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# Surface and structural properties of titania-supported Ru catalysts for hydrogenolysis of glycerol

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# ABSTRACT

A series of catalysts with different Ru contents supported on titania were prepared by conventional impregnation (IM) and deposition–precipitation (DP) methods. These catalysts were characterized by X-ray diffraction, temperature programmed reduction, transmission electron microscopy, X-ray photoelectron spectroscopy and CO chemisorption. The catalysts were evaluated for selective hydrogenolysis of glycerol. The glycerol conversion and the selectivity towards 1,2-propanediol depend on the method of catalyst preparation and on the Ru content. The catalysts with low Ru content exhibited maximum conversion, in turn was related to its dispersion. The catalysts prepared by DP method showed stable activity upon reuse. The high activity of Ru/TiO<sub>2</sub> catalyst is due to the presence of well-dispersed nano size Ru particles on titania. The low activity of the IM catalyst is because of large domains of Ru and because of the presence of residual Cl<sup>-</sup> ions.

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# 1. Introduction

The use of renewable feedstock is essential for the sustainable development of society. The conversions of renewable feedstock into chemicals and fuels are important in the present scenario, as the availability of fossil fuels is limited. Catalysts play an important role to convert biorenewable feedstock to commodity chemicals and clean fuels [1–6]. In recent times, synthesis of biodiesel by transesterification of vegetable oils and fats is identified as one of the important conversion processes of renewable feedstock [7]. Biodiesel production in the European Union was estimated to be about 6 Mt in 2006 and is forecasted to increase to about 12 Mt in 2010 [8]. Recently, a European Union Directive stated that by the end of 2010, traffic fuels should contain at least 5.75% of renewable bio-components [1]. The global biodiesel market is estimated to reach 37 billion gallons by 2016, growing at an average annual rate of 42%.

Glycerol is the by-product in biodiesel synthesis and has been identified as one of the top ten building blocks in the bio refinery feed stocks [9–11]. Production of glycerol is increasing with increase of biodiesel production and this leads to a glut in the market. Utilization of crude glycerol is an alternative route to increase the profitability of biodiesel production [12]. Glycerol is a highly functionalized molecule and a variety of value added chemicals could be derived from glycerol by different reactions [1,13,14]. The broad overviews on the chemistry of glycerol and its conversion to new products are presented in the latest reviews [12–14]. Conversion of glycerol into valuable chemicals by a green catalytic process is a challenging area of research. Among different possible valuable chemicals, glycerol to propanediols is an important reaction.

Selective hydrogenolysis of glycerol yields to 1,2-propanediol (1,2-PD), 1,3-propanediol (1,3-PD) and ethylene glycol (EG) as main products [15,16]. The diols are used widely in the synthesis of pharmaceuticals, polymers, agricultural adjuvants, plastics and transportation fuel [17–19]. The commercial route to produce propylene glycol or ethylene glycols is by the hydration of propylene oxide or ethylene oxide derived from propylene or ethylene [11,15,19–23]. Heterogeneous catalytic conversion of glycerol to propanediol is an economically and environmentally attractive process [12].

Two types of catalysts are used for glycerol hydrogenolysis reaction. Mainly, Cu based mixed oxides and supported noble metal catalysts are the types of catalysts used for this reaction [18,19,21,23–28]. Among noble metal catalysts, supported Ru metal catalysts are more active for selective hydrogenolysis of glycerol than other catalysts [25–28]. Addition of solid acid catalyst to a supported noble metal catalyst enhances the conversion and selectivity in hydrogenolysis of glycerol compared to the results for supported noble metal catalyst alone [16,28]. It is reported that addition of solid acid to metal catalysts enhances the

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conversion and selectivity of the reaction, as the reaction proceeds via dehydration of glycerol to acetol over solid acid and consecutive hydrogenation on metal catalyst [16,28-30]. The authors reported the role of solid acid as co-catalyst and the direct relation between acidity of the co-catalysts with glycerol conversion has been elucidated [11]. Both acid and metal functionalities are required for hydrogenolysis of glycerol. Use of a single catalyst for the selective conversion of glycerol to 1,2-PD is more advantageous. Alhanash et al. [23] prepared a bifunctional catalyst by loading Ru onto a heterpoly acid salt  $C_{s_2,5}H_{0,5}(PW_{1,2}O_{4,0})$ . This catalyst showed about 96% selectivity to 1,2-propanediol with 21% glycerol conversion at 150 °C for 10 h. Feng et al. [29] studied in detail about the Ru supported catalysts for glycerol hydrogenolysis. The effect of both support and catalyst reduction temperatures were studied and the results suggested that the support can influence the metal particle size and thereby its activity. Among the TiO<sub>2</sub>, SiO<sub>2</sub>, NaY, and  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports, TiO<sub>2</sub> is a better support for obtaining high glycerol conversion whereas SiO<sub>2</sub> is choice of support for getting high selectivity to 1,2-PD. Even so the Ru/TiO<sub>2</sub> catalyst exhibited high glycerol conversion the selectivity towards 1,2-PD is low. The role of support is explained, but the detailed reasons for the low selectivity are not yet explored. The role of precursor and method of preparation of the catalysts are also important and there is a need to understand these in detail. The precursor of Ru is also important and the precursor with Cl- ion leads lower selectivity to 1,2-PD due to the excessive hydrogenolysis to propanediols [31].

In the present work, titania supported Ru catalysts are prepared by both impregnation and deposition precipitation methods and are studied for glycerol hydrogenolysis. The role of method of preparation and Ru content on glycerol hydrogenolysis was studied. The influences of metal particle size, metal support interaction, surface species and the morphology of the catalyst derived from different characterized methods are correlated with the observed hydrogenolysis activity.

# 2. Experimental

# 2.1. Catalyst preparation

Titania supported Ru catalysts were prepared by conventional impregnation (IM) and deposition–precipitation (DP) methods using aqueous solutions of RuCl<sub>3</sub>·*n*H<sub>2</sub>O. In the conventional IM method, a calculated amount of aqueous metal precursor solution was added to TiO<sub>2</sub> and excess water was evaporated on a water bath followed by oven drying for 12 h at 120 °C. In the DP method, the support was suspended in the aqueous solution of RuCl<sub>3</sub>·*n*H<sub>2</sub>O; Ru(OH)<sub>3</sub> was exclusively precipitated on the support by the slow addition of 1 M Na<sub>2</sub>CO<sub>3</sub> solution until the pH of the solution reached a value of 10.5. The resultant solid was filtered and washed with deionized water several times until no chloride ion was detected in the filtrate as confirmed by AgNO<sub>3</sub> test. The solid thus obtained was oven dried at 120 °C for 12 h. Each catalyst was reduced in H<sub>2</sub> flow at 300 °C for 2 h before its use for glycerol hydrogenolysis. The numbers indicate the wt.% of Ru on support.

## 2.2. Catalyst characterization

The BET surface areas of the catalyst samples were calculated from N<sub>2</sub> adsorption–desorption data acquired on an Autosorb-1 instrument (Quantachrome, USA) at liquid N<sub>2</sub> temperature.

Powder X-ray diffraction (XRD) patterns of the catalysts were recorded on a Rigaku Miniflex (Rigaku Corporation, Japan) X-ray diffractometer using Ni filtered Cu K $\alpha$  radiation ( $\lambda$  = 1.5406 Å) with a scan speed of 2° min<sup>-1</sup> and a scan range of 10–80° at 30 kV and 15 mA.

Temperature programmed reduction (TPR) experiments were carried out on an Auto Chem 2910 (Micromeritics) instrument. In a typical experiment ca.100 mg of oven-dried samples was taken in a quartz sample tube. Prior to TPR runs, the catalyst sample was pre-treated in argon gas at 300 °C for 2 h. After pretreatment, the sample was cooled to ambient temperature and the carrier gas consisting of 5% hydrogen balance argon (50 mL/min), was allowed to pass over the sample. The temperature of the sample was increased from ambient to 800 °C at a heating rate of 10 °C/min and the hydrogen consumption was monitored with a thermal conductivity detector.

X-ray photoelectron spectroscopy (XPS) measurements were conducted on a KRATOS AXIS 165 with a DUAL anode (Mg and Al) apparatus using Mg K<sub> $\alpha$ </sub> anode. The non-monochromatized Al K<sub> $\alpha$ </sub> X-ray source (hv = 1486.6 eV) was operated at 12.5 kV and 16 mA. Before acquisition of the data each sample was out-gassed for about 3 h at 100 °C under vacuum of  $1.0 \times 10^{-7}$  T to minimize surface contamination. The XPS instrument was calibrated using Au as standard. For energy calibration, the carbon 1s photoelectron line was used. The carbon 1s binding energy was taken as 285 eV. Charge neutralization of 2 eV was used to balance the charge up of the sample. The spectra were deconvoluted using Sun Solaris Vision-2 curve resolver. The location and the full width at half maximum (FWHM) value for the species were first determined using the spectrum of a pure sample. Symmetric Gaussian shapes were used in all cases. Binding energies for identical samples were, in general, reproducible within  $\pm 0.1$  eV.

CO chemisorption measurements were carried out using an Auto Chem 2910 instrument. Prior to adsorption measurements, each catalyst sample (100 mg) was reduced in a flow of hydrogen (50 ml/min) at 300 °C for 2 h, and flushed subsequently in He flow for an hour at 300 °C, and cooled to ambient temperature in the same gas flow. CO uptake was measured by injecting a number of CO pulses through a calibrated on-line sampling valve, CO pulses were injected until there was no more adsorption by catalyst. Ruthenium metal surface area and dispersion and average particle size were calculated assuming the stoichiometric factor for CO to Ru as 1.

The morphological features of the catalysts were monitored using a JEOL JEM 2000EXII transmission electron microscope, operating between 160 and 180 kV. The specimens were prepared by dispersing the samples in methanol using an ultrasonic bath and evaporating a drop of resultant suspension onto the lacey carbon support grid.

## 2.3. Activity measurements

Hydrogenolysis of glycerol was carried out in 80 ml haste alloy PARR 4843 autoclave. In a typical experiment, the required quantities of glycerol diluted with deionized water and of catalyst were taken. Prior to the experiment the supported Ru catalyst was reduced at 300 °C for 2 h with H<sub>2</sub> (60 ml/min). The autoclave was purged with H<sub>2</sub> flow to drive off the air present in autoclave. After purging, the reaction temperature and the hydrogen pressure were raised to the required temperature and pressure. After the reaction, the autoclave was cooled, the gas products were collected in a Teflon bag, and the liquid products were separated from the catalyst by filtration. The liquid products were analyzed by gas chromatography (Shimadzu 2010) using a flame ionization detector by separating them on Inno wax capillary column. Products were identified by using GC-MS (Shimadzu, GCMS-QP2010S) analysis. The gas phase products were analyzed using a gas chromatograph equipped with a Porapak Q column and a thermal conductivity detector. The products identified during glycerol hydrogenolysis are 1,2-PD, 1,3-PD, 1-propanol (1-PO), and 2-propanol (2-PO) as hydrogenolysis products and EG, ethanol, methanol, ethane and methane are as degradation products.

Catalyst	BET surface area (m <sup>2</sup> /g)	Dispersion (%)	Specific metal area (m²/g)	Particle size (nm) <sup>a</sup>
TiO <sub>2</sub>	52	-	-	-
1Ru/TiO <sub>2</sub> (DP)	51	53.0	4.5	1.1
2Ru/TiO <sub>2</sub> (DP)	49	42.0	8.0	1.2
5Ru/TiO <sub>2</sub> (DP)	47	29.4	7.2	3.4
5Ru/TiO <sub>2</sub> (IM)	44	9.7	2.4	10.2
7Ru/TiO <sub>2</sub> (DP)	40	18.6	5.1	6.3

# Table 1 Physico-chemical properties of Ru/TiO<sub>2</sub> catalysts.

<sup>a</sup> Particle size determined from CO chemisorption.

Conversion of the glycerol was calculated on the basis of the following equation:

$$Conversion(\%) = \frac{moles of glycerol consumed}{moles of glycerol initially charged}$$

The selectivity of the products was calculated on carbon basis.

Selectivity (%) = 
$$\frac{\text{moles of carbon in specific product}}{\text{moles of carbon in all delected products}} \times 100.$$

# 3. Results and discussion

#### 3.1. Catalyst characterization

The physico-chemical properties of the catalysts are reported in Table 1. The specific surface area of support  $TiO_2$  was found to be  $52 \text{ m}^2/\text{g}$ . The decrease in the BET surface area of the catalysts with increase in Ru loading is presumably a result of pore blockage by the crystallites of Ru.

The XRD patterns of the reduced catalysts are shown in Fig. 1. The XRD pattern of the 5 wt.% Ru/TiO<sub>2</sub> prepared by IM method appears in the same figure. The catalyst samples exhibited peaks at  $2\theta$  value of 25.3, 37.8, 48.1 and 54 corresponding to the anatase phase of titania. Small peaks related to rutile phase of titania were observed at  $2\theta$  values of 27.4, 36.1 and 54.3. No characteristic peak related to metallic Ru was found at a loading of below 5 wt.% of Ru. A peak at the  $2\theta$  value of 44.03 related to metallic Ru was observed for the catalysts with loading of 5 wt.% of Ru. However the catalyst prepared by IM method showed the presence of Ru crystallites. The absence of a crystallographic pattern of Ru metal at low Ru content might be due to the presence of nano (<40 Å) Ru particles in a highly dispersed state on the support.



**Fig. 1.** X-ray diffraction patterns of the supported Ru catalysts ( $\blacksquare$ ) anatase; (#) rutile of TiO<sub>2</sub>; and (\*) Ru.

The reducibility of Ru/TiO<sub>2</sub> catalysts was investigated by TPR; the profiles of the catalysts are shown in Fig. 2. The TPR pattern of the catalyst prepared by IM method is also shown in the same figure for comparison. The catalysts exhibited one main reduction peak between 120 and 130 °C related to the single stage reduction of RuO<sub>2</sub> to Ru. Another reduction peak at high temperature around 240–260 °C, which is prominent for catalysts with high Ru content, is due to the reduction of bulk RuO<sub>2</sub> present on the surface. The IM catalyst showed the main reduction peaks at 194 and 234 °C. The reduction of Ru at high temperature for IM catalyst might be due to the presence of residual Cl<sup>-</sup> ions. The presence of residual Cl<sup>-</sup> hinders easy reduction of metal oxide.

XPS analysis was carried out for reduced Ru/TiO<sub>2</sub> catalysts and the patterns are shown in Fig. 3. Since the binding energy of Ru  $3d_{5/2}$ (~280 eV) overlapped with that of C 1s (~284 eV), it was difficult to resolve the small Ru peak out from the large peak of C 1s. After a careful deconvolution, peaks at 280, 283, 286 and 288 eV were detected for the catalysts. The B.E. of 280 and 283 eV is related to the chemical states of Ru<sup>0</sup> and Ru<sup>n+</sup> respectively. The Ru/TiO<sub>2</sub> catalysts prepared by the DP method showed an additional Ru doublet with a B.E. of 283.4 eV attributed to Ru(IV) species [32]. The Ru(IV) species are formed when the pre-reduced catalysts are exposed to run XPS analyzes. The B.E. of 288 eV may be an Auger signal of a Na impurity that may be present in the catalyst. No such Auger signal is observed for the catalyst prepared by IM method.

The dispersion of Ru was measured by CO chemisorption; the results are summarized in Table 1. The average particle size was calculated based on CO chemisorption values by assuming spherical particles. The CO chemisorption results suggest that the Ru particles were highly dispersed on the support, with a particle size <5 nm. The crystallite size of Ru particles increased with Ru loading due to the formation of crystalline Ru particles, as noticed from XRD. The crystallite size of Ru measured from CO chemisorption is in



Fig. 2. Temperature programmed reduction profiles of the catalysts.



**Fig. 3.** XPS spectra of reduced Ru/TiO<sub>2</sub> catalysts.

good agreement with XRD results. The dispersion of Ru decreased with increase in Ru loading. It is observed a very high dispersion for the catalyst with 2 wt.% of Ru. The dispersion values are decreased at high Ru loading due to the formation of large Ru ensembles. Comparing the dispersion and particle size of the 5 wt.% Ru/TiO<sub>2</sub> catalysts prepared by IM and DP methods reveal that the catalyst prepared by the DP method possesses smaller Ru particles with higher dispersion than the catalyst prepared by the IM method.

The morphological features of 5 wt.% Ru catalysts prepared by both IM and DP method were studied by transmission electron microscopy. The micrographs of these catalysts are shown in Fig. 4. The images reveal that the catalysts prepared by the DP method possess uniformly distributed nano Ru particles on TiO<sub>2</sub>. The TEM image of IM catalyst exhibited large ensembles of Ru particles. The particle size of Ru estimated by TEM measurement is comparable with the values obtained from CO chemisorption measurements. The catalyst prepared by the DP method allowed Ru to disperse uniformly on TiO<sub>2</sub> thus leading to the formation of nano-sized Ru particles. Smaller Ru metal particles are formed for Ru supported catalysts prepared by Cl<sup>-</sup> free precursor [31]. In the case of IM method, the aqueous solution of RuCl<sub>3</sub> that was used as precur-

## Table 2

Glycerol hydrogenolysis activity over Ru/TiO<sub>2</sub> catalysts.

Catalyst	Conversion (%)	Selectivity (%)			
		1,2-PD	EG	Acetol	Others
5Ru/TiO <sub>2</sub> (DP)	44	58	17	4	21
5Ru/TiO <sub>2</sub> (IM)	31	59	24	2	15

Reaction conditions: glycerol conc.: 20 wt.%,  $H_2$  pressure: 60 bar, reaction time: 8 h, reaction temperature: 180 $^\circ C$ , catalyst wt.: 6%.

sor contains polymeric species which favors the sintering in the presence of  $Cl^-$ . These  $Cl^-$  ions remain on the support [33,34].

# 3.2. Glycerol hydrogenolysis activity

# 3.2.1. Effect of method of catalyst preparation

The catalytic activity of Ru/TiO<sub>2</sub> catalysts prepared by both IM and DP methods was studied for glycerol hydrogenolysis; results are presented in Table 2. The glycerol conversions and selectivities varied with changes in catalyst preparation method. The catalyst prepared by the DP method showed better activity than the catalyst prepared by the IM method. Hydrogenolysis activity of titania was also tested and there was no reaction without Ru. The difference in activity with change in preparation method might be due to the difference in the nature of the Ru species. The catalysts were prepared using RuCl<sub>3</sub> as precursor; during preparation, chloride species might be present on surfaces for the catalyst prepared by IM method. The Cl<sup>-</sup> species are not easily removed completely during reduction for IM catalyst. The XPS analysis suggests the presence of surface Cl<sup>-</sup> species for the catalyst prepared by the IM method. In case of the catalyst prepared by the DP method the RuCl<sub>3</sub> was precipitated to Ru(OH)3 and the chloride species are removed completely. TPR pattern of the catalyst prepared by the IM method also supports the presence of residual Cl<sup>-</sup> as it showed a high temperature reduction peak (Fig. 2). In the case of DP catalyst, the  $Ru(OH)_3$ is easily reduced during pretreatment, leading to well dispersed Ru particles on the support. CO chemisorption and TEM results suggest the presence of well-dispersed Ru particles compared to IM catalyst. The presence of highly dispersed Ru particles in the case of the DP method catalyst is responsible for the high glycerol conversion.

# 3.2.2. Effect of ruthenium loading

As the catalysts prepared by the DP method showed better activity, a series of catalysts with different Ru contents were prepared; these catalyst activities for glycerol hydrogenolysis are shown in Table 3. The high glycerol conversion of about 46% with 82% com-



(a) IM catalyst

(b) DP catalyst

Fig. 4. TEM images of Ru/TiO<sub>2</sub> catalysts.

Table 3
Effect of Ru content on hydrogenolysis of glycerol

Catalyst	Conversion (%)	Selectivity (%)				
		1,2-PD	EG	Acetol	Others	
$1 \text{Ru}/\text{TiO}_2$ (DP)	35	64	18	2	16	
$2Ru/1iO_2$ (DP) $5Ru/TiO_2$ (DP)	46 44	63 58	19 17	2 4	16 21	
7Ru/TiO <sub>2</sub> (DP)	40	64	18	7	11	

Reaction conditions: glycerol conc.: 20 wt.%, H<sub>2</sub> pressure: 60 bar, reaction time: 8 h, reaction temperature: 180 °C, catalyst wt.: 6%.

bined glycol selectivity was achieved at a loading of 2 wt.% of Ru. Low Ru metal loading (2 wt.%) was sufficient to achieve optimum glycerol conversion when the catalysts are prepared by the DP method. The high activity for the catalyst with low Ru was mainly because of well-dispersed nano Ru particles. The 2-wt.% Ru/TiO<sub>2</sub> catalyst exhibited the highest dispersion (Table 2). The presence of the large particles for the catalysts with high Ru content might be the reason for the decrease in activity. The XRD and CO chemisorption results suggest the presence of large particles with low dispersion for the catalyst with high Ru on titania.

In order to understand the role of support TiO<sub>2</sub> for glycerol hydrogenolysis, we carried out the reaction with Ru/TiO<sub>2</sub> in the presence of N<sub>2</sub> gas instead of H<sub>2</sub>. Very low conversion (3%) of glycerol was observed. However, the main product was acetol. At the same time, the reaction was also carried with TiO<sub>2</sub> in the presence of H<sub>2</sub>. There is no conversion of glycerol, suggesting that TiO<sub>2</sub> cannot promote the hydrogenlosis of glycerol. These results suggest that Ru is responsible for the dehydration and hydrogenation, leading to the formation of 1,2-PD. Chiu et al. [35] reported the formation of acetol from glycerol during catalytic reactive distillation over transition metal catalysts. The formation of acetol during the reaction as seen in Tables 2 and 3 further suggests that the Ru based catalysts are following dehydration followed by hydrogenation route. Supported Ru, Pd, Ni and copper-chromite catalysts dehydrate glycerol to acetol. The intrinsic property of TiO<sub>2</sub> is mainly in enhancing the dispersion of Ru. The high activity of 2 wt.%Ru/TiO<sub>2</sub> catalyst supports the above observation where the catalyst with high dispersion showed maximum activity.

## 3.2.3. Effect of reaction temperature

As the 2-wt.% Ru/TiO<sub>2</sub> catalyst showed better activity, this catalyst was studied as system catalyst to evaluate the reaction parameters for glycerol hydrogenolysis. The influence of reaction temperature on the hydrogenolysis of glycerol was studied; the results are shown in Fig. 5. The glycerol conversion gradually increased from 34 to 67% as the temperature of the reaction increased from 160 to 220 °C. The optimum reaction temperature lies between 180 and 200 °C, as at these temperatures it showed high selectivity to desired 1,2-PD with reasonable conversion. High glycerol conversion was obtained above 200 °C; however the selectivity to 1,2-PD and EG was relatively low. It is known that, at high temperature, propanediol will undergo further hydrogenolysis to yield lower alcohols [12,20].

# 3.2.4. Influence of hydrogen pressure

The influence of  $H_2$  pressure on hydrogenolysis was studied by carrying out the reaction under various values of  $H_2$  pressure from 20 to 80 bar. Fig. 6 shows the effect of hydrogen pressure on conversion and selectivity during glycerol hydrogenolysis. The glycerol conversion gradually increased with increase in reaction pressure. There was not much variation in selectivity with change in  $H_2$  pressure. The high conversion of glycerol with increase in  $H_2$  pressure is due to the availability of more amounts of hydrogen for the hydrogenation of acetol that formed during the reaction.



Fig. 5. Effect of reaction temperature on glycerol hydrogenolysis over  $Ru/\text{TiO}_2$  catalysts.

 $\it Reaction\ conditions:\ glycerol\ conc.:\ 20\ wt.\%,\ H_2\ pressure:\ 60\ bar,\ reaction\ time:\ 8\ h,\ catalyst\ wt.:\ 6\%.$ 

# 3.2.5. Effect of reaction time

Fig. 7 shows the effect of reaction time on hydrogenolysis of glycerol. About 33.6% of conversion and 77% combined selectivity towards 1,2-PD and EG within 4 h of reaction time was achieved. Glycerol conversion increased with increase in a reaction time from 4 to 16 h. High glycerol conversion of about 56% was achieved at a reaction time of 16 h. The selectivity to 1,2-PD increased with time and at the same time selectivity to EG is decreased. At short reaction times, Ru promotes the cleavage of C–C bond along with hydrogenation, leading to formation of EG. This is expected at initial stages, as the Ru is more active and promotes the secondary reaction by the cleavage of 1,2-PD.

#### 3.2.6. Influence of glycerol concentration

Influences of glycerol concentration or water content on glycerol hydrogenolysis were studied; the results are presented in Fig. 8. A decrease in glycerol conversion was noticed with increase in glycerol concentration. It is known that glycerol conversion is higher at low glycerol concentration [12,17]. The low conversion at high glycerol concentration is as expected, since the available number of Ru sites is constant. No formation of any other by-products at high glycerol concentration.



Fig. 6. Effect of hydrogen pressure on glycerol hydrogenolysis over  $\mbox{Ru}/\mbox{Ti}\mbox{O}_2$  catalysts.

Reaction conditions: glycerol conc.: 20 wt.%, reaction time: 8 h, reaction temperature: 180 °C, catalyst wt.: 6%.



**Fig. 7.** Variation of glycerol activity with reaction time over Ru/TiO<sub>2</sub> catalysts. *Reaction conditions*: glycerol conc.: 20 wt.%, H<sub>2</sub> pressure: 60 bar, reaction temperature:  $180 \degree$ C, catalyst wt.: 6%.



**Fig. 8.** Influence of glycerol concentrations during its hydrogenolysis over Ru/TiO<sub>2</sub> catalysts.

Reaction conditions:  $\rm H_2$  pressure: 60 bar, reaction time: 8 h, reaction temperature: 180  $^\circ C$ , catalyst wt.: 6%.

## 3.2.7. Effect of salt on hydrogenolysis of glycerol

Glycerol, which is to be obtained from the biodiesel industry, contains trace amounts of alkali salts like sodium sulphate and other impurities. Each transesterification reaction is carried out over base catalysts like sodium hydroxide and the products will be neutralized in down stream process with acid. The nuetralization leads to the formation of salts. The hydrogenolysis of crude glycerol and the glycerol with added sodium salts was carried over the present catalyst to test its tolerance towards impurities; the results are shown in Table 4. Synthetically 5% sodium sulphate was added to pure glycerol to study the effect of salt on glycerol hydrogenolysis. The crude glycerol was obtained as a by-product from transesterification of sunflower oil with methanol using NaOH as catalyst. The reaction was carried out at room temperature with 6:1 molar ratio of methanol to oil and 1% of sodium hydroxide catalyst by weight of sunflower oil. The crude glycerol contained excess methanol and other impurities and is highly basic (pH=14). The crude glycerol was purified by sequential removal of NaOH with the addition of sulphuric acid. Excess methanol and water were removed by the evaporation.

The demethanolized crude glycerol was used for hydrogenolysis of glycerol to propanediols. The hydrogenolysis of crude glycerol Table 4

Hydrogenolysis of crude glycerol over 2-wt.% Ru/TiO<sub>2</sub> (DP) catalyst.

Catalyst	Conversion (%)	Selectivity (%)			
		1,2-PD	EG	Acetol	Others
2Ru/TiO <sub>2</sub> (DP)	46	63	19	2	16
2Ru/TiO <sub>2</sub> (DP) <sup>a</sup>	44	63	19	2	16
2Ru/TiO <sub>2</sub> (DP) <sup>b</sup>	42	59	22	2	17

Reaction conditions: glycerol conc.: 20 wt.%, H<sub>2</sub> pressure: 60 bar, reaction time: 8 h, reaction temperature: 180 °C, catalyst wt.: 6%.

<sup>a</sup> Crude glycerol.

<sup>b</sup> Glycerol with 5% sodium sulphate.

# Table 5

Activity of titania supported Ru catalysts during Recycling experiments.

No. of cycles	Conversion (%)	Selectivity (%)			
		1,2-PD	EG	Acetol	Others <sup>a</sup>
Fresh	46	63	19	2	16
Cycle-I	48	64	18	3	15
Cycle-II	49	64	18	3	15
Cycle-III	51	63	18	4	15

Reaction conditions: glycerol conc.: 20 wt.%, H<sub>2</sub> pressure: 60 bar, reaction time: 8 h, reaction temperature: 180 °C, catalyst wt.: 6%.

results in a maximum conversion of about 43% with 63% selectivity toward 1,2-propanediol and 19% selectivity towards ethylene glycol. These results are similar to the results obtained using analytical grade glycerol. It is noteworthy to mention that the present catalyst is resistant towards the salts and other impurities present in glycerol.

#### 3.2.8. Reusability of the catalyst

It is important to study the reusability of glycerol hydrogenolysis catalyst. The hydrogenolysis was carried out under relatively harsh conditions and the glycerol contains impurities. There is a possibility of structural changes during the reaction and poisoning of active metal sites. Recyclability of the catalyst was studied; the results are listed in Table 5. The catalyst was separated after the reaction by centrifugation and washed with distilled water, followed by methanol. This semi-dried catalyst is used for recyclic experiments, as the recovery of the catalyst was quantitative. The recycling results suggest the consistent activity upon reuse. In fact, the conversion of glycerol increased marginally during the recycling above that of the fresh catalyst. The selectivity towards 1,2-PD and EG remains same during recycling. A marginal increment of glycerol conversion with reuse might be due to complete reduction of Ru during reaction, as hydrogen is present in the reaction. This might be allowing Ru to maintain its high dispersion on TiO<sub>2</sub> during the experiments [30].

The used catalyst was characterized by XRD, XPS and TEM and results were compared with values of the virgin catalyst (Fig. 9). The XRD patterns of the fresh and three times-used catalysts are presented in Fig. 9a. Both fresh and used catalysts showed similar XRD patterns. This suggests that the catalysts structural features were intact during reaction. The XPS analysis also implies that the surface species retained their identity upon reuse (Fig. 9b). TEM images of fresh and used catalysts (Fig. 9c) suggest that similar morphology was maintained during hydrogenolysis of glycerol. There was no indication of any agglomeration during the glycerol hydrogenolysis. The results suggest the structural stability of the catalyst under glycerol hydrogenolysis conditions.

# 4. Conclusions

Selective hydrogenolysis of glycerol to propylene glycol was studied over titania supported Ru catalysts prepared by both IM and DP methods. Catalyst preparation method can influence the



**Fig. 9.** Characterization of used catalyst (a) X-ray diffraction, TiO<sub>2</sub>: (■) anatase and (#) rutile; (b) XPS; and (c) TEM images.

Used

conversion and selectivity during glycerol hydrogenolysis. Catalysts prepared by the DP method showed higher conversion than catalysts prepared by the IM method. Low Ru content is sufficient to achieve maximum conversion if the catalyst was prepared by the DP method. The catalyst with low Ru content exhibited maximum activity, which is related to the nature of the Ru species. The support titania provides the platform for good dispersion of nano size Ru particles, which are responsible for high activity. The presence of residual chlorine has a detrimental effect on glycerol hydrogenolysis for supported Ru catalysts. The catalyst is active even when crude glycerol and glycerol with alkali salts was used. The catalyst showed similar conversion values and selectivities upon reuse without loss of any activity and selectivity with intact morphology of the catalyst. The conversion of glycerol and the selectivity to 1,2-PD also depend on the reaction temperature, hydrogen pressure, reaction time and glycerol concentration.

Fresh

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