Hydrogenolysis of glycerol catalyzed by Ru-Cu bimetallic catalysts supported on clay with the aid of ionic liquids

Tao Jiang,* Yinxi Zhou, Shuguang Liang, Huizhen Liu and Buxing Han*

Received 22nd January 2009, Accepted 25th March 2009
First published as an Advance Article on the web 9th April 2009
DOI: 10.1039/b901425j

Glycerol is a well-known renewable chemical, and its effective transformation to valuable chemicals accords well with the principles of green chemistry. In this work, a series of Ru-Cu bimetallic catalysts were prepared using cheap and abundant clay, bentonite, as the support. Bentonite was modified with a functional ionic liquid 1,1,3,3-tetramethylguanidinium lactate (TMGL) in an attempt to develop highly efficient catalysts. Hydrogenolysis of aqueous solution of glycerol was performed with the immobilized Ru-Cu catalyst under temperatures of 190–240 °C and pressures of 2.5–10 MPa. The bimetallic catalysts were very efficient for promoting the hydrogenolysis of glycerol. 100% of glycerol conversion and 85% yield of 1,2-propanediol could be achieved at 230 °C and 8 MPa. The conversion of glycerol and the selectivity to 1,2-propanediol did not decrease after the catalyst was used 5 times. TMGL played a crucial role in fabricating the new catalysts. The catalysts were characterized by FT-IR, XPS, SEM and TEM, and the reasons for the excellent performances of the catalyst were also discussed.

Introduction

With the gradual depletion of fossil resources, an urgent task is to replace fossil resources with renewable materials. Commodity chemicals that are currently used to produce pharmaceuticals, plastics and transportation fuels are expected to be produced from renewable materials in future. This strategy is especially crucial for the sustainable development of the society and economy. Much effort, therefore, has been devoted to the conversion and utilization of renewable feedstocks and chemicals in recent years.[1,2] Glycerol is one of the top-12 building block chemicals identified by the U.S. Department of Energy.[3] As a biomass-derivate, glycerol can be commercially produced by the microbial fermentation of sugars such as glucose and fructose.[4–6] In addition, glycerol is a byproduct in a large amount from the production of biodiesel by transesterification of plant and animal oils with methanol.[7] 10 wt% of glycerol is produced in manufacturing biodiesel fuel. It is no doubt that development of chemical processes to convert low-cost glycerol to more valuable chemicals is of great importance. Recently, several excellent papers have given overviews on the recent development in the conversion of glycerol into value-added chemicals.[8–11]

It is known that glycerol can be catalytically converted into functionalized and value-added chemicals *via* a variety of reaction routes, such as oxidation, hydrogenolysis, dehydration, pyrolysis, steam reforming, etherification, esterification, oligomerization and polymerization, *etc.* The hydrogenolysis of glycerol produces oxygenated chemicals including ethylene glycol (EG) and propylene glycol. Propylene glycol is presently produced through petroleum routes, such as the ethylene oxide route (Shell technology)[12] or acrolein (Degussa-DuPont technology)[13] for the production of 1,3-propanediol (1,3-PDO) and the hydrolysis of propylene oxide with water for manufacturing 1,2-propanediol (1,2-PDO). 1,3-PDO is mainly used as a starting material for producing polymers and 1,2-PDO is often used directly as intermediates or additives to produce antifreezing agent, lubricants, foods, cosmetics, and resins.[9,14] Increasing attention has consequently been paid to the hydrogenolysis of glycerol to produce 1,3-PDO and 1,2-PDO, and about 10 papers were published in 2008. Solid catalysts have exhibited unique advantages in separation and recovery of catalysts. Metals including Cu, Ni, Pd, Pt, Ru, Rh, Cr, and Au have been extensively used as the active components for hydrogenolysis of glycerol, and the reactions were conducted at temperatures of 453–513 K and hydrogen pressures of around 6–10 MPa.[15–22]

Among the metals used, ruthenium has shown a high activity for the hydrogenolysis of glycerol,[23–26] but C–C bond cleavage is often unavoidable[27,28] resulting in the high yields to products of small molecules, including methane, methanol, CO, and CO_2, *etc.* The work by Davis *et al.* indicated that Ru favored the formation of EG over 1,2-PDO. C–C bond cleavage is thought to occur primarily *via* a metal-catalyzed reaction route over Ru.[29,30] Montassier *et al.*[16] carried out the hydrogenolysis of glycerol under 30 MPa H_2 at 533 K. Mainly methane was obtained in the presence of RANEY® Ni, Ru, Rh and Ir catalysts, while 1,2-PDO was the main product when RANEY® Cu was used as a catalyst. Cu also exhibited good performance for the hydrogenolysis of glycerol in other works.[31,32] Chaminand *et al.* reported the hydrogenolysis of glycerol over CuO/ZnO catalysts. At 180°C and 80 bar hydrogen pressure 100% selectivity to 1,2-PDO can be obtained in water when the conversion of glycerol was 19%.[23] More recently, Xia and coworkers prepared

---

Beijing National Laboratory for Molecular Sciences (BNLMS), Centre for Molecular Science, Institute of Chemistry, Chinese Academy of Sciences, Beijing, 100190, China. E-mail: Jiangt@iccas.ac.cn, Hanbx@iccas.ac.cn; Fax: +86 10 62562821; Tel: +86 10 62562821

highly dispersed copper nanoparticles supported on silica by the precipitation–gel technique, which showed 94.3% selectivity toward 1,2-PDO with 73.4% glycerol conversion at 473 K and a total pressure of 9 MPa.[33]

Recently, the preparation of catalysts assisted by ionic liquids (ILs) has attracted much attention.[34] For example, Mehnert *et al.* dispersed 1-butyl-3-methylimidazolium hexafluorophosphate ([bmim][PF_6]) and 1-butyl-3-methylimidazolium tetrafluoroborate ([bmim][BF_4]) on silica gel to provide a solvent environment for the Rh complex. The as-prepared catalyst showed excellent catalytic activity and stability for hydrogenation.[35] More interestingly, some functional ILs exhibit a strong ability to stabilize nanoparticles. Different Pd or Ru nanoparticle catalysts have been prepared with the assistance of guanidinium-based IL, which also showed outstanding catalytic performance for the hydrogenation of benzene and olefins.[36,37] More recently, a series of very effective supported catalysts for different organic reactions have been prepared using different ILs and solid supports.[38–40]

Natural clay minerals are a type of environmentally benign material. Bentonite (BEN) is a clay consisting predominantly of montmorillonite. It has a layered structure, large surface areas, and cation exchange capacity. The special properties of bentonite make it a valuable material for a wide range of applications, such as pharmaceuticals, cosmetics, environment, agriculture, and catalysis, *etc.* Bentonite is potentially a good catalyst support. For example, an excellent catalyst has been prepared using ion-exchanged montmorillonite for the hydrogenation of benzene.[41] A montmorillonite-enwrapped scandium has been used as a heterogeneous catalyst for the Michael reaction.[42]

As discussed above, both Ru and Cu can catalyze the reaction, with certain advantages. A combination of them may produce a more efficient catalyst. In this work, a series of Ru-Cu bimetallic catalysts were prepared using bentonite as the support with the aid of 1,1,3,3-tetramethylguanidinium lactate (TMGL). Hydrogenolysis of glycerol was performed with the immobilized Ru-Cu catalyst (designated as Ru-Cu/TMG-BEN). The results demonstrated that the catalyst was highly active and selective for the hydrogenolysis of glycerol to produce 1,2-PDO. The IL played a crucial role in fabricating the new catalysts. As far as we know, this is the first work on the hydrogenolysis of glycerol carried out using Ru-Cu bimetallic catalysts.

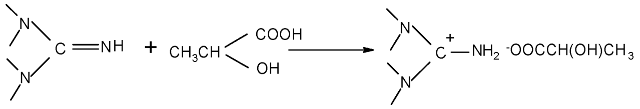
Experimental

Materials

The clay mineral used in this work is a smectite rich white bentonite provided by Zhejiang Sanding Scientific and Technology Co., Ltd., China. The composition of the clay was 58.98% SiO_2, 19.82% Al_2O_3, 3.73% MgO, 5.18% Na_2O, 0.42% K_2O, 0.87% CaO, 1.31% Fe_2O_3, 0.10% TiO_2, 0.74% P_2O_5, and 0.08% FeO. It was microporous and cation-rich. The cation exchange capacity (CEC) of the bentonite was 99 mmol/100 g. H_2 was purchased from Beijing Analytical Instrument Factory with a purity of 99.99%. Glycerol, 1,2-propanediol, ethylene glycol, n-butanol, and N,N-dimethylformamide (DMF) were purchased from Sinopharm Chemical Reagent Co., Ltd. $NaBH_4$, $Cu(NO_3)_2 \cdot 3H_2O$, and $RuCl_3 \cdot 3H_2O$ were A.R. grade and produced by Beijing Chemical Reagents Company. All chemicals were used as received.

Catalyst preparation

In this work, bentonite was modified with ionic liquid 1,1,3,3-tetramethylguanidinium lactate (TMGL), which was prepared directly by neutralization of 1,1,3,3-tetramethylguanidine with lactic acid at room temperature (Scheme 1).[43] Before being used as the supports, bentonite was treated with TMGL to exchange the Na cations with the IL cations. The molar ratio of IL to the CEC of bentonite was 1.2:1. Bentonite was first dispersed in an aqueous solution of TMGL and stirred for 6 h at room temperature. After being separated from the solution by filtration, bentonite was treated for the second time with the same procedures. Then bentonite was washed three times with deionized water, and dried at 120°C overnight, which was labeled as TMG-BEN.



Scheme 1 The synthesis of TMGL.

The Ru or Cu catalysts supported on TMG-BEN were prepared by the following procedures: 1 g of TMG-BEN was dispersed in an aqueous solution of $RuCl_3 \cdot 3H_2O$ (0.0776 g, 0.297 mmol Ru; 20 mL of deionized water) or $Cu(NO_3)_2 \cdot 3H_2O$ (0.0717 g, 0.297 mmol Cu; 20 mL of deionized water), and the mixture was stirred for 2 h at room temperature. Then water was removed under vacuum. The obtained catalyst was reduced in a flow of pure H_2 at 220°C for 3 h. The as-obtained catalyst was designated as Ru/TMG-BEN and Cu/TMG-BEN, respectively.

The Ru-Cu bimetallic catalysts supported on TMG-BEN were prepared by the following procedures: 1 g of the modified bentonite was added to the aqueous solution of $RuCl_3 \cdot 3H_2O$ (0.0776 g, 0.297 mmol Ru; 20 mL of deionized water), and the mixture was stirred for 2 h at room temperature. Then $NaBH_4$ was used to reduce Ru. The solid was washed with deionized water and dried at 100 °C. Then the supported Ru catalyst was added to the aqueous solution of $Cu(NO_3)_2 \cdot 3H_2O$ (0.0239 g, 0.1 mmol Cu; 20 mL of deionized water), and the mixture was stirred for 2 h at room temperature. After being reduced with $NaBH_4$ the solid was washed with deionized water and dried at 100 °C. Finally, the solid was reduced in a flow of pure H_2 at 220 °C for 3 h and then 300 °C for 3 h. The as-made catalysts were labeled as Ru-Cu/TMG-BEN. The content of Ru in this catalyst was 3 wt% of the support and the molar ratio of Ru to Cu was 3/1. The catalysts with other Ru/Cu ratios were prepared using the same procedures. For comparison, the Ru-Cu bimetallic catalyst supported on unmodified bentonite was also prepared using a similar method, which was referred to as Ru-Cu/BEN.

Catalyst characterization

Fourier transform infrared spectroscopy (FT-IR) spectra were determined using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. The morphology of the catalysts was observed with a transmission electron microscope (TEM, Tecnai 20, Philips). The X-ray photoelectron spectrum (XPS) data of the as-prepared samples were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Mg$K\alpha$ radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1 s line at 284.8 eV from adventitious carbon. X-ray Diffraction (XRD) was performed on a X'PERT SW X-ray diffractometer operated at 30 kV and 100 mA with CuKa radiation. Scanning electron microscope (SEM) examination was carried out on a scanning electron microscope (JEOL, JSM-4300) operated in a high-vacuum mode at 15 kV, which provided general textural information of the samples. Thermogravimetric analysis of TMG-BEN was performed on a TGA Q50 V20.7 Build 32 thermogravimetric analysis system in the atmosphere at a heating rate of 20 °C per min.

Catalytic activity measurement

The hydrogenolysis of glycerol was carried out in a 7 mL autoclave reactor under stirring. Typically, the reactor was charged with glycerol (5 mmol, 0.46 g) and the catalyst (0.084 g, 0.3 mol% of Ru/glycerol) in 1.0 mL deionized water, and purged with 2.0 MPa hydrogen three times before the reaction. An air bath was used to heat the reactor and its temperature was controlled by a PID temperature controller (model SX/A-1, Beijing Tianchen Electronic Company). The temperature fluctuation of the constant temperature air bath was ±0.1 °C. After the autoclave was heated to the reaction temperature, hydrogen was charged up to the desired pressure. After a required period, the autoclave was cooled and the gases were released and collected. The liquid products were analyzed using a GC (Agilent 6820) equipped with a PEG-20M (30 m) capillary column and a FID detector. n-Butanol was employed as the internal standard to calculate the product compositions and DMF was used as the solvent. The gas product was analyzed using a GC (Agilent 4890) equipped with a packed carbon molecular sieve column (2 m long, 3 mm o.d.) and a TCD detector.

Recycling procedure of Ru-Cu/TMG-BEN

In the recycling experiment, the catalyst was separated by centrifugation and washed with deionized water three times. Then the catalyst was dried at 60 °C under vacuum for 3 h and 100 °C for 2 h in air. The catalyst was reused in the next run directly. Reaction conditions were as follows: catalyst, Ru-Cu/TMG-BEN (Ru 3 wt%, Ru/Cu 3/1); catalyst amount, 0.3 mol% Ru/glycerol; reaction temperature, 225 °C; reaction time, 20 h; glycerol, 5 mmol (0.46 g); water, 1.0 mL; initial pressure, 10.0 MPa.

Results and discussion

In the experiments, 1,2-PDO, 1,3-PDO, ethylene glycol (EG), 1-propanol (1-PO), 2-propanol (2-PO), C_2H_5OH, and CH_3OH were detected in the liquid products. CH_4 and CO_2 were observed in the gas products. Conversion of glycerol is defined as the ratio of number of moles of glycerol consumed in the reaction to the total moles of glycerol initially added. Selectivity to liquid product is defined as the ratio of number of moles of glycerol consumed to produce liquid product to the number of moles of converted glycerol. Composition of liquid product was calculated based on C-based moles of each component in the liquid product.

Effect of Ru/Cu molar ratio

A series of Ru/Cu bimetallic catalysts were prepared using TMGL modified BEN as the support by changing the molar ratio of Ru and Cu. In all of the catalysts, the content of Ru was 3 wt% of the support. Table 1 summarized the results of these catalysts in catalyzing the hydrogenolysis of aqueous glycerol. When Ru/TMG-BEN catalyst was used (Table 1, Entry 1), the conversion of glycerol could reach 90.7%. But obvious cleavage of C–C bonds was observed and the selectivity to liquid product was only 27.4%. A large amount of gas product (CH_4 and CO_2) was detected. This is consistent with the results of other researchers.[16,29,30] In addition, the content of EG in the liquid product was more than 30%, which is also high compared with the results using other catalysts in Table 1. EG is formed *via* the cleavage of the C–C bond, further demonstrating that Ru is active for cleavage of the C–C bond. On the contrary, Cu/TMG-BEN exhibited low conversion of glycerol (26.5%), but high selectivity to liquid product, especially 1,2-PDO (Table 1, Entry 8), indicating Cu catalysts have poor activity towards C–C bond

Table 1 Effect of molar ratio of Ru/Cu on the catalytic performance of Ru-Cu/TMG-BEN in the hydrogenolysis of glycerol

				C-based composition of liquid products/mol%		
Entry	Molar ratio of Ru/Cu	Conversion of glycerol/%	Selectivity to liquid product/%	1,2-PDO	EG	Others[a]
1	3/0	90.7	27.4	62.3	32.7	5.0
2	3/0.5	71.9	34.4	57.6	37.3	5.1
3	3/1	70.9	46.1	71.7	23.6	4.7
4	3/2	66.1	40.4	70.3	24.8	4.9
5	3/3	64.4	30.6	69.5	28.6	1.9
6	3/4	41.7	23.4	72.7	23.7	3.6
7	3/9	27.0	22.0	79.4	17.9	2.7
8	0/3	26.5	59.1	83.1	11.6	5.3

Reaction conditions: catalyst, Ru-Cu/TMG-BEN (Ru 3 wt%); temperature, 195 °C; reaction time, 18 h; catalyst amount, 0.6 mol% Ru/glycerol; glycerol, 5 mmol (0.46 g); water, 1.0 mL; Initial pressure at 195 °C, 10.0 MPa.[a] Including 1-propanol (1-PO), 2-propanol (2-PO), C_2H_5OH, and CH_3OH.

Table 2 Effect of H_2 pressure on the performance of Ru-Cu/TMG-BEN

T/°C	P/MPa	Conversion of glycerol/%	Selectivity to liquid product/%	C-based composition of liquid products/mol%		
				1,2-PDO	EG	Others[a]
210	10	71.4	65.0	83.3	14.7	2.0
	8	71.5	67.0	85.7	12.3	2.0
	6	77.4	66.3	84.6	12.9	2.5
	5	87.6	67.0	84.5	13.5	2.0
	2.5	81.6	31.3	87.3	7.3	5.4
230	10	100.0	98.5	86.4	9.4	4.2
	8	100.0	99.5	85.4	7.6	7.0
	6	100.0	79.1	83.4	3.3	13.3

Reaction conditions: catalyst, Ru-Cu/TMG-BEN (Ru 3 wt%, Ru/Cu 3/1); reaction time, 18 h; catalyst amount, 0.3 mol% Ru/glycerol; glycerol, 5 mmol (0.46 g); water, 1.0 mL.[a] Including 1-propanol (1-PO), 2-propanol (2-PO), C_2H_5OH, and CH_3OH.

cleavage and good activity towards C–O bond hydrogenation. The results in Table 1 indicate that addition of Cu to Ru/TMG-BEN could restrain the catalyst from catalyzing the cleavage of the C–C bond and increase the selectivity to 1,2-PDO and other liquid products. With the decreased molar ratio of Ru to Cu, the conversion of glycerol gradually decreased and there were maxima in both of the selectivity to liquid product and the content of 1,2-PDO in the liquid product (Table 1, Entries 2–7). When the molar ratio of Ru/Cu was 3/1, Ru-Cu/TMG-BEN exhibited the best performance (Table 1, Entry 3).

Effect of reaction conditions

In this work, the effects of reaction temperature, reaction time and H_2 pressure on the reaction were investigated systematically using the catalyst Ru-Cu/TMG-BEN with Ru/Cu molar ratio of 3/1 because it was the best catalyst, as can be seen from Table 1.

The effect of pressure was studied at 210 °C and 230 °C, and the results are given in Table 2. The data in the table indicate that the pressure did not affect the content of 1,2-PDO in the liquid product considerably. At 210 °C, the selectivity to liquid product was low when the pressure was low (2.5 MPa). At 230 °C, glycerol could be converted completely at the pressures studied. The selectivity to liquid product also approached 100% under 8 MPa and 10 MPa, and the content of 1,2-PDO was 86%. Therefore, the yield of 1,2-PDO could be as high as 85.1% at the optimized reaction conditions.

Table 3 presents the results at 10 MPa and different temperatures. The conversion of glycerol increased with the rising temperature and reached 100% at 230 °C and 240 °C. The selectivity to liquid product also increased with increasing temperature. The content of 1,2-PDO in the liquid product reached a maximum at 230 °C. At 240 °C, the content of 1,2-PDO in the liquid product decreased to 76.1%, indicating that high temperature promoted the formation of small molecular products.

In order to investigate the effect of TMG on the properties of the as-prepared catalyst, the reaction was conducted using Ru-Cu/TMG-BEN and Ru-Cu/BEN at the same reaction conditions. As shown in Table 3, when the reaction was conducted for 18 h, the conversion of glycerol over the two catalysts was all 100% (Table 3, Entry 5 and Entry 8), and the content of 1,2-PDO in the liquid product was similar. The selectivity to liquid product over Ru-Cu/TMG-BEN was 98.5%, which was much higher than 78.1% catalyzed by Ru-Cu/BEN. When the reaction was conducted for a short time of 10 h, the conversion of glycerol over the two catalysts was all less than 100% (Table 3, Entry 6 and Entry 9). Although the content of 1,2-PDO in

Table 3 Effect of reaction temperature on the performance of Ru-Cu/TMG-BEN

Entry	T/°C	Glycerol conversion/%	Selectivity to liquid product/%	C-based composition of liquid products/mol%		
				1,2-PDO	EG	Others[a]
1	190	48.8	34.0	60.7	32.9	6.4
2	200	59.2	59.6	74.3	22.1	3.6
3	210	71.4	65.0	83.3	14.7	2.0
4	220	90.0	75.7	84.4	13.1	2.5
5	230	100.0	98.5	86.4	9.4	4.2
6	230[b]	86.9	97.3	87.1	9.8	3.1
7	240	100.0	98.9	76.1	9.3	14.6
8	230[c]	100.0	78.1	87.1	9.5	3.4
9	230[d]	80.1	72.1	85.9	11.2	2.9

Reaction conditions: catalyst, Ru-Cu/TMG-BEN (Ru 3 wt%, Ru/Cu 3/1); catalyst amount, 0.3 mol% Ru/glycerol; reaction time, 18 h; glycerol, 5 mmol (0.46 g); water, 1.0 mL; initial pressure, 10.0 MPa.[a] Including 1-propanol (1-PO), 2-propanol (2-PO), C_2H_5OH, and CH_3OH. [b] Reaction time, 10 h. [c] Conducted using the catalyst unmodified with IL, Ru-Cu/BEN (Ru 3 wt%, Ru/Cu 3/1); reaction conditions were the same. [d] Conducted with Ru-Cu/BEN (Ru 3 wt%, Ru/Cu 3/1); reaction time, 10 h.

the liquid product over the two catalysts were similar, Ru-Cu/TMG-BEN showed higher activity and higher selectivity to liquid product than Ru-Cu/BEN. Therefore, Ru-Cu/TMG-BEN exhibited better performance than Ru-Cu/BEN.

Catalyst characterization

Some typical catalysts were characterized by XPS. Fig. 1 displays the XPS spectra of Ru/TMG-BEN, Cu/TMG-BEN, and Ru-Cu/TMG-BEN (Ru/Cu, 3/1 in moles). The binding energy of Ru in Ru/TMG-BEN can be observed at 280.4 eV (Ru3d5, Fig. 1a), and the binding energy of Cu in Cu/TMG-BEN is 933.3 eV (Cu2p3, Fig. 1b). In catalyst Ru-Cu/TMG-BEN, the binding energy of Ru is shifted to 280.6 eV, and that of Cu to 934.0 eV. Therefore, there existed strong interaction between Ru and Cu and some electrons might be transferred from Ru to Cu in the Ru-Cu catalysts.

The morphology and microstructure of the support and catalysts were studied by SEM and TEM. Fig. 2 shows the SEM images of the pristine bentonite (a) and Ru-Cu/TMG-BEN (b). Clearly, the morphology of Ru-Cu/TMG-BEN was similar to that of bentonite. The TEM images of Ru-Cu/TMG-BEN and Ru-Cu/BEN are also shown in Fig. 2. In catalyst Ru-Cu/TMG-BEN, the diameters of the metal particles were in the range of 5–8 nm (Fig. 2c), and the particle size in Ru-Cu/BEN was similar (Fig. 2e). However, after these two catalysts were used separately once, the size of the nanoparticles on the surface of the two catalysts was quite different. For the former, most nanoparticles were still in the range of 5–8 nm (Fig. 2d). The metal particles in catalyst Ru-Cu/BEN aggregated and the size of the nanoparticles increased to about 50 nm (Fig. 2f). It can be deduced that the main reason for the better performance of Ru-Cu/TMG-BEN is that the particle size was unchanged in the reaction process, while the metal particles in Ru-Cu/BEN became larger and larger during the reaction, and therefore, the performance of the catalyst was relatively poor. This indicates that TMG played an important role in dispersing and stabilizing the metallic particles in the catalyst because the only difference of the two catalysts was that ionic liquid TMGL was utilized when preparing Ru-Cu/TMG-BEN.

Bentonite has a layered structure and negative charge in the silicate layers. On the basis of these special characteristics, it can exchange cations with IL or other reagents to compensate the negative charge. There are successful examples which demonstrate that the interactions between nanoparticles and polymers or surfactants can be used to intercalate nanoparticles into the interlayer spaces of montmorillonite. For example, Dékány *et al.* proved rhodium particles can be stabilized by polymers and by the lamellae of layered silicates of montmorillonite.[44] Király *et al.* prepared ultrafine Palladium particles on ationic and nionic clays, mediated by oppositely charged surfactants.[45] In the as-prepared catalyst, TMG ions were fixed on the surface or interlayer of bentonite by electrostatic force after ion-exchange. On the other hand, TMG cations have the ability to stabilize nanoparticles, which stems from their electron-donor properties[46,47] and has been demonstrated in other work.[36–38] The metal particles combined with TMG ions on the surface of the bentonite with the assistance of coordination interaction. In this way, the nanoparticles were supported on the surface or interlayer of bentonite by combination of coordination and electrostatic force. The coordination interaction existed between metallic particles and TMG, and the electrostatic force between TMG and bentonite. Both the electrostatic and coordination forces are very strong, which prohibit aggregation

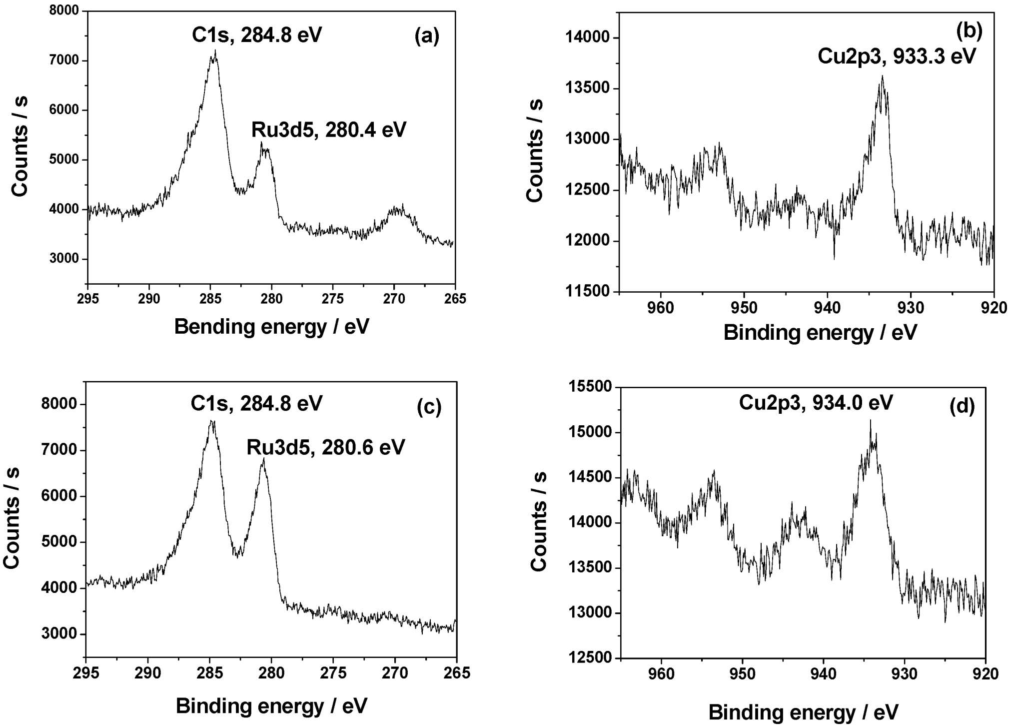


Fig. 1 XPS spectra of catalyst: (a) Ru/TMG-BEN, (b) Cu/TMG-BEN, (c) and (d) Ru-Cu/TMG-BEN (Ru/Cu, 3/1 in moles).

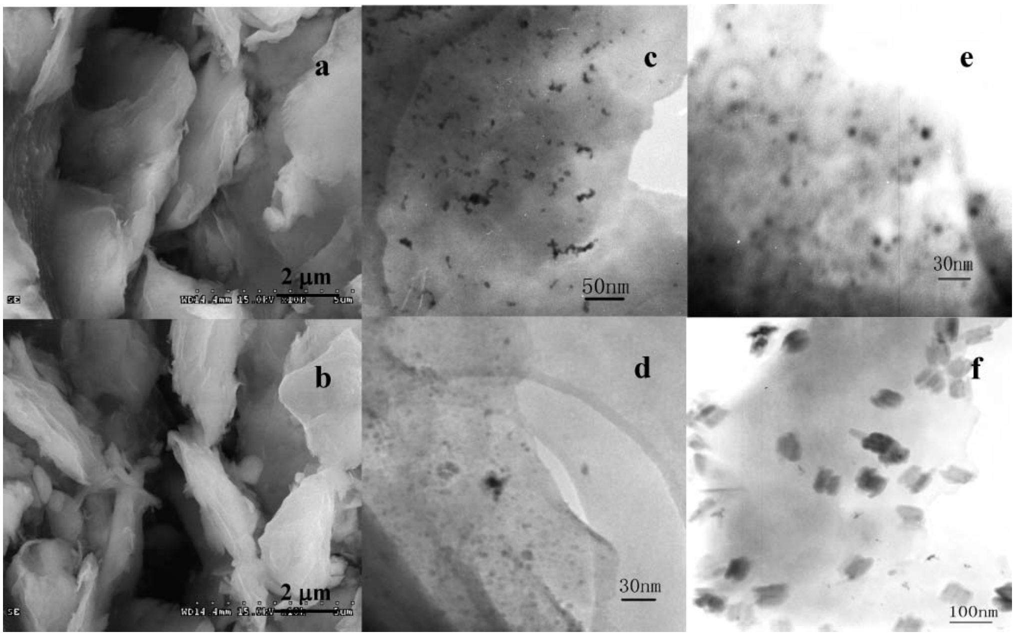


Fig. 2 SEM images of (a) pristine bentonite; (b) Ru-Cu/TMG-BEN; (c) TEM images of fresh catalyst A (Ru-Cu/TMG-BEN); (d) Catalyst A after one run; (e) fresh catalyst B (Ru-Cu/BEN); and (f) catalyst B after one run.

of the nanoparticles effectively. Therefore, the catalyst was stable during the reaction. After reaction, the organic products were collected and analyzed by AAS (atomic absorption spectrum) analysis for Ru and Cu metals, and metal leaching was not detected. Results of recyclability of Ru-Cu/TMG-BEN also supported this from another aspect. It can be seen from Fig. 3 that the activity and selectivity of the catalyst did not change after recycling 4 times.

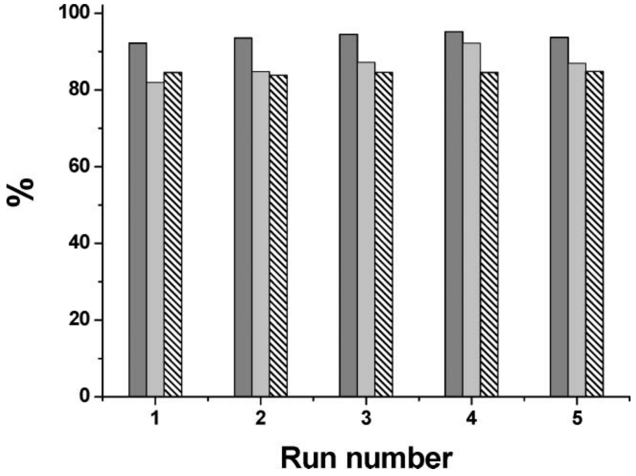


Fig. 3 Results of the recycle of catalyst Ru-Cu/TMG-BEN. ■ Glycerol conversion; □ Selectivity to liquid product; ▨ 1,2-PDO content in liquid product.

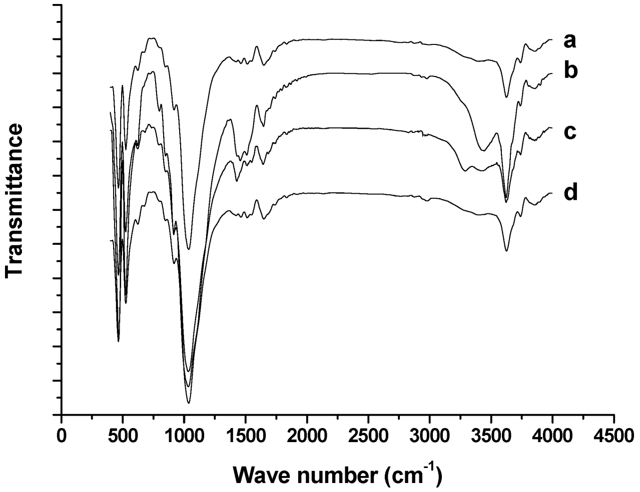


Fig. 4 FT-IR spectra of the pristine bentonite and the as-prepared catalysts: a) the pristine bentonite, b) TMG-bentonite, c) fresh catalyst A (Ru-Cu/TMG-bentonite), and d) catalyst A after one run.

Some characterizations were conducted to confirm the existence of TMG cations on the surface of the catalyst. The presence of the cation of the ionic liquid TMGL in this catalyst was supported by the fact that the catalyst contained 10 wt% organic compound, as determined by TGA. The existence of the TMG cations was also supported by the FT-IR spectra (Fig. 4). The specific peaks of CH_3 group at 1414 cm^{-1}, 1463 cm^{-1}, and 2967 cm^{-1}, and the peak of C=N bond at 1640 cm^{-1} can be observed in the spectrum of Ru-Cu/TMG-BEN which accord well with the FT-IR spectrum of TMG-BEN (Fig. 4). In addition, Fig. 4d shows the FT-IR spectrum of Ru-Cu/TMG-BEN after one run. The specific peaks of the CH_3 group and C=N bond can also be observed clearly, indicating that TMG cations still existed on the surface of bentonite after the reaction. Therefore the metal particles in Ru-Cu/TMG-BEN did not aggregate.

Conclusions

In conclusion, the Ru-Cu bimetals has been successfully supported on bentonite, a cheap and abundant clay, with the aid of ionic liquid TMGL. The cations of TMGL are necessary for the excellent stability of the catalyst. Ru and Cu exhibits excellent combination for catalyzing the hydrogenolysis of aqueous glycerol to produce 1,2-PDO. The catalyst was most efficient with a molar ratio of Ru to Cu of 3/1. 100% conversion of glycerol and 85% yield of 1,2-PDO could be achieved at 230 °C and 8 MPa. The catalyst modified with IL showed excellent recyclability. We believe that more efficient catalysts can be prepared by combination of functional ionic liquids, clays and metals for different reactions.

Acknowledgements

The authors wish to thank the National Natural Science Foundation of China (20733010) for financial support.

References

1 T. Miyazawa, Y. Kusunoki, K. Kunimori and K. Tomishige, *J. Catal.*, 2006, **240**, 213–221.
2 G. W. Huber, J. N. Chheda, C. J. Barrett and J. A. Dumesic, *Science*, 2005, **308**, 1446–1450.
3 S. Fernando, S. Adhikari, C. Chandrapal and N. Murali, *Energy Fuels*, 2006, **20**, 1727–1737.
4 T. Werpy and G. Petersen, Top Value Added Chemicals from Biomass, vol. 1, Results of Screening for Potential Candidates from Sugars and Synthesis Gas, US DOE Report, 2004.
5 C. S. Gong, J. X. Du, N. J. Cao and G. T. Tsao, *Appl. Biochem. Biotechnol.*, 2000, **84**, 543–560.
6 P. L. Rogers, Y. J. Jeon and C. J. Svenson, *Process Saf. Environ. Prot.*, 2005, **83**, 499–503.
7 G. W. Huber, S. Iborra and A. Corma, *Chem. Rev.*, 2006, **106**, 4044–4098.
8 M. Pagliaro, R. Ciriminna, H. Kimura, M. Rossi and C. D. Pina, *Angew. Chem. Int. Ed.*, 2007, **46**, 4434–4440.
9 A. Behr, J. Eilting, K. Irawadi, J. Leschinski and F. Lindner, *Green Chem.*, 2008, **10**, 13–30.
10 C. H. Zhou, J. N. Beltramini, Y. X. Fan and G. Q. Lu, *Chem. Soc. Rev.*, 2008, **37**, 527–549.
11 Y. G. Zheng, X. L. Chen and Y. C. Shen, *Chem. Rev.*, 2008, **108**, 5253–5277.
12 D. Zimmerman and R. B. Isaacson, US Pat., 3 814 725, 1974 (Shell).
13 P. N. Caley and R. C. Everett, US Pat., 3 350 871, 1967 (DuPont).
14 E. P. Maris and R. J. Davis, *J. Catal.*, 2007, **249**, 328–337.
15 S. Ludwig and E. Manfred, US Pat., 5,616,817, 1997.
16 C. Montassier, D. Giraud and J. Barbier, *Stud. Surf. Sci. Catal.*, 1988, 165–170.
17 M. A. Dasari, P.-P. Kiatsimkul, W. R. Sutterlin and G. J. Suppes, *Appl. Catal. A: Gen.*, 2005, **281**, 225–231.
18 L. Huang, Y. L. Zhu, H. Y. Zheng, Y. W. Li and Z. Y. Zeng, *J. Chem. Technol. Biotechnol.*, 2008, **83**, 1670–1675.
19 I. Furikado, T. Miyazawa, S. Koso, A. Shimao, K. Kunimori and K. Tomishige, *Green Chem.*, 2007, **9**, 582–588.
20 C.-W. Chiu, A. Tekeei, J. M. Ronco, M.-L. Banks and G. J. Suppes, *Ind. Eng. Chem. Res.*, 2008, **47**, 6878–6884.
21 T. Kurosaka, H. Maruyama, I. Naribayashi and Y. Sasaki, *Catal. Commun.*, 2008, **9**, 1360–1363.
22 J. Chaminand, L. Djakovitch, P. Gallezot, P. Marion, C. Pinel and C. Rosier, *Green Chem.*, 2004, **6**, 359–361.
23 L. Ma, D. H. He and Z. P. Li, *Catal. Commun.*, 2008, **9**, 2489–2495.
24 J. Feng, H. Y. Fu, J. B. Wang, R. X. Li, H. Chen and X. J. Li, *Catal. Commun.*, 2008, **9**, 1458–1464.
25 D. G. Lahr and B. H. Shanks, *Ind. Eng. Chem. Res.*, 2003, **42**, 5467–5472.
26 D. G. Lahr and B. H. Shanks, *J. Catal.*, 2005, **232**, 386–394.
27 C. Montassier, J. C. Menezo, L. C. Hoang, C. Renaud and J. Barbier, *J. Mol. Catal.*, 1991, **70**, 99–110.
28 B. Casale and A. M. Gomez, US Pat., 5 276 181, 1994.
29 E. P. Maris, W. C. Ketchie, M. Murayama and R. J. Davis, *J. Catal.*, 2007, **251**, 281–294.
30 E. P. Maris and R. J. Davis, *J. Catal.*, 2007, **249**, 328–337.
31 S. Wang and H. C. Liu, *Catal. Lett.*, 2007, **117**(1–2), 62–67.
32 M. Balaraju, V. Rekha, P. S. Sai Prasad, R. B. N. Prasad and N. Lingaiah, *Catal. Lett.*, 2008, **126**, 119–124.
33 Z. W. Huang, F. Cui, H. X. Kang, J. Chen, X. Z. Zhang and C. G. Xia, *Chem. Mater.*, 2008, **20**, 5090–5099.
34 A. P. Umpierre, G. Machado, G. H. Fecher, J. Morais and J. Dupont, *Adv. Synth. Catal.*, 2005, **347**, 1404–1412.
35 C. P. Mehnert, E. J. Mozeleski and R. A. Cook, *Chem. Commun.*, 2002, 3010–3011.
36 J. Huang, T. Jiang, H. X. Gao, B. X. Han, Z. M. Liu, W. Z. Wu, Y. H. Chang and G. Y. Zhao, *Angew. Chem. Int. Ed.*, 2004, **43**, 1397–1399.
37 J. Huang, T. Jiang, B. X. Han, W. Z. Wu, Z. M. Liu, Z. L. Xie and J. L. Zhang, *Catal. Lett.*, 2005, **103**, 59–62.
38 X. M. Ma, Y. X. Zhou, J. C. Zhang, A. L. Zhu, T. Jiang and B. X. Han, *Green Chem.*, 2008, **10**(1), 59–66.
39 Y. L. Gu, C. Ogawa, J. Kobayashi, Y. Mori and S. Kobayashi, *Angew. Chem. Int. Ed.*, 2006, **45**, 7217–7220.
40 M. R. Castillo, L. Fousse, J. M. Fraile, J. I. García and J. A. Mayoral, *Chem.-Eur. J.*, 2006, **13**, 287–291.
41 S. D. Miao, Z. M. Liu, B. X. Han, J. Huang, Z. Y. Sun, J. L. Zhang and T. Jiang, *Angew. Chem. Int. Ed.*, 2006, **45**(2), 266–269.
42 T. Kawabata, T. Mizugaki, K. Ebitani and K. Kaneda, *J. Am. Chem. Soc.*, 2003, **125**, 10486–10487.
43 H. X. Gao, B. X. Han, J. C. Li, T. Jiang, Z. M. Liu, W. Z. Wu, Y. H. Chang and J. M. Zhang, *Synth. Commun.*, 2004, **34**, 3083–3089.
44 S. Papp, J. Szél, A. Oszkó and I. Dékány, *Chem. Mater.*, 2004, **16**(9), 1674–1685.
45 Z. Király, B. Veisz, Á. Mastalir and Gy. Köfaragó, *Langmuir*, 2001, **17**(17), 5381–5387.
46 S. Aoki, K. Iwaida, N. Hanamoto, M. Shiro and E. Kimura, *J. Am. Chem. Soc.*, 2002, **124**, 5256–5257.
47 P. J. Bailey and S. Pace, *Coordin. Chem. Rev.*, 2001, **214**, 91–141.