity slightly decreases due to the formation of overhydrogenolysis products (propanols). The reaction pathways over Ru/SiO_2 catalyst were explored using intermediate and final products as reactants. The production of 1,2-propanediol is favorable as it is formed with high selectivity from acetol and its overhydrogenolysis to propanols is very limited. The results suggest that ethylene glycol is a primary product originating from the direct degradation of glycerol.

INTRODUCTION

Biodiesel is considered as a potential environmentally friendly substitute of petroleum diesel fuel. The global biodiesel market is estimated to reach 180 million tonnes by 2016, growing at an average annual rate of 42%.[1] For every 9 kg of biodiesel produced, about 1 kg of crude glycerol byproduct is also formed.[2] This overproduction of crude glycerol resulted in a decrease of its price and it seems to be impossible for the current market to absorb this surplus. It is of high interest that this crude glycerol can serve as a renewable feedstock for the chemical industry, replacing fossil-derived products. In addition, glycerol has been identified by the U.S. Department of Energy as one of the top 12 building-block chemicals that can be derived from biobased feedstocks and converted to high-value biobased chemicals or materials.[3]

Among the various processes of converting glycerol to marketable chemicals, glycerol hydrogenolysis to propanediols has attracted significant interest. The hydrogenolysis of glycerol to 1,2- and 1,3-propanediol is an attractive innovative pathway for the production of renewable value-added products. 1,2-Propanediol (propylene glycol) is a major commodity chemical with a 4% annual market growth. Typical uses of 1,2-propanediol are in unsaturated polyester resins, functional fluids, pharmaceuticals/cosmetics, paints, etc. Propylene glycol is currently produced from petroleum derivatives such as propylene oxide by chemical catalytic routes.[4,5]

Glycerol hydrogenolysis usually takes place under elevated hydrogen pressures and mild temperatures in the presence of suitable catalytic materials. Initial H_2 pressures of 0.5−10 MPa and temperatures of 120−240 °C have been reported in open literature[6−20] and patents.[21−23] The hydrogenolysis reaction is suggested to proceed via dehydration of glycerol to hydroxyacetone (acetol) and 3-hydroxypropanal by acid catalysis and subsequent hydrogenation to the glycols by metal catalysts.[6,18] Another mechanism proposed[24] for this reaction involves dehydrogenation of glycerol to glyceraldehyde followed by dehydration to 2-hydroxyacrolein and hydrogenation to 1,2-propanediol with a Ru/C catalyst under neutral/slightly basic aqueous polyol solutions.

Several researchers have focused on the use of Ru metal catalysts on supports such as carbon,[12−15,18] TiO_2[11,19] and acidic heteropoly salts.[8] For example, with the use of Ru-based on C as a hydrogenation catalyst along with an Amberlyst resin as a solid acid catalyst, the performance was rather poor with 55% selectivity to 1,2-propanediol at 13% glycerol conversion.[18] The promoting effect of Re metal addition to Ru[25−27] and Rh[28] was investigated by various groups in order to improve the activity and propylene glycol selectivity. Suppes's group[6] performed the glycerol hydrogenolysis reaction with various commercial catalysts and found copper−chromite to be the most effective catalyst with 54.8% glycerol conversion and 85% propylene glycol selectivity. In addition, catalysts prepared using a template preparation method to increase the surface area[29] and Cu−ZnO catalysts[7,30] have been used for selective production of 1,2-propanediol.

In our previous study[20] the hydrogenolysis of glycerol was investigated on supported Ru catalysts focusing on the effect of

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the supporting material (γ-Al_2O_3, SiO_2, ZrO_2) and the type of ruthenium precursors (chloride, nitrate). We found that the total acidity of the catalytic material (induced either by the support and/or by the metal precursor) strongly affected glycerol activity and product selectivity.

Several research groups have examined the effect of the operating conditions on glycerol hydrogenolysis reaction. For example the effect of reaction temperature[6,18,25,31,32] was examined in the presence of various catalysts such as commercial Cu−Cr, Ru/C + Amberlyst resin, Ru/C, Ru/γ-Al_2O_3 + $Re_2(CO)_{10}$ and Co/MgO. However, there is a lack of a detailed description of the overall reaction performance in terms of the byproduct formation with respect to reaction temperature. In addition, the influence of hydrogen pressure was studied by different research groups[1,6,18,25,31,32] varying hydrogen pressure from 0 to 10 MPa. Glycerol concentration effect was also examined in order to explore the role of water addition in the reaction mixture.[6,8,31,32] Typically, 10−20 wt % or 80 wt %[6] glycerol aqueous solutions were used in literature reports.

We present here the results of the systematic parametric study of glycerol hydrogenolysis operating conditions on the performance of 5 wt % Ru/SiO_2 catalyst which has been proved to be the most selective to 1,2-propanediol according to our recent work.[20] As the first reaction step is dehydration, this catalyst presents the optimum acidity in order to achieve satisfactory conversion and 1,2-propanediol selectivity. The effect of reaction temperature, hydrogen pressure, and glycerol concentration were investigated. An attempt to gain insight into the hydrogenolysis reaction pathways was performed using intermediate and final products as reactants.

EXPERIMENTAL SECTION

Materials. Ultrahigh purity gases were used in the hydrogenolysis tests: hydrogen (Air-Liquide, 99.999%) and nitrogen (Air-Liquide, 99.995%). SiO_2 (Saint-Gobain, Norpro) and $RuNO(NO_3)_3$(Alfa-Aesar, Ru content 31.3%) were employed in the catalyst preparation. Glycerol (Panreac 99.5%), 1,2-propylene glycol (Riedel-de Haen, 99.5%), 1,3-propylene glycol (Riedel-de Haen, 98%), ethylene glycol (Baker, 99.8%), hydroxyacetone (Alfa-Aesar, 95%), and acetonitrile (Merck, 99.9%) were used for the experiments.

Methods. Supported 5 wt % Ru catalyst was prepared using the wet impregnation method. Silica (particle size 45−106 μm, S_{BET} = 106 $m^2 \cdot g^{-1}$) was used as the supporting material, and $RuNO(NO_3)_3$, as the metal precursor. The details of the preparation procedure are reported in our previous work.[20]

Surface areas of the fresh and used samples were determined by N_2 adsorption at 77 K, using the multipoint BET analysis method, with an Autosorb-1 Quantachrome flow apparatus. Prior to the measurements, the samples were dehydrated in vacuum at 250 °C overnight.

X-ray diffraction (XRD) patterns were obtained by employing a Siemens D500 diffractometer, with Cu Kα radiation. The Scherrer equation was used to calculate the crystal size of metal particles from the X-ray patterns.

Details of the programmed temperature reduction with H_2 and NH_3 desorption procedures are elsewhere provided.[20]

Activity Test. Glycerol hydrogenolysis was carried out in a 450-mL stainless-steel batch reactor (Parr Instruments) equipped with an electronic temperature controller, a mechanical stirrer, and a tube for the sampling of the liquid phase. Reaction conditions varied were initial hydrogen pressure (2−8 MPa) and temperature (180−240 °C). The above tests were conducted with 120 mL of pure glycerol (100% concentration) and catalyst weight of 0.9 g. The effect of the initial glycerol concentration (100% to 20%) was also explored. The catalyst collected after the reaction was used one more time in order to test its reusability. Experiments with 1,2-propanediol, 1,3-propanediol, ethylene glycol, and hydroxyacetone (acetol) as reactants were performed under similar experimental conditions. It is important to notice that the Ru/SiO_2 catalyst was not reduced prior to the reaction. The temperature used ($180 < T < 240$ °C) and hydrogen environment were sufficient to convert the oxidic form of ruthenium to the metallic form, which is considered as the active phase. The main advantage of Ru-based catalysts compared with Cu-based catalysts is that the prereduction step can be avoided. This is a very important issue because the need of catalyst prereduction burdens the whole hydrogenolysis process with an additional cost.

The reaction sequence was as follows: loading of the reactor with glycerol substrate and the appropriate amount of catalyst, N_2 flushing for 10 min at 0.2 MPa, H_2 flushing for 5 min at 0.5 MPa, and increase of temperature and H_2 pressure to the desired conditions under constant stirring. The reaction was allowed to run for 5 h under the above-mentioned conditions, during which time liquid samples were periodically removed. After each sampling, the reactor was backfilled with hydrogen to retain the constant pressure. At the end of the reaction, the system was allowed to cool down to room temperature, and the gas products were collected in a gas bag.

Liquid samples were analyzed by GC (Agilent 7890A) equipped with DB-Wax (30 m × 0.53 mm × 1.0 μm) column and a flame ionization detector. Acetonitrile was used as a solvent for the GC analysis. The multiple point internal standard method was used for the quantification of the conversion and selectivity determination. Gas analysis was performed in Varian 3700 GC equipped with two columns, Porapak Q and Molecular Sieve-5A in series bypass configuration and a thermal conductivity detector. The liquid products identified were: 1,2-propanediol, ethylene glycol, hydroxyacetone (acetol), 1-propanol, 2-propanol, methanol, and ethanol. Small amounts of oligomerization products were also detected. The gaseous products were mainly methane, carbon dioxide, carbon monoxide, and ethane. The glycerol conversion and the liquid product selectivity were calculated by using equations presented elsewhere,[20] unless otherwise stated. The carbon balance closure was 95 ± 5%.

RESULTS AND DISCUSSION

Catalyst Characterization. The main physicochemical characteristics of the Ru/SiO_2-supported catalyst are summarized in Table 1. The specific surface area of the fresh catalyst and used samples reveals only a slight change. The crystalline phases in the fresh and used catalysts were investigated by X-ray diffraction (Figure 1). XRD analysis clearly shows the formation of crystalline ruthenium oxide (RuO_2) on the as-synthesized calcined material. The diffractogram of the first-time used sample shows peaks characteristic of metallic Ru, indicating that, during reaction, ruthenium from the oxidic form is reduced to metallic Ru as expected, since the reaction proceeds under reducing conditions.

The XRD findings qualitatively agree with the reduction characteristics of the Ru/SiO_2 catalyst as determined by H_2-TPR (Table 1). One main reduction peak centered at 187 °C was

Table 1. Physicochemical characterization of 5 wt % Ru/SiO_2 catalyst

BET surface area ($m^2 \cdot g^{-1}$)				
fresh	1st time used	2nd time used	T_{max} of reduction (°C)	total acidity (μmol $NH_3 \cdot g^{-1}$)
98.3	99.9	109.2	187	13

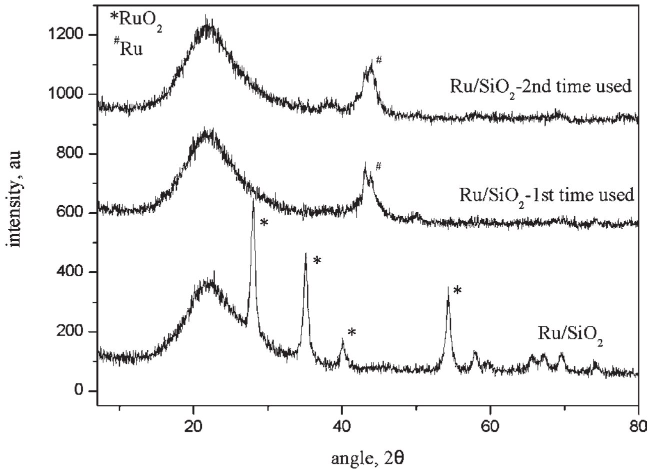


Figure 1. XRD patterns of 5 wt % Ru/SiO_2 as fresh and used catalysts.

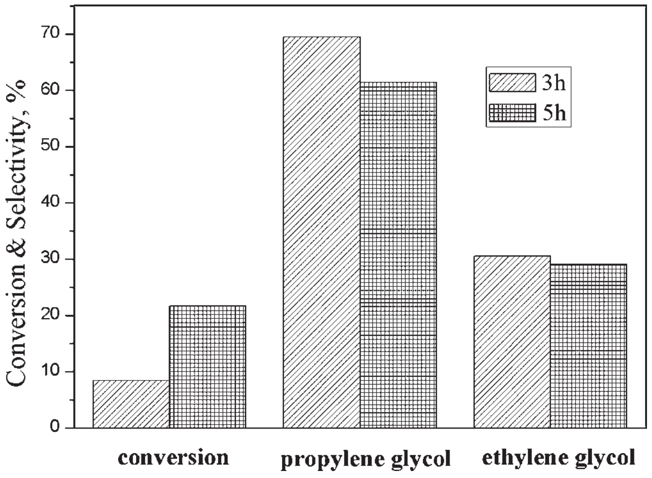


Figure 2. Activtity and product distribution at 3 and 5 h of the reaction period. Catalyst: 5 wt % Ru/SiO_2, P = 8 MPa, catalyst/glycerol = 0.006 (wt), 5 h, pure glycerol.

assigned to the reduction of RuO_2 to metallic Ru.[20] As a consequence, the conditions used in the reactor, reaction temperature >180 °C and hydrogen atmosphere, can be considered sufficient for the reduction of the oxidic phase to the metallic active phase, rendering prereduction not necessary. Total acidity of the catalyst was determined by NH_3-TPD. As expected, the acidity of the catalyst is relatively low (13 μmol $NH_3 \cdot g^{-1}$). The profile of the desorbed ammonia consisted of a broad peak located in the temperature range 150−300 °C and a high temperature shoulder up to 500 °C indicating the presence of weak/medium acid sites.[20]

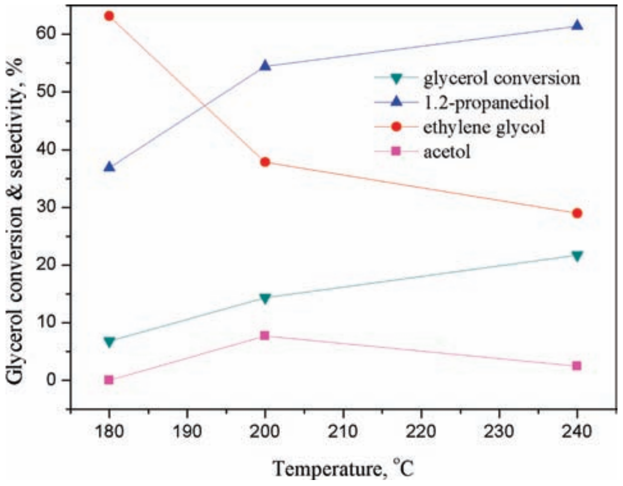


Figure 3. Effect of temperature on glycerol conversion and product selectivity, catalyst: 5 wt % Ru/SiO_2, P = 8 MPa, catalyst/glycerol = 0.006 (wt), 5 h, pure glycerol.

Catalytic Results. *Activity and Product Distribution.* In glycerol hydrogenolysis tests, the reaction time commonly used exceeds 10−12 h.[6,8,17,18] In most of the cases, only the final results are analyzed. In this work, glycerol conversion and main product selectivities at a temperature of 240 °C were examined at 3 and 5 h reaction periods, and the results are presented in Figure 2 After 3 h testing, glycerol conversion is around 15% and further increases with time reaching the value of 22% after 5 h testing. The distribution of reaction products is quite interesting. The major reaction product is propylene glycol with its selectivity reaching maximum value of 69 at 15% glycerol conversion obtained at 3 h. Apart from propylene glycol, ethylene glycol is also formed in considerable amounts (selectivity at ∼30%). Final selectivity after 5 h testing for propylene glycol is moderately lower (∼61%). Worthy to notice is that ethylene glycol selectivity does not practically change with time on stream. These results imply that most probably glycerol and/or propylene glycol undergo sequential reactions leading to the formation of heavier products. Indeed, heavier than glycerol products with selectivity 5.8% (probably oligomerization products) were detected during the last half of the experiment. The extent of excessive hydrogenolysis of propylene glycol to propanols was negligible over the present Ru/SiO_2 catalyst. Methanol, with 1.3% selectivity was also observed after 5 h testing.

Effect of Reaction Temperature. Reaction temperature significantly affects the conversion of glycerol/propylene glycol selectivity, but also byproduct and intermediate product formation. In general, temperature increment favors the activity and propylene glycol selectivity.[6] In the present study the influence of temperature on the conversion and selectivity was explored over a range of 180−240 °C keeping constant at 8 MPa the hydrogen pressure. The results of glycerol conversion and propylene glycol, ethylene glycol, and acetol selectivity after 5 h reaction time are presented in Figure 3. As expected, glycerol conversion increases with temperature. The temperature rise favors propylene glycol selectivity, as its selectivity from the value of 35% at 180 °C almost doubles (∼61%) at 240 °C. In contrast, ethylene glycol selectivity decreases from 63% at 180 °C to 30% at 240 °C. It is known from the literature[33] that higher temperature favors C−O bond cleavage compared to C−C bond scission (C−C:

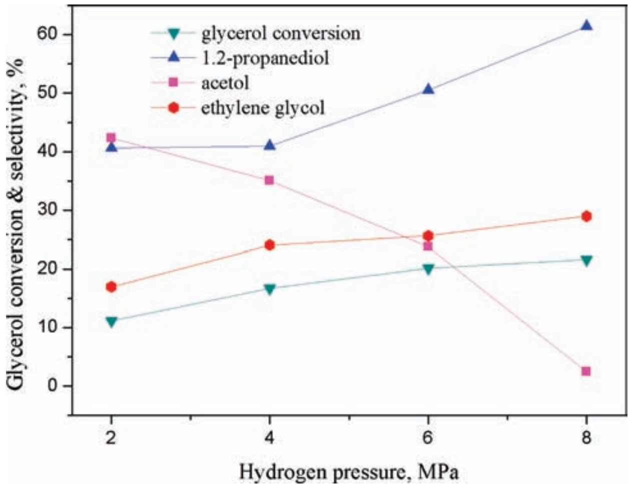


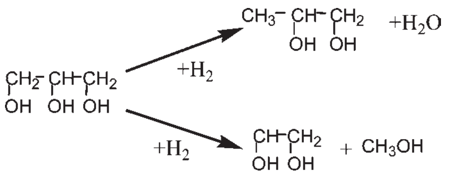
Figure 4. Effect of hydrogen pressure on glycerol conversion and product selectivity, catalyst: 5 wt % Ru/SiO_2, T = 240 °C, catalyst/glycerol = 0.006 (wt), 5 h, pure glycerol.

$\Delta H^{f,298}$ = 347 kJ/mol, C−O: $\Delta H^{f,298}$ = 358 kJ/mol). As propylene glycol is formed via C−O bond cleavage reaction while ethylene glycol is formed via C−C cleavage, temperature increment will favor propylene glycol production over ethylene glycol formation. However, final selectivity of the main products is affected not only by their formation rates but also by sequential reactions rates as well. Experiments with propylene glycol and ethylene glycol as initial reactants at 240 °C (will be further analyzed in section Mechanistic Implications of Glycerol Conversion Routes over Ru/SiO_2) showed that propylene glycol is a more stable product compared with ethylene glycol, as the rate of consumption of the latter is higher, leading to the formation mainly of gas products.

Acetol, which is considered as the intermediate of glycerol hydrogenolysis to propylene glycol is always detected in the product mixture. Its selectivity value reaches a maximum 7.8% at 200 °C with a further decrease to 2.5% at 240 °C. Further temperature increment (>240 °C) results in a decrease of propylene glycol selectivity due to the promotion of excessive hydrogenolysis to propanols and/or lower alcohols.[6,31]

Effect of Hydrogen Pressure. In the case of the liquid-phase process, the glycerol hydrogenolysis reaction typically takes place under elevated pressures usually from 3 to 10 MPa. Hydrogen leads to an increase in glycerol conversion and propylene glycol selectivity, but it also favors the formation of degradation products. The effect of hydrogen pressure was studied in the range from 2 to 8 MPa at constant temperature 240 °C. The results are illustrated in Figure 4. The increase of hydrogen pressure positively affects both glycerol conversion and propylene glycol selectivity. The more pronounced effect of hydrogen pressure is on acetol selectivity. At the lowest hydrogen pressure, 2 MPa, about 10% of glycerol is converted to a mixture of 1,2-propanediol, ethylene glycol, and acetol. Under these conditions acetol is the main reaction product with a selectivity value of 42%. Hydrogen pressure seems to be insufficient for the hydrogenation of this intermediate to the desired 1,2-propanediol. The acetol selectivity declines rapidly from 42 to 2.5% with the increase of hydrogen pressure from 2 to 8 MPa. The decrease in acetol selectivity is associated with the increase in propylene glycol. The main degradation byproduct, ethylene glycol, also increases with pressure rise, but to a lesser extent compared with propylene glycol. The influence of hydrogen pressure on the glycerol hydrogenolysis reaction supports the simplified Scheme 1, according to which the presence of hydrogen positively affects the kinetics of both the hydrogenolysis and degradation reactions. The positive effect of hydrogen pressure on glycerol conversion can be additionally associated with the surface state of ruthenium, which is in situ reduced from RuO_2 to metallic Ru, thus affecting the available metal active sites.

Scheme 1. Glycerol hydrogenolysis to 1,2-propanediol and ethylene glycol



Effect of Glycerol Concentration. The production of 1,2-propanediol from glycerol hydrogenolysis is proposed to occur via dehydration/hydrogenation reactions,[6,18] and although water is generated during the reaction, the majority of previous literature works[8,16−18,31,32] used very dilute aqueous glycerol solutions. The influence of water in glycerol hydrogenolysis is very important from a techno-economical point of view because the presence of water results in an increase of both capital and operation costs. In addition, water has been reported[34] to be responsible for Cu/C catalyst deactivation. The influence of water content on the glycerol hydrogenolysis reaction was studied using pure glycerol (100 wt %) and 50 and 20 wt % aqueous glycerol solutions under the standard conditions of 240 °C and 8 MPa hydrogen pressure. The amount of the catalyst used in each test was adapted so as to keep constant the catalys-to-glycerol weight ratio at 0.006. Glycerol conversion shows slight variations with dilution, implying that water acts only as a solvent (Table 2). This result was expected as the experiments were performed using constant weight ratio catalyst/substrate. Wawrzetz et al.[35] studied the reactions of glycerol in water over a bifunctional Pt/γ-Al_2O_3 catalyst using 20 wt % aqueous glycerol solution at 225 °C and 29 bar total N_2 pressure. Their results showed the formation of H_2 and CO_2 as the main gaseous products due to the glycerol reforming reaction. In our case, the addition of water does not favor glycerol reforming along with the hydrogenolysis reaction, as the experiments were conducted under hydrogen atmosphere and the presence of hydrogen shifts the equilibrium of the reforming reaction to the opposite direction.

Product distribution is strongly affected by the glycerol concentration. In the highly diluted glycerol solution, selectivity of 1,2-propanediol is 90.2% in contrast to the undiluted glycerol where the selectivity is 60.5%. The presence of water is unlikely to influence the first proposed dehydration step as this step is not equilibrium limited. Water seems to retard the C−C bond-cleavage reactions as the selectivity to ethylene glycol drastically reduces with the increase of its content. In addition, water disfavors the oligomerization reactions (leading to the undesired C_{4+}, products heavier than glycerol), which vanish in the tests with diluted glycerol. It is worth mentioning that, with the use of aqueous solutions of glycerol, 1,3-propanediol is also formed in very small amounts (selectivity less than 2%).

Table 2. Effect of water content on glycerol hydrogenolysis over 5 wt % Ru/SiO_2[a]

		selectivity, %		
reactant	conversion, %	1,2-propanediol	ethylene glycol	C_{4+}
pure glycerol	21.7	60.5	28.7	5.8
50 wt % H_2O + 50 wt % glycerol	23	71.2	19.5	–
80 wt % H_2O + 20 wt % glycerol	18	90.2	9.7	–

[a] T = 240 °C, P = 8 MPa, 5h, catalyst/glycerol = 0.006 (wt).

Table 3. Reuse of Ru/SiO_2 catalyst in glycerol hydrogenolysis[a]

		selectivity, %		
catalyst	conversion, %	1.2-propanediol	ethylene glycol	propanols
Ru/SiO_2-1st time used	21.7	60.5	28.7	–
Ru/SiO_2-2nd time used	20.6	50.9	26.6	7

[a] T = 240 °C, P = 8 MPa, 5 h, pure glycerol.

Table 4. Intermediate and final product reactions in the presence of hydrogen[a]

	reactants			
products	1,2-propanediol	1,3-propanediol	ethylene glycol	hydroxyacetone
	Conversion, %			
	18.0	18.0	29.0	100.0
	Selectivity, %			
1,2-propanediol	–	–	–	78.3
1,3-propanediol	–	–	–	–
hydroxyacetone	9.3	–	–	–
ethylene glycol	–	–	–	–
1-propanol	–	39.4	–	–
2-propanol	–	–	–	–
methanol	–	2.0	3.9	–
ethanol	–	12.7	9.8	–
CO	–	–	36.2	–
CO_2	0.2	0.1	0.3	1.8
CH_4	83.9	24.5	46.0	17.3
C_2H_6	6.6	21.3	3.9	2.6

[a] P = 8 MPa, T = 240 °C, catalyst/substrate = 0.006 (wt), 5 h test, pure components.

Despite that propylene glycol selectivity is favored by the presence of water, the use of diluted solutions is considered as a drawback[6] for the commercialization of this process. The addition of water burdens the process as the final product will need an extra separation step and the reactor volume will increase in order to keep the same productivity levels as for pure glycerol.

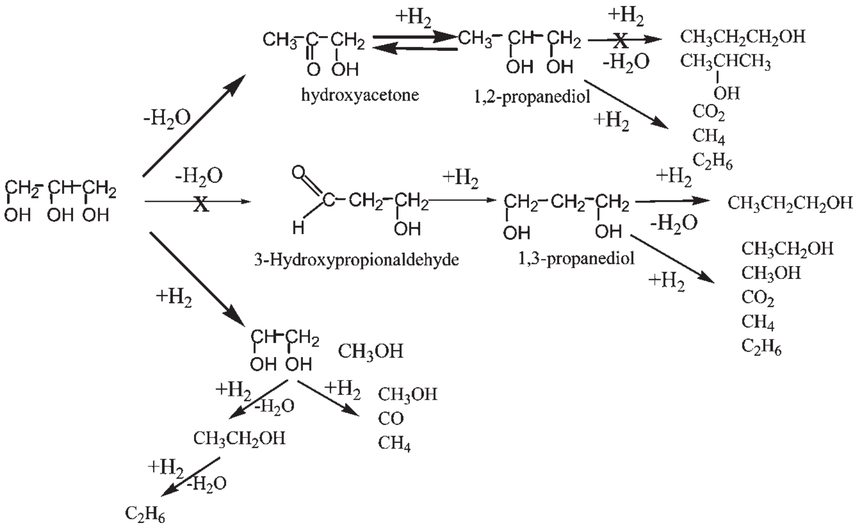
In summary, the parametric study showed that temperature (240 °C) and increased hydrogen pressure (8 MPa) positively affect glycerol conversion and 1,2-propanediol selectivity. In addition, Ru/SiO_2 catalyst proved to be highly active given that the tests were conducted with undiluted glycerol and very low catalyst/glycerol ratio at relatively short reaction time. The productivity to the desired product, 1,2-propanediol over Ru/SiO_2 catalyst is $0.74\ mol_{1,2\text{-propanediol}}\cdot g_{Ru}^{-1}\cdot h^{-1}$. Even though direct comparison with literature is not possible due to limited availability of data under the same conditions, it is noteworthy to report that with a conventional Ru/C catalyst plus tungsten phosphoric acid on ZrO_2 at 180 °C and 6 MPa, the productivity is $0.21\ mol_{1,2\text{-propanediol}}\cdot g_{Ru}^{-1}\cdot h^{-1}$.[31] Further comparison with CuO/ZnO catalyst, one of the most promising and extensively studied catalyst in glycerol hydrogenolysis, is also in favor to the Ru/SiO_2 catalyst as the productivity of the former does not surpass $1.2\ mol_{1,2\text{-propanediol}}\cdot g_{Cu}^{-1}\cdot h^{-1}$ at 200 °C and 5 MPa H_2.[30] The above support the conclusion that the present Ru/SiO_2 catalyst is highly active in the glycerol hydrogenolysis reaction with good selectivity to propylene glycol.

Reuse of Catalytic Material. A first indication about the stability of Ru/SiO_2 catalyst was obtained after testing of the same catalyst sample in two sequential runs. The catalyst was recovered by filtration and drying at 120 °C for 17 h and then reused without any other pretreatment. Table 3 shows the results of the catalytic experiments for the first-time and second-time used Ru/SiO_2 catalyst. Glycerol conversion remains practically constant in the two experiments with the used catalytic material, indicating that Ru/SiO_2 catalyst is rather stable in terms of activity. The main physicochemical characteristics, BET surface area and crystal phases, did not change as evidenced from the measurements of the first- and second-time used samples (see Table 1 and Figure 1). Ruthenium remained in its metallic form finely dispersed on silica with crystallite sizes around 5 nm (first-time used 5.2 nm, second-time used 4.9 nm), implying that silica stabilizes ruthenium crystallites, preventing sintering and consequent decline of activity. Another indication about the stability of Ru on silica was provided by the absence of any metal leaching as checked by visual observation of the color of the reaction liquids which remained transparent or light yellow (depending on the concentration of the intermediate acetol in the solution) and testing with ICP which did not show any measurable concentration of the metal in the liquid.

However, the selectivity of 1,2-propanediol decreases by 11% in the two consecutive runs (Table 3). The reason for the loss of selectivity is the increase to the extent of the propylene glycol sequential hydrogenolysis to propanols. Indeed, propanols (1- and 2-) with a 7% selectivity were observed. The reason that 1,2-propanediol selectivity decreases with the second round of catalyst testing still remains unclear to us and is the subject of further study. Miyazawa et al.[17] also observed higher selectivities to propanols with reused Ru/C + A70 (Amberlyst resin) catalysts.

Mechanistic Implications of Glycerol Conversion Routes over Ru/SiO_2. In order to understand the reaction sequence and product distribution, tests of the products (1,2-propanediol, 1,3-propanediol, ethylene glycol) and the proposed[6,18] intermediate hydroxyacetone (acetol), were conducted over Ru/SiO_2, employing conditions similar to that of glycerol. Table 4, presents the conversion and the product selectivities (based on total products, gases, and liquids). The reactivity order of the tested

Scheme 2. Reaction pathways of glycerol hydrogenolysis and degradation over Ru/SiO_2 catalyst



products and the intermediate is as follows: acetol > ethylene glycol > 1,3-propanediol = 1,2-propanediol.

Pure 1,2-propanediol (propylene glycol) is a rather stable component exhibiting low reactivity over Ru/SiO_2 catalyst. The conversion attained explains its high selectivity in the glycerol hydrogenolysis tests. In our previous work[20] we found that in the presence of this catalyst the selectivity to propanols was negligible. The present results of the propylene glycol reaction support the above, as the selectivity to propanols is also zero. These monoalcohols are formed by hydrogenolysis (dehydration/hydrogenation) of 1,2-propanediol. It seems that Ru/SiO_2 catalyst presents optimum acidity inhibiting the dehydration/hydrogenation reactions. Propylene glycol is mainly converted to gaseous products with methane being the dominant one with 83.9% selectivity. The presence of the lower alkanes CH_4 and C_2H_6 in the gaseous products might be due to degradation and overhydrogenolysis reactions. In the liquid phase the only product observed is acetol with 9.3% selectivity. The formation of acetol from the reaction of 1,2-propanediol implies that the hydrogenation of acetol intermediate to propylene glycol is a reversible equilibrium-limited reaction.

In the glycerol hydrogenolysis reaction over Ru/SiO_2 catalyst, the formation of 1,3-propanediol seems not to be favored, as this product was not detected in the liquid mixture. In contrast with what has been reported in the literature,[18] 1,3-propanediol conversion is as high as that of 1,2-propanediol (Table 4). The reason might be that in the present study the test was performed with pure reactants and not with aqueous solutions.[18] The product spectrum is quite interesting as the 1,3-propanediol follows a different pathway from that of 1,2-propanediol. The dehydration/hydrogenation route to 1-propanol proceeds with rates comparable to that of C−C bond cleavage. These reactions lead to a mixture of degradation products, such as ethanol, ethane, and methane. As the 1,3-propanediol was not detected under the conditions applied in the glycerol hydrogenolysis tests, it is possible that the rate of its formation is very low. Miyazawa et al.[18] report that the active species for 3-hydroxypropionaldehyde formation, which is considered the intermediate to 1,3-propanediol, is Ru in hydrated form. The formation of hydrated Ru species, is unlikely under the conditions applied in the present tests as no water was used. The presence of small amounts of 1,3-propanediol (2% selectivity) in the liquid products formed from the glycerol hydrogenolysis using aqueous mixtures confirms the above assumptions about the active sites responsible for the formation of 1,3-propanediol.

Acetol is considered as the intermediate for the production of 1,2-propanediol from glycerol over acidic catalysts.[6,18] The hydrogenation of acetol can easily proceed on Ru/SiO_2 as evidenced from the complete conversion (100%) along with the high selectivity to 1,2-propanediol (78.3%). The detection of gaseous products, mainly of methane, implies that part of the formed propylene glycol may undergo further degradation to lower alkanes. These results suggest its high reactivity under reaction conditions as the reason for the very low concentration to the product mixture. Actually, acetol was always detected even in small quantities (<2.5%) in the liquid products over Ru/SiO_2 catalyst at the present conditions.

The main byproduct obtained from glycerol hydrogenolysis is ethylene glycol with selectivities ranging from 30% to 65%, depending on the operating conditions. Ethylene glycol hydrogenation behaviour was also examined in a separate test (Table 4). Ethylene glycol shows moderately higher activity in hydrogen atmosphere than propylene glycol, forming a variety of products. Methanol and ethanol with total selectivity of 13.7% are the two liquid products formed. The reaction of ethylene glycol mainly resulted in gas products formation, CH_4 (46%), CO (36.2%), and ethane in smaller amounts. The fact that ethylene glycol is not formed as a product in the reactions of acetol, 1,2-propanediol, and 1,3-propanediol implies that it is a degradation product formed directly from C−C bond scission of the glycerol molecules. The excessive hydrogenolysis of ethylene glycol produces ethanol and secondary ethane, while methanol and gas products (CO and CH_4) are formed via hydrogenation/degradation reactions.

All the above are summarized in Scheme 2, where the favorable and not favorable routes (presented with an "X" arrow) in the presence of the Ru/SiO_2 catalyst are presented. As can be seen in the reaction scheme, the formation of 1,2-propanediol is favorable and originates from the combination of two distinct steps, glycerol dehydration to hydroxyacetone (acetol intermediate) and subsequent very fast hydrogenation to 1,2-propanediol. It is worth underlining the importance of the mild acidity of the Ru/SiO_2, inhibiting the overhydrogenolysis of 1,2-propanediol to propanols. The formation of ethylene glycol and gas products that derive from glycerol degradation reactions is also favorable due to the use of Ru metal, being active both in C−O and C−C bond scission. Finally, the dehydration of the central −OH glycerol group (main route for the formation of 1,3 propanediol) is not favorable in the presence of the Ru/SiO_2 catalyst under the conditions used.

■ CONCLUSIONS

The parametric study (effect of reaction temperature, hydrogen pressure, and glycerol concentration) showed that the activity and propylene glycol selectivity is favored by the increase of temperature and hydrogen pressure. The addition of water did not affect the conversion, acting merely as a solvent, but positively influenced the 1,2-propanediol selectivity attaining a value of 90.2% with aqueous 20% glycerol solutions. The 5 wt % Ru/SiO_2 catalyst proved to be stable after the second time used in terms of conversion, but propylene glycol selectivity slightly decreased, due to the excessive hydrogenolysis reaction to propanols. Finally, the reaction pathways were explored, and the results indicate that the production of 1,2-propanediol is favorable along with the prevention from the excessive hydrogenolysis to propanols, while the formation of 1,3-propanediol is not favorable in the presence of the Ru/SiO_2 catalyst. In addition, the formation of ethylene glycol is confirmed to originate from the direct degradation of glycerol.

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