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Accepted Article

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To be cited as: *Chem. Asian J.* 10.1002/asia.201700412

Link to VoR: http://dx.doi.org/10.1002/asia.201700412

A Journal of
ACES
Asian Chemical Editorial Society

A sister journal of **Angewandte Chemie** and **Chemistry – A European Journal**

WILEY-VCH

Chemistry - An Asian Journal 10.1002/asia.201700412

Efficient generation of lactic acid from glycerol over Ru-Zn-Cu(I)/HAP catalyst

Zhiwei Jiang,[a] Zhanrong Zhang,[a] Tianbin Wu,[a] Pei Zhang,[a] Jinliang Song,[a] Chao Xie,[a] and Buxing Han*[a,b]

Abstract: The biodiesel production process generates a significant amount of glycerol as a by-product. Its valorization has attracted worldwide attention in terms of improving the overall effectiveness and profitability of bio-diesel production. Herein, we report hydroxyapatite (HAP) supported Ru-Zn-Cu(I) (Ru-Zn-Cu(I)/HAP) as effective catalysts for the transformation of glycerol to lactic acid (LA).The catalysts were characterized by different techniques. The effects of catalyst composition, reaction time and temperature on conversion and the product distribution were investigated. It was revealed that Ru nanoparticles of less than 2 nm were dispersed uniformly on HAP. Cu(I) could effectively inhibit the cleavage of C-C bonds, leading to improved yields of LA. Under optimized conditions, the yield of LA could achieve 70.9% over Ru-Zn-Cu(I)/HAP. Furthermore, the catalyst could be reused at least four times without obvious loss of activity and selectivity.

Introduction

Efficient use of natural resources in a sustainable and environmentally benign manner is important for the transition from the current petro-based economy to a future bio-based economy.[1] The production of biodiesel via transesterification of triglycerides is a promising and attractive approach for the generation of renewable energy.[2] However, during this process, glycerol (around 10 wt.%) is inevitably generated as a by-product.[3] Valorization of the surplus glycerol to value-added products such as high-value chemical compounds is therefore of great importance, in terms of improving the overall effectiveness and profitability of bio-diesel production plants. In this context, many studies have demonstrated the potential of glycerol as a bio-derived building block for the synthesis of variousvalue-added chemical products, such as propanediols[4], pyruvaldehyde,[5] glyceric acid,[6] acrylic acid,[7] and acrolein[8].

Among the various products that can be derived from glycerol, lactic acid (LA) is an important bio-based platform chemical and has been extensively employed in various industrial sectors such as food, pharmaceutical and chemical industries.[9] In addition, this trend is also promoted by the growing interest in the utilization of LA for the production of biodegradable and biocompatible polylactic acid which is a sustainable bioplastic material.[10] Nowadays, LA is manufactured primarily *via* anaerobic fermentation of edible carbohydrates (e.g. glucose or sucrose).[11] However, this technology suffers from poor productivities and generally involves complicated processes. It is thus desirable to develop alternative methods enabling an effective large-scale production of LA.

The conversion of glycerol to LA has been studied in both homogeneous[12] and heterogeneous phases.[13] Lu et al. investigated the conversion of glycerol to LA using homogenous iridium-based catalytic systems under H_2-acceptorless conditions and high yield of LA could be obtained.[12b] In heterogeneous catalytic systems, the conversion of glycerol to LA was investigated under reductive conditions or in the presence of hydrogen acceptor. Maris et al. used commercial carbon-supported Ru and Pt catalysts to generate LA from glycerol in basic solutions at 473 K and 40 bar H_2.[13e] Shen et al. found that the selectivity of LA could reach 86% at 30% glycerol conversion with a TiO_2 supported bimetallic Au-Pt catalyst, using oxygen as hydrogen acceptor.[13a] The use of oxygen as hydrogen acceptor leads to many undesired side reactions, rendering the overall process less effective. To address this drawback, ethylene was utilized as hydrogen acceptor with heterogeneous monometallic Pt catalyst, the selectivity of LA could be up to 95%.[13d]

During the conversion of glycerol to LA, the dehydrogenation of glycerol is the rate-determining step and Ru is well known to be active for this transformation.[12c, 13e] Notably, copper could also promote the dehydrogenation reaction and suppress the undesired C-C bond rupture.[14] Moreover, some studies proposed that LA was generated from glyceraldehyde via 1, 2-hydride shift.[15] Zn^{2+} could potentially enhanced the 1, 2-hydride shift and improve the yield of LA.[16]

Hydroxyapatite (HPA) has high ion-exchange and adsorption abilities, and therefore the active species can be immobilized stably on its surface. HAP supported Ru,[17] Cu,[18] Zn,[19] Ag,[20] Pd,[21] Au[22] have shown excellent catalytic performances in a wide range of chemical reactions such as oxidative cleavage of alkenes, CO_2 cycloaddition reactions, epoxidation of styrene, and partial hydrogenation of benzene to cyclohexene.

To the best of our knowledge, HAP as a catalyst support for glycerol conversion has not been reported. Herein, we prepared

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Ru/HAP, Ru-Zn/HAP Ru-Zn-Cu(I)/HAP by an ion-exchange method. The effects of catalyst composition and reaction conditions on the distribution of liquid and gaseous products were investigated. It was found that the catalysts had satisfactory performance for the reaction. Especially, Ru-Zn-Cu(I)/HAP was very active and selective for the reaction.

Results and Discussion

Catalyst characterization

The XRD patterns of the HAP and as-prepared Ru/HAP, Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP catalysts are shown in Figure 1. The XRD patterns of Ru/HAP catalyst was in good consistency with the parent HAP. This indicates that there were no transformations of the catalyst support framework during preparation of the Ru/HAP. In addition, new diffraction peaks were observed in the XRD patterns of Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP catalysts, suggesting the formation of new crystals for Zn-HAP and Cu(I)-HAP. The characteristic diffraction band of Ru (2θ = 44°) cannot be observed due to the small size and high dispersion of the Ru particles on the HAP.

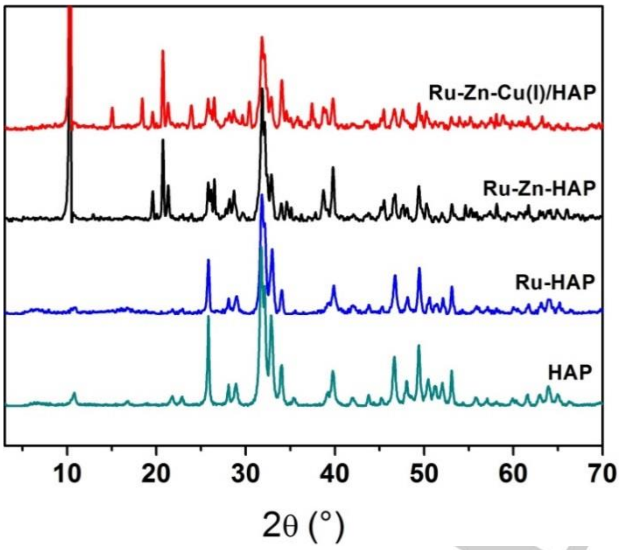


Figure 1. XRD patterns of HAP and the synthesized Ru/HAP, Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP.

Figure 2 illustrates the TEM images of the Ru-HAP, Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP catalysts. It can be seen from Figure 2a-c that the Ru nanoparticles dispersed uniformly on the surface of the HAP, suggesting that HAP had excellent ion-exchange ability to adsorb the Ru precursors and prevented the aggregation of metallic particles during the reduction process. Figure 2d shows the high resolution TEM (HRTEM) image of the Ru-Zn-Cu(I)/HAP and the histogram of Ru particle size distribution. The average particle sizes are around 1.6 nm. The lattice fringes with interplanar spacing about 2.05 Å visualized in the inserted figure of Figure 2d are ascribable to the (101) planes of *hcp* Ru, indicating that the Ru NPs are crystalline. No metallic Zn particles were observed in the TEM images of the Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP (Figure 2b and 2c). In addition, elemental distribution images of Ru-Zn-Cu(I)/HAP further illustrate the co-existence of Ru, Zn and Cu elements (Figure S1).

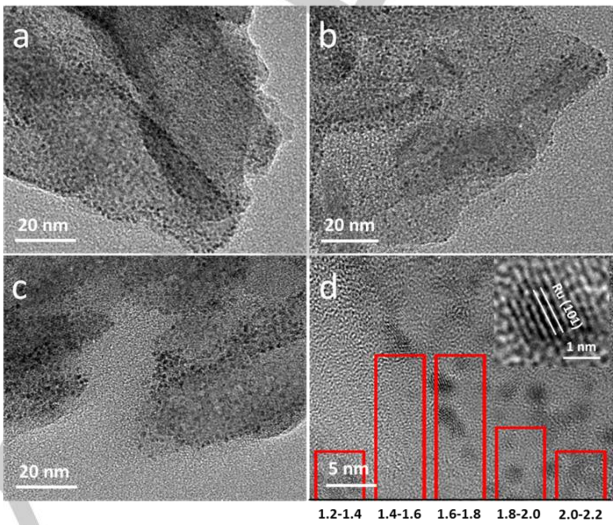


Figure 2. TEM images of (a) Ru/HAP, (b) Ru-Zn/HAP, (c) Ru-Zn-Cu(I)/HAP, (d) HRTEM and Ru particle size distribution of Ru-Zn-Cu(I)/HAP, the corresponding PSD histogram of the Ru NPs is given in the insert.

X-ray photoelectronspectroscopy (XPS) was used to characterize the surface composition of Ru-Zn-Cu(I)/HAP catalyst (Figure 3). Characteristic band for Cl 2p, I 3d or N 2p cannot be observed, indicating that the Cl^-, I^- and NO_3^- were completely removed. The narrow scan spectra of Zn 2p, Ru 3d and Cu 2p are shown in Figure 3b, 3c and 3d. In Figure 3b, the peak centered at 1022.6 eV was assigned to Zn 2p$_{3/2}$, corresponding with 1022.5 eV of Zn^{2+} reported elsewhere.[24] The Zn 2p spectra of Zn/HAP and Ru/Zn/HAP are given in Figure S2. The binding energies (BEs) of Zn 2p$_{3/2}$ in the Zn/HAP (1022.4 eV) and Ru/Zn/HAP (1022.6 eV) were close to the value reported in the literature, demonstrating that valence of Zn has not changed during the substitution procedure.[25]

Figure 3c shows the Ru 3d spectrum of the Ru-Zn-Cu(I)/HAP catalyst. The binding energy of 281.1 eV is assigned to Ru(0) 3d$_{5/2}$, indicating that the metallic Ru was formed during the reduction process. No peak for Ru^{n+} ion was observed in the spectrum. The peak of Ru(0) 3d$_{3/2}$ overlapped with the C 1s peak. For comparison, the Ru 3d spectrum of the Ru/HAP and Ru-Zn/HAP are shown in Figure S3. The BEs of Ru (0) 3d$_{5/2}$ in Ru-Zn-Cu(I)/HAP (281.1 eV), Ru-Zn/HAP (281.1 eV) and Ru/HAP (280.9) were higher than that of metallic Ru (280.0 eV).[26] The higher energy value may be attributed to the electron properties of the HAP framework. The interaction between Ru and the oxygen in the HAP framework renders the Ru surface electron deficient, resulting in the increase of the BE of Ru (0) particles.[27]

Figure 3d shows the Cu 2p spectrum of the Ru-Zn-Cu(I)/HAP. The BE of Cu $2p_{3/2}$ (933.9 eV) was higher than that of Cu(II) species (933.4 eV) on the HAP support (Figure S4). Moreover, the BE of Cu $2p_{3/2}$ in the Cu(I)/HAP reported in the literature was 934.2 eV,[18] demonstrating that Cu(I) and Cu(II) coexisted in fresh Ru-Zn-Cu(I)/HAP. The existence of Cu(II) may be attributed to the oxidation of Cu(I) during the XPS sampling procedure.

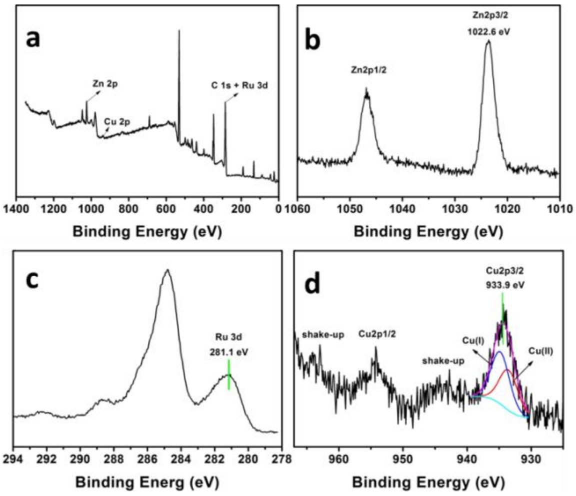


Figure 3. XPS spectra of the Ru-Zn-Cu(I)/HAP catalyst (a) full spectrum; (b) Zn 2p spectrum; (c) Ru 3d spectrum; (d) Cu 2p spectrum.

As shown in the TEM images and the XPS spectra of Ru-Zn-Cu(I)/HAP, Zn^{2+} exchanged onto HAP could not be reduced by hydrogen at 200 °C. Ru^{3+} ions were reduced to Ru nanoparticles supported on HAP by H_2. The electronegativity of Ru in Ru-Zn-Cu(I)/HAP was higher that of the metallic Ru due to a tendency to attract the electrons from the oxygen in the HAP framework. Cu(I) was successful exchanged onto Ru-Zn/HAP through hydrothermal method, and didn't affect the chemical state of the Ru and Zn on Ru-Zn/HAP. Furthermore, the acidity of Ru/HAP, Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP were characterized by NH_3-TPD of, as shown in Figure S5. The results indicate that Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP had higher acidity than Ru/HAP, which was attributed to addition of Zn^{2+}. The higher acidity of Ru-Zn/HAP and Ru-Zn-Cu(I)/HAP could be favorable to 1,2-hydride shift, and thus enhanced the selectivity of LA.

Catalytic activity

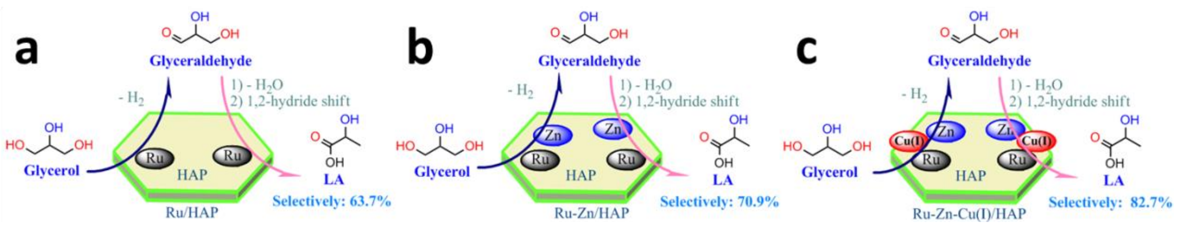
The conversion of glycerol to LA with the production of hydrogen was carried out at 140 °C under vacuum condition in the presence of a base (NaOH to glycerol molar ratio of 1.5). The results of the catalytic reactions are compiled in Table 1. Blank reactions carried out demonstrated that glycerol was not converted under our reaction conditions in the absence of catalyst or base. This is consistent with the results reported by Liu et al.[13a] Ru/HAP showed high activity with 100% conversion, while a relatively low LA selectivity of 63.7%, due to the formation of formic acid (FA) and 1,2-PROP (Table 1, entry 1). Moreover, the gas product contained a large amount of methane (13.7 mol%) besides hydrogen. Maris et al also reported the similar results.[13e] We can infer from this experimental result that the dehydrogenation of glycerol to glyceraldehydes is base-assisted in the present of Ru NP-based catalyst. 1,2-PROP was formed from hydrogenation of pyruvaldehyde or its tautomer with hydrogen.[13d] The degradation product was primarily formic acid with CO_2 and methane gas products because Ru is effective for the cleavage of C-C hydrocarbon bonds.[13e]

To investigate the influence of the different ions on the glycerol conversion in the present of Ru/HAP, several salts were studied (Table 1, entries 2 to 5). Upon adding $ZnSO_4$ in the reaction system, a higher selectivity (78.4%) of LA was obtained compared to that of Ru/HAP without $ZnSO_4$, with a lower glycerol conversion (74.5%) and relative high yields of FA and methane. This reveals that Zn^{2+} could improve effectively the formation of LA through benzilic acid rearrangement and could not suppress the effect of Ru. Cu based catalysts has been demonstrated conversion of glycerol to LA with high yield.[13c] $CuSO_4$ and Cu_2O

Table 1. Reaction results over different catalysts for the conversion of glycerol to LA[a]

entry	catalyst	additive	Conv. GLY(%)	liquid prod. (%)	sel.liquid prod. (%) LA	FA	PROP	EG	GLYA	TA	methane sel. (%)
1	Ru/HAP	----	100.0	68.7	63.7	28.5	6.0	1.3	0.3	0.2	13.7
2	Ru/HPA	$CuSO_4$	100.0	64.0	57.3	8.2	0.9	0.3	6.6	24.7	0.3
3	Ru/HAP	Cu	94.3	67.1	45.4	22.4	29.4	1.2	1.1	0.5	12.5
4	Ru/HAP	$ZnSO_4$	74.5	65.2	78.4	13.0	3.5	4.2	0.8	0.4	2.4
5	Ru/HAP	Cu_2O	100.0	85.4	69.5	5.3	8.7	0.5	12.0	4.5	0.7
6	Ru-Zn/HAP	----	72.3	70.9	75.7	13.6	4.9	5.1	0.7	0.2	1.3
7	Ru-Zn/HAP	Cu_2O	73.9	98.9	83.5	6.5	2.1	0.8	5.5	1.6	0.2
8[b]	Ru-Zn/HAP	Cu_2O	100.0	87.5	83.9	10.0	1.8	0.6	2.0	1.7	0.3
9[c]	Ru-Zn-Cu(I)/HAP	-----	100.0	88.7	82.7	8.1	2.1	0.7	2.5	2.2	0.2

[a] Reaction conditions: 20 mg catalyst, 2 mg additive, 0.1 g glycerol (GLY), 0.065 g NaOH (NaOH to glycerol molar ratio of 1.5), 2 mL water, 140 °C, 12 h. [b] 21 h. [c] 21 h.



Scheme 1. Proposed reaction pathway for glycerol conversion over Ru/HAP (a), Ru-Zn/HAP (b), and Ru-Zn-Cu(I)/HAP (c).

could effectively decline the production of FA and methane. Moreover, Cu_2O could raise notably the yield of the liquid products, suggesting that Cu_2O effectively restrained the the cleavage of C-C hydrocarbon bonds. In addition, 1,2-PROP yield would increase in the presence of Cu metal (Table entry 3), which is consistent with the results of Cu/Al_2O_3 catalyst.[28]

Over Ru-Zn/HAP, high selectivity of LA (75.7%) and hydrogen (99.8%) at a glycerol conversion of 73.9%, but the yield of liquid product was relatively low (Table1 entry 6). By adding Cu_2O in the above reaction system, the selectivity of LA (83.5%) and the yield of liquid products (98.9%) were both significantly enhanced (Table entry 7). By increasing the reaction time from 12 to 21 h, the glycerol conversion, catalyzed by Ru-Zn/HAP in the present of Cu_2O, reached 100%, maintaining the high LA selectivity of 83.9% (Table 1, entry 8). Finally, the Ru-Zn-Cu(I)/HAP was also used to convert glycerol with a high yield of LA (70.9%) and a high selectivity of hydrogen (99.8%). The gas chromatogram of the gas products was shown in Figure S6. This suggested that Cu(I) reduced effectively the degradation of the intermediates for glycerol conversion, leading to a high selectivity of LA in liquid products and a low selectivity of methane in gas products.

It has been well established that LA is generated from glycerol via dehydrogenation of glycerol to glyceraldehyde, base-catalyzed dehydration and 1,2-hydride shift of the intermediate. As shown in Scheme 1a, LA selectivity was was relatively low on Ru/HAP, most probably due to the cleavage of C-C bonds over this catalyst. The selectivity of LA increased significantly over Ru-Zn/HAP because of the presence of Zn active sites (Scheme 1b), as Zn^{2+} ions favored the 1,2-hydride shift of pyruvaldehyde to LA. As Cu(I) was introduced into the Ru-Zn/HAP catalyst, the cleavage of C-C bonds was restrained notably, resulting in the improved catalytic performance for glycerol conversion (Scheme 1c).

The effect of reaction time

The effect of reaction time on glycerol dehydrogenation was investigated on the Ru-Zn-Cu(I)/HAP catalyst. As displayed in Figure 4, glycerol conversion increased from 49% to 100% when the reaction time was increased from 6 to 24 h. In addition, the selectivity for GLYA was found to gradually decline with the increase in reaction time, while the selectivity for FA enhance from 4.9 to 8.1, suggesting that the GLYA would further degrade during the reaction process. It should be noted that the selectivity for LA was very high (81.9~83.2) in the full time range, indicating the high efficiency of the Ru-Zn-Cu(I)/HAP catalyst for glycerol conversion.

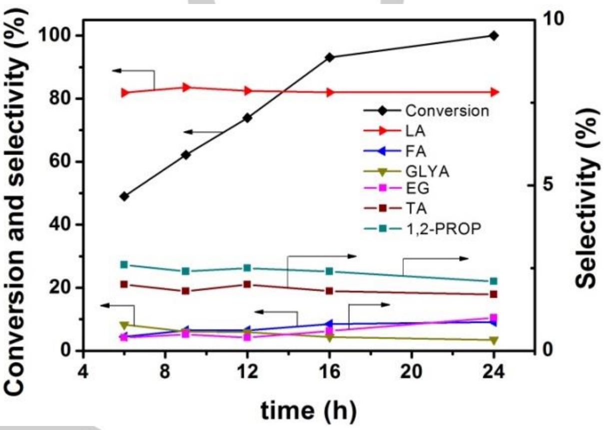


Figure 4. Time course of glycerol conversion over Ru-Zn-Cu(I)/HAP catalyst. Reaction conditions: 20 mg catalyst, 0.1 g glycerol, NaOH, 0.065g, and 2 mL water, 140 °C.

Table 2. Reaction results over Ru-Zn-Cu(I)/HAP catalyst for conversion of glycerol to LA at different temperatures [a]

	Temperature		**sel.liquid prod. (%）**					
Entry	(°C)	Conv. (%)	LA	FA	PROP	EG	GLYA	TA
1	100	26.7	80.1	9.5	0.5	0.6	6.2	3.1
2	120	42.2	81.8	8.6	1.4	0.6	5.4	2.2
3	140	72.8	83.6	7.8	2.2	0.4	4.4	1.6
4	160	83.6	80.9	10.3	4.6	0.5	2.2	1.5

[a] Reaction conditions: 20 mg catalyst, 0.1 g glycerol, NaOH, 0.065 g, and 2 mL water, reaction time of 12 h.

The effect of reaction temperature

The effect of reaction temperature on the glycerol conversion and product distribution is summarized in Table 2. Glycerol conversion was enhanced with increasing temperature. The selectivity of LA increased from 80.1% at 100 °C to 83.6% at 140 °C. However, the selectivity reduced to 80.9% at 160 °C. Nevertheless, the selectivity of 1,2-PROP slightly increased from 0.5% to 4.6% with the increasing of reaction temperature. Conversely, the selectivity for GLYA and TA marginally declined.

In addition, the high reaction temperature also favored the production of FA from glycerol. Hence, an appropriate reaction temperature was necessary for the conversion of glycerol to LA.

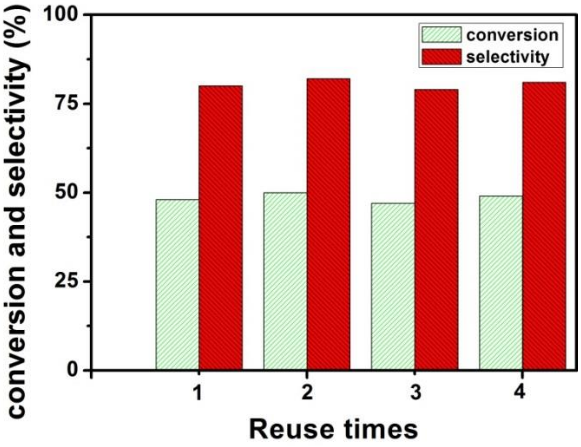


Figure 5. Reusability of the Ru-Zn-Cu(I)/HAP for glycerol conversion. Reaction conditions: 20 mg catalyst, 0.1 g glycerol, NaOH, 0.065 g, and 2 mL water, 6 h.

Reuse of the catalyst

The reusability of the Ru-Zn-Cu(I)/HAP catalyst for the glycerol conversion was investigated under the optimized reaction conditions (Figure 5). The catalyst could be reused at least four times without notable changes. From the TEM images of the fresh catalyst and the catalyst reused after four cycles (Figure 6), it is obvious that Ru nanoparticles were still highly dispersed on HAP (Figure 6b) and the change of the morphology of the catalyst was not obvious. The thermogravimetric (TG) and ICP experiments of the fresh catalyst and the catalyst reused after four cycles was examined. The TG study indicate that the thermal stabilization of the Ru-Zn-Cu(I)/HAP catalyst after reused was not changed compared to the fresh catalyst (Figure S7). ICP analysis showed that the contents of Ru, Zn, and Cu in Ru-Zn-Cu(I)/HAP before and after reaction was nearly the same. This indicates that the Ru-Zn-Cu(I)/HAP was stable as catalyst for converting glycerol to LA under the given reaction conditions.

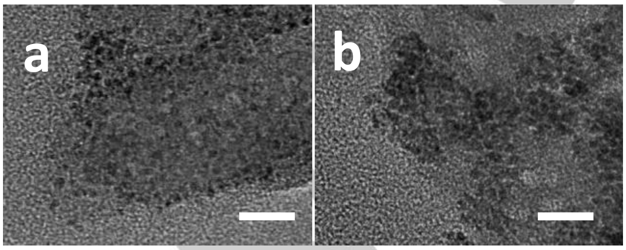


Figure 6. TEM images of fresh Ru-Zn-Cu(I)/HAP (a) and the Ru-Zn-Cu(I)/HAP after reused four times (b). The scar bar is 10 nm.

Conclusions

In summary, Ru/HAP, Ru-Zn/HAP, and Ru-Zn-Cu(I)/HAP catalysts have been prepared by an ion-exchange method. They can be used for transformation of glycerol into LA effectively in alkaline aqueous solutions. The Ru-Zn-Cu(I)/HAP is most effective for the reaction and the yield of LA can reach 70.9% at 140 °C. Compared to the Ru/HAP catalyst, the introduction of Zn^{2+} into the catalyst could significantly promote the selectivity of LA and Cu(I) could effectively inhibit the cleavage of C-C bonds, leading to high yields of LA. The catalyst is stable and can be reused for at least four times without decreasing its catalytic activity and selectivity.

Experimental Section

Materials

Glycerol (GLY, 98%), lactic acid (0.1 N), tartronic acid (TA, 98%) were purchased from Alfa Aesar. Formic acid (FA, >98%) was obtained from Fluka. Acetic acid (1 N) was provided by Aladdin. H_2SO_4 (98%), acetic acid (AA, 99%), 1,2-propylene glycol (PROP), ethylene glycol (EG), glyceric acid (GLYA) $Zn(NO_3)_2{\cdot}6H_2O$, Ruthenium (III) chloride trihydrate ($RuCl_3{\cdot}3H_2O$), sodium hydroxide (NaOH), $Cu(NO_3)_2{\cdot}3H_2O$, Cu_2O, Cu powder, CuI, acetonitrile, hydroxyapatite ($[Ca_5(PO_4)_3OH]$) were all A. R. grade and purchased from Sinopharm Chemical Reagent Co. Ltd.

Catalyst preparation

The Ru, Ru-Zu catalysts supported on HAP with various contents were prepared by ion-exchange method. In a typical procedure, HAP (1 g) was dispersed in double deionized water (300 mL) under vigorous stirring for 2 h at room temperature. Then a certain amount of $RuCl_3$ aqueous solution (Ru: 10 wt.%) with various amounts of $Zn(NO_3)_2$ was added into the HPA suspension. After being stirred for 2 h, the slurry was heated and refluxed at 110 °C for 24 h. The obtained solid was collected by filtration and washed with deionized water until the Cl^- and NO_3^- were not detectable. The as-prepared catalyst was dried under vacuum at 60 °C overnight and was then reduced in pure H_2 at 200 °C for 2 h and subsequently cooled slowly to room temperature in Ar. The catalysts without Zn are denoted as Ru/HAP. When the nominal Ru/Zn wight ratio in the catalyst was 10:10 (i.e., Ru-Zn/HAP), the actual loadings of Ru and Zn determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES) were 7.49 wt% and 9.78 wt%, respectively. For the preparation of Ru-Zn-Cu(I)/HAP, CuI (0.19g, 1mmol) was dissolved in acetonitrile-water (70 mL, 60:10). 0.5 g Ru-Zn/HAP was dispersed in the CuI solution under vigorous stirring for 1h. The obtained mixture was sealed in a 100 mL Teflon lined autoclave, heated to 140 °C in an oil bath and kept for 24 h. After cooled to room temperature, the obtained solid was washed with acetonitrile until I^- was not detectable. The the solid materials were washed with ethanol followed by drying *in vacuo* overnight at 60 °C, yielding the Ru-Zn-Cu(I)/HAP catalyst with Cu content of 0.49 wt% as measured by ICP-AES: 0.49 wt%).

Catalyst characterization

The contents of the Ru, Zn and Cu in the catalysts were determined by ICP-AES (PROFILE. SPEC, Leeman). Powder X-ray diffraction (XRD) patterns were recorded on a Rigaku D/max-2500 X-ray diffractometer using Cu Kα radiation (λ = 0.1406 nm). The structural properties were characterized by transmission electron microscopy (TEM, JEOL JEM-2100F). The X-ray photoelectron spectroscopy (XPS) data were obtained with an ESCALab 220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure was about 3×10^{-9} mbar. The binding energies were referenced to the C 1s line at 284.8 eV from adventitious carbon. Temperature-programmed desorption of ammonia (NH_3-TPD) was performed on Micromeritics' AutoChem 2950 HP Chemisorption Analyzer. Thermogravimetric analysis (TGA) was carried out on a Pyris TGA (Perkin-Elmer) at a heating rate of 10 °C/min between 50 and 800 °C under nitrogen atmosphere.

Catalytic conversion of glycerol

The conversion of glycerol was performed in a 10 mL Teflon-lined stainless steel autoclave equipped with a magnetic stirrer, which was similar to that used previously.[23] In a typical experiment, 0.1 g glycerol, 20 mg catalyst, 0.065 g NaOH, and 2 mL water were introduced into the reactor. The air in the reactor was removed by vacuum. The reaction mixture was stirred at a given temperature in an oil bath for a known time. After reaction, the reactor was immediately quenched in an ice-water bath.

Product analysis

The liquid samples were collected by removing the solid catalyst via centrifugation, and analyzed without pretreatment by high performance liquid chromatography (HPLC, Shimadzu, LC-15C) equipped with UV and RID detectors, using a BP-800 H^+ column (Benson Polymeric Inc. USA) and 5 mmol L^{-1} sulfuric acid aqueous solution as the mobile phase (0.6 mL min^{-1} flow rate at 55 °C). The gas product was analyzed using a GC (Agilent 4890) equipped with a packed carbon molecular sieve column and a TCD detector. The yields of organic chemicals were calculated based on the following equation.

$$\text{Yield} = \frac{\text{moles of carbon in the organic cheimcal}}{\text{moles of carbon in feedstock}} \times 100\% (1)$$

Reuse of the catalysts

To test the reusability of the synthesized catalysts, the catalyst was separated from the liquid by centrifugation, washed with water until pH reaches around 7 and dried under vacuum at 60 °C. Then they were directly reused for the next run without reduction.

Acknowledgements

This work was supported by National Natural Science Foundation of China (21603236, 21373230, 21503238), and Chinese Academy of Sciences (QYZDY-SSW-SLH013).

Keywords: Glycerol conversion • Lactic acid • Heterogeneous catalysis • Hydroxyapatite

[1]. He, M.; Sun, Y.; Han, B., *Angew. Chem. Int. Ed.* **2013,** *52* (37), 9620-9633.

[2]. Morales, M.; Dapsens, P. Y.; Giovinazzo, I.; Witte, J.; Mondelli, C.; Papadokonstantakis, S.; Hungerbuhler, K.; Perez-Ramirez, J., *Energy Environ. Sci.* **2015,** *8* (2), 558-567.

[3]. (a) Bozell, J. J.; Petersen, G. R., *Green Chem.* **2010,** *12* (4), 539-554; (b) Janaun, J.; Ellis, N., *Renew. Sustainable Energy Rev.* **2010,** *14* (4), 1312-1320.

[4]. (a) Iqbal, S.; Kondrat, S. A.; Jones, D. R.; Schoenmakers, D. C.; Edwards, J. K.; Lu, L.; Yeo, B. R.; Wells, P. P.; Gibson, E. K.; Morgan, D. J.; Kiely, C. J.; Hutchings, G. J., *ACS Catal.* **2015,** *5* (9), 5047-5059; (b) Jiang, T.; Zhou, Y.; Liang, S.; Liu, H.; Han, B., *Green Chem.* **2009,** *11* (7), 1000-1006.

[5]. Lari, G. M.; Garcia-Muelas, R.; Mondelli, C.; Lopez, N.; Perez-Ramirez, J., *Green Chem.* **2016,** *18* (17), 4682-4692.

[6]. Brett, G. L.; He, Q.; Hammond, C.; Miedziak, P. J.; Dimitratos, N.; Sankar, M.; Herzing, A. A.; Conte, M.; Lopez-Sanchez, J. A.; Kiely, C. J.; Knight, D. W.; Taylor, S. H.; Hutchings, G. J., *Angew. Chem. Int. Ed.* **2011,** *50* (43), 10136-10139.

[7]. (a) Li, X.; Zhang, Y., *ACS Catal.* **2016**, 2785-2791; (b) Liu, L.; Wang, B.; Du, Y.; Zhong, Z.; Borgna, A., *Appl. Catal. B* **2015,** *174–175* (0), 1-12.

[8]. (a) Wang, Z.; Wang, L.; Jiang, Y.; Hunger, M.; Huang, J., *ACS Catal.* **2014,** *4* (4), 1144-1147; (b) Zhang, H.; Hu, Z.; Huang, L.; Zhang, H.; Song, K.; Wang, L.; Shi, Z.; Ma, J.; Zhuang, Y.; Shen, W.; Zhang, Y.; Xu, H.; Tang, Y., *ACS Catal.* **2015,** *5* (4), 2548-2558.

[9]. Dusselier, M.; Van Wouwe, P.; Dewaele, A.; Makshina, E.; Sels, B. F., *Energy Environ. Sci.* **2013,** *6* (5), 1415-1442.

[10]. Drumright, R. E.; Gruber, P. R.; Henton, D. E., *Adv. Mater.* **2000,** *12* (23), 1841-1846.

[11]. Liu, S. Q., *Int. J. Food Microbiol.* **2003,** *83* (2), 115-131.

[12]. (a) Sharninghausen, L. S.; Campos, J.; Manas, M. G.; Crabtree, R. H., *Nat Commun* **2014,** *5*, 6084; (b) Lu, Z.; Demianets, I.; Hamze, R.; Terrile, N. J.; Williams, T. J., *ACS Catal.* **2016,** *6* (3), 2014-2017; (c) Li, Y.; Nielsen, M.; Li, B.; Dixneuf, P. H.; Junge, H.; Beller, M., *Green Chem.* **2015,** *17* (1), 193-198; (d) Tao, M.; Zhang, D.; Deng, X.; Li, X.; Shi, J.; Wang, X., *Chem. Commun.* **2016,** *52* (16), 3332-3335; (e) Tao, M.; Dan, Z.; Guan, H.; Huang, G.; Wang, X., *Sci. Rep.* **2016,** *6*, 29840.

[13]. (a) Shen, Y.; Zhang, S.; Li, H.; Ren, Y.; Liu, H., *Chem. Eur. J.* **2010,** *16* (25), 7368-7371; (b) Purushothaman, R. K. P.; van Haveren, J.; van Es, D. S.; Melián-Cabrera, I.; Meeldijk, J. D.; Heeres, H. J., *Appl. Catal. B* **2014,** *147*, 92-100; (c) Roy, D.; Subramaniam, B.; Chaudhari, R. V., *ACS Catal.* **2011,** *1* (5), 548-551; (d) Oberhauser, W.; Evangelisti, C.; Tiozzo, C.; Vizza, F.; Psaro, R., *ACS Catal.* **2016,** *6* (3), 1671-1674; (e) Maris, E. P.; Davis, R. J., *J. Catal.* **2007,** *249* (2), 328-337.

[14]. Han, Z.; Li, S.; Jiang, F.; Wang, T.; Ma, X.; Gong, J., *Nanoscale* **2014,** *6* (17), 10000-10008.

[15]. Katryniok, B.; Kimura, H.; Skrzynska, E.; Girardon, J.-S.; Fongarland, P.; Capron, M.; Ducoulombier, R.; Mimura, N.; Paul, S.; Dumeignil, F., *Green Chem.* **2011,** *13* (8), 1960-1979.

[16]. (a) Bicker, M.; Endres, S.; Ott, L.; Vogel, H., *J. Mol. Catal. A Chem.* **2005,** *239* (1–2), 151-157; (b) Hirano, Y.; Sagata, K.; Kita, Y., *Appl. Catal. A* **2015,** *502*, 1-7.

[17]. Ho, C.-M.; Yu, W.-Y.; Che, C.-M., *Angew. Chem. Int. Ed.* **2004,** *43* (25), 3303-3307.

[18]. Saha, D.; Adak, L.; Mukherjee, M.; Ranu, B. C., *Org. Biomol. Chem.* **2012,** *10* (5), 952-957.

[19]. Mori, K.; Mitani, Y.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K., *Chem. Commun.* **2005,** (26), 3331-3333.

[20]. Mitsudome, T.; Arita, S.; Mori, H.; Mizugaki, T.; Jitsukawa, K.; Kaneda, K., *Angew. Chem. Int. Ed.* **2008,** *47* (41), 7938-7940.

[21]. Mori, K.; Hara, T.; Mizugaki, T.; Ebitani, K.; Kaneda, K., *J. Am. Chem. Soc.* **2004,** *126* (34), 10657-10666.

[22]. Liu, Y.; Tsunoyama, H.; Akita, T.; Tsukuda, T., *Chem. Commun.* **2010,** *46* (4), 550-552.

[23]. Jiang, Z.; Zhang, Z.; Song, J.; Meng, Q.; Zhou, H.; He, Z.; Han, B., *ACS Sustainable Chem. Eng.* **2016,** *4* (1), 305-311.

[24]. Li, J.; Li, Y.; Zhang, L.; Zuo, Y., *Appl. Surf. Sci.* **2008,** *254* (9), 2844-2850.

[25]. Zhang, P.; Wu, T.; Jiang, T.; Wang, W.; Liu, H.; Fan, H.; Zhang, Z.; Han, B., *Green Chem.* **2013,** *15* (1), 152-159.

[26]. Kaga, Y.; Abe, Y.; Yanagisawa, H.; Kawamura, M.; Sasaki, K., *Surf. Sci. Spectra* **1999,** *6* (1), 68-74.

[27]. Zahmakıran, M.; Román-Leshkov, Y.; Zhang, Y., *Langmuir* **2012,** *28* (1), 60-64.

[28]. Cai, F.; Zhu, W.; Xiao, G., *Catal. Sci. Technol.* **2016,** *6* (13), 4889-4900.

10.1002/asia.201700412

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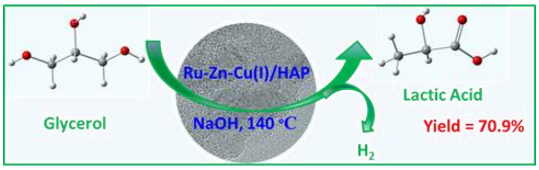

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