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Selective oxidation of 1,2-propanediol to lactic acid over Cu modified Au/hydrotalcite catalysts

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Catalytic oxidation of biomass-derived 1,2-propanediol to valuable lactic acid were investigated over various Cu modified Au supported on Mg-Al hydrotalcite (HT). Compared to those of individual Au-HT, the better catalytic performance was achieved over Cu modified Au-HT catalysts, mainly due to the suppressive generation of byproducts. The structural properties of Cu-Au/HT catalysts were determined by XRD, SEM, HRTEM, and N₂ physical adsorption, and strong interaction was discovered in the Cu modified Au-HT catalysts. The controlled experience verified that the secondary hydroxyl in 1,2propanediol is unreactive over Au/HT catalysts modified with Cu, which intensively inhibited the generation of main byproducts formic acid and acetic acid. These findings provided useful guidance for the design of more efficient and stable nano-catalysts for oxidizing glycols to organic acids containing hydroxides.

Introduction

Lactic acid is an important fine chemical widely used in the cosmetic, textile and food industries, and a major monomer for production of eco-friendly poly-lactic acid (PLA).¹⁻⁴ Traditional routes for synthesis of lactic acid in industry generally use HCN, acrylonitrile or Cl_2 as raw materials, which are expensive, inadequate and environmentally unfriendly.^{2, 5} Currently, commercial lactic acid is mainly produced by microbial fermentation, whereas the efficiency is limited by low productivity and space-time yield and generating large amount of $CaSO_4$ by-product.^{6, 7} Therefore, chemical synthesis of lactic acid from renewable biomass with high efficiency has attracted increasing attention.

The oxidation of glycerol and its derivative of 1,2-propanediol, obtained from bio-diesel industry, into lactate acid, provides an alternative and efficient process for production of lactate acid because of the structural analogy of C₃ skeleton.⁸⁻¹⁰ Recent years, numerous significant works found that supported Pt, Au, Pd, Ag and heteropolyacid catalysts present excellent catalytic performance for glycerol and 1,2-propanediol transforming into lactate acid,^{2, 11-17} and some representative results are shown in Table 1. For example, Ma et al.¹⁸ found that 1,2-propanediol conversion of 97 % and lactic acid selectivity of 84 % were achieved over an 1.4%Au/Mg(OH)₂ catalyst at the reaction condition of 60 °C and 0.3 MPa O₂. Yin et al.¹³ reported that 1,2propanediol was oxidized to lactate acid with 88 % selectivity at 98 % 1,2-propanediol conversion at reaction condition of 60 °C

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and 1.0 MPa air on an AuPd/Mg(OH)₂ catalyst. The oxidation of 1,2-propanediol mentioned above provided a promising route for lactate acid synthesis. Nevertheless, there is still room for improving the selectivity to lactate acid by suppressing the generation of byproducts.^{11, 15}

Due to two types of hydroxides in 1,2-propanediol, two competitive pathways probably take place in the its oxidation (Scheme 1).¹¹⁻¹⁵ Generally, the oxidative reaction dehydrogenation of primary hydroxyl into lactaldehyde and secondary hydroxyl into hydroxyacetone occur concurrently. Subsequently, the two main intermediates of lactaldehyde and hydroxyacetone converted to lactate acid or other by-products via different pathways, respectively. Lactaldehyde could be directly oxidized to lactic acid quantitatively, while the conversion of hydroxyacetone into lactic acid also via arrangement reaction of reactive intermediate of pyruvaldehyde, which also easily transforming into byproducts at reation conditions. Therefore, it is a feasible mean to improve lactic acid selectivity by limiting the pathway 2.

In the previous work, the oxidation efficiency of primary alcohol into aldehyde on Au/SiO₂ catalysts is enhanced by adding copper promoter, indicating that copper is a potential candidate to change the pathway of 1,2-propanediol oxidation.¹⁹ Herein, various Au catalysts supported on Mg-Al hydrotalcite (HT) were prepared for selective oxidation of 1,2propanediol to lactic acid. The secondary reactions were obviously suppressed over the Au catalysts modified by Cu addition, which in favor of increasing lactic acid selectivity. Additionally, the structure characterization for different catalysts was conducted for confirming structure-activity relationship, and the possible reaction mechanism was proposed.

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⁺ Footnotes relating to the title and/or authors should appear here.

⁵⁸ Electronic Supplementary Information (ESI) available: [details of any supplementary

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Substrate	Catalyst	Reaction Conditions	Conversion (%)	Lactic acid selectivity (%)	Ref
1,2-propanediol	1.4%Au/Mg(OH)2	60 °C,0.3 MPa O ₂ , NaOH	97	84	18
1,2-propanediol	0.75% Au-0.25% Pd/Mg(OH) ₂	60 °C, 1.0 MPa O ₂ , NaOH	98	88	13
1,2-propanediol	0.5% Au-0.5% Pd/hydroxyapatite	80 °C, 0.1 MPa O ₂ , NaOH	89	92	14
1,2-propanediol	0.5% Au-0.5% Pt/C	40 °C, 0.3 MPa O2, NaOH	78	86	20
1,2-propanediol	98.5%Cu@1.5%Au Nanoparticles	100 °C, 1.0 MPa O ₂ , NaOH	90	76	21
1,2-propanediol	0.025% Au-1% Pt/TiO2	90 ℃, 0.5 MPa air, NaOH	96	87	12
Glycerol	1%Au/CeO ₂	90 ℃, 0.1MPa air, NaOH	98	83	22
Glycerol	0.4%Au-0.3%Pt/CeO ₂	100 ℃, 0.5MPa air, NaOH	99	80	23



Scheme 1 Reaction route of oxidation of 1,2-propanediol into lactate.¹¹⁻¹⁵

Experimental

Materials

All the reagents used were analytical grade. The Mg(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O, NaOH and Na₂CO₃ were produced by Xilong Scientific Co., Ltd. Cu(NO₃)₂·3H₂O was purchased from Damao Chemical Reagent Factory. HAuCl₄·3H₂O and NaBH₄ was bought from Chengdu Chron Chemicals Co., Ltd. and Wuhan Pego Technology, Ltd., respectively.

Catalyst preparation

Preparation of HT support. The HT support was prepared by coprecipitation method reported in previous work.²⁴ Briefly, a mixed solution of Mg(NO₃)₂ and Al(NO₃)₃ (Mg²⁺: Al³⁺ = 3: 1) and solution of NaOH (8.0 M) were dropped concurrently into 100 mL Na₂CO₃ solution (Al³⁺: CO₃²⁻ = 2 : 1) with mechanical stirring at 30 °C, while maintaining the pH at approximately 10. After aging at 80 °C for 24 h, the obtained precipitate was filtered and washed with deionized water until pH~7. And then, the sample was dried at 120 °C overnight and calcined at 500 °C for 3 h in air.

Preparation of Au/HT and Cu-Au/HT catalysts. In the catalysts preparation, deposition-precipitation method and incipient wetness impregnation method were used to loaded Au and Cu on the support, respectively. Firstly, the Cu modified HT was prepared by impregnating over calcined HT support with an aqueous solution containing the certain amount of Cu(NO₃)₂, following by drying at 120 °C for 12 h and reducing at 350 °C in a H₂ atmosphere for 3 h. Sequentially, the prescribed amount of HAuCl₄ solution and prepared Cu/HT or HT samples was added

into a flask to obtain suspension at room temperature. After stirring for 1 h, aqueous solution of NaBH₄ solution (NaBH₄/Au (mol/mol) = 5) was dropped slowly into the suspension. After aging at room temperature for 6 h, the black precipitates were filtered and washed several times with deionized water until no Cl⁻ was detected in the spent washing liquid, following by drying 120 $^{\circ}$ for 12 h. The nominal content of Au in these catalysts was at 0.6 wt%. The catalysts were denoted as xCu-Au/HT, where *x* represents the nominal copper loading (wt%).

Catalyst characterization. X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/MAX-2400 diffractometer with nickel filtered Cu K_{α} radiation at 40 kV and 30 mA. N₂ physical adsorption-desorption measurements were carried out on a Micromeritics TriStar II instrument. The BET specific surface area and average pore size were calculated by the Brunauer-Emmett-Teller (BET) method and Barrett-Joyner-Halenda (BJH) method, respectively. Inductively coupled plasma-atomic emission spectroscopy (ICP-AES) measurements were performed using an Agilent 725-ES. Before tested, the samples were dissolved by aqua regia and then diluted by deionized water. Scanning electron microscopy (SEM) was performed on a scanning electron microscope (Vega3 Tescan) operated at an acceleration voltage of 20 kV. Transmission electron microscopy (TEM) was observed on a transmission electron microscope (TF20) operated at an acceleration voltage of 200 kV, and the particle size was statistically measured from the TEM micrographs by counting more than 200 particles. High angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) and energy-dispersive X-ray spectroscopy (EDX) analyses were conducted on a Tecnai G2 F20 transmission electron microscope operated at an acceleration voltage of 200 kV.

Catalytic test and product analysis. The 1,2-propanediol oxidation reactions were carried out in a stainless steel autoclave (100 ml) at a stirring speed of 800 rpm. In a typical run, 30 g 1,2-propanediol aqueous solution (10 wt%), 3.15 g of NaOH (NaOH/1,2-propanediol (mol/mol) = 2) and 1.0 g catalyst were added into the autoclave. Then, the reactor was purged with O_2 (> 99.99%) three times, pressurized with O_2 to 1.0 MPa and then heated to the setting temperature, which kept constant during the reaction. The products and remained reactant were analyzed by a Shimadzu LC-20A high-

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performance liquid chromatography (HPLC) with a refractive index detector (RID) and an RSpak KC-811 column after acidizing with H_3PO_4 aqueous (1 mol L⁻¹). Products were also identified on an Agilent 7890A/5975C GC-MS with a HP-5MS column. The

detected liquid products after acidulation were electrice acid, formic acid and acetic acid. The conversion 3300^{10} and 3200^{10} selectivity were calculated as following:

Conversion (%) = $\frac{\text{mol of 1,2-propanediol charged - mol of 1,2-propanediol left}}{(\%)}$

mol of 1,2-propanediol charged

mol of Carbon atoms in product

Results and discussion

Catalyst characterization

XRD patterns of dried HT support, calcined HT support and prepared catalysts are shown in Fig. 1. The diffraction peaks at 11.7°, 23.6°, 35.0°, 39.7°, 47.1°, 60.9° and 62.4° observed in the pattern of HT support, Au/HT and Cu-Au/HT catalysts could be assigned to the (003), (006), (009), (105), (108), (110), and (113) lattice planes in Mg-Al hydrotalcite, respectively. After calcination at 500 °C for 3 h, the characteristic diffraction peaks of Mg-Al hydrotalcite greatly weakened, and diffraction peaks of MgO at 42.9° and 62.3° were found. It is worth noting that the obvious diffraction peaks attributed to Mg-Al hydrotalcite appear again in the patterns of Au/HT and Cu-Au/HT catalysts prepared by reductive precipitation method. This finding indicates that the structure for layered double hydroxide



Fig. 1 XRD patterns of HT support, calcined HT support and prepared catalysts

rebuilds from metallic oxides, which could attribute to the "memory effects" of the hydrotalcite structure.^{25,26} The characteristic peak intensity of hydrotalcite decreased gradually from dried HT to Au/HT and Cu-Au/HT catalysts, indicating the declining crystallinity of sample with heteroatom Au and Cu loading. Additionally, no characteristic peaks attributed to Au (JCPDA 65-2807) or Cu (JCPDA 04-0836) species were observed in the XRD patterns, indicating that Au and Cu particles were well dispersed on the HT support.

SEM images of dried HT support, Au/HT and Cu modified Au/HT catalysts are shown in Fig. 2. A solid lamellar with layered structure can be observed in the image of dried HT support. And many stacking holes with different diameters and shapes were formed by unordered agglomerate of Mg-Al hydrotalcite sheets. Referring to their parents, no obvious difference present in both Au/HT and Cu-Au/HT catalysts, indicating that the layered structure is reserved with addition of Cu and Au during calcination and reduction treatments, which also verified by XRD results.

TEM images of dried HT support, Au/HT and Cu modified Au/HT catalysts are given in Fig. 3 and particle dispersion results obtained from the TEM images are listed in Table 2. The porous structure, caused by the removal of CO₂ and H₂O during the pretreatment process, is observed in all images of samples, which is responsible for their high surface area. The welldistributed particles of about 8 nm in diameter are present in the Au-HT catalyst, while smaller particles of 5.5-7.0 nm are well dispersed in the entire Cu promoted Au-HT catalyst. These findings indicate that Cu prevented the aggregation of Au nanoparticles, which is consistent with the Pt-Cu catalysts supported on activated carbon and SiO₂ in previous works due to the strong interactions between Cu and noble metals.^{27, 28} From the HRTEM images of Au/HT and 0.5Cu-Au/HT (Fig. S1), the particles observed in both samples show similar lattice fringes of 0.24 nm, which is close to the {1 1 1} lattice spacing of fcc metallic gold. These results indicate that the observed particles in the TEM images of 0.5Cu-Au/HT are mainly Au particles, instead of the Cu particles or Au-Cu alloy particles. Furthermore, no obvious change of morphology feature was found in the sample with different copper loading. It is worth noting that mean particle size of Au in Au/HT catalyst was 8.0 nm, while diffraction peaks weren't observed in its XRD pattern. The strongest diffraction peak of Au⁰ (JCPDA 65-2870) is at 38.2°, which is near the wide peak of Mg-Al hydrotalcite at 39.7°, so that this peak of Au may be covered by peak of Mg-Al hydrotalcite. Moreover, the intensity of other peaks of Au weren't strong enough to be observed in the XRD pattern. This

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42 43 may be the reason for that diffraction peaks of Au didn't appear in the XRD pattern of Au-HT catalyst.

In order to investigated the interaction between Au and Cu, the elemental mapping and line-scan tests were conducted on 0.5Cu-Au/HT, and the results are shown in Fig. 4. It can be seen from the elemental mapping results that the dispersions of Cu element and Au element were different. The Cu element existed on the surface of the support with two different statuses, Cu particle with high dispersion and aggregated Cu particle. However, the Au nanoparticle dispersed mainly at the area consisting of large Cu particles. From the line-scan profiles, it can be found that the atomic ratio of Au/Cu in the metal particles was constant. These findings are probably attributed to strong interaction between Au and Cu. Moreover, the atomic number of Au was much higher than that of Cu in position of the metal particles, which may be the reason 1010 1010 1010 1010 1010 1010 1010 100

To further understand the structure of HT support, Au/HT and Cu modified Au/HT catalysts, their textural properties are given in Table 2. The contents of Au and Cu in these catalysts determined by ICP-AES were close to the nominal values. The BET specific surface area of Au/HT catalyst was 225 m² g⁻¹, similar to that of HT support, indicating the pretreatment process do not influence textural structure significantly. The surface area of Au catalysts modified by copper with 0.05~2.0 wt% loading increased to 270~290 m² g⁻¹. Meanwhile, the



Fig. 2 SEM images of (a) HT support, (b) Au/HT, (c) 0.05Cu-Au/HT, (d) 0.1Cu-Au/HT, (e) 0.25Cu-Au/HT, (f) 0.5Cu-Au/HT, (g) 1Cu-Au/HT, and (h) 2Cu-Au/HT samples.



Fig. 3 TEM images of (a) HT support, (b) Au/HT, (c) 0.05Cu-Au/HT, (d) 0.1Cu-Au/HT, (e) 0.25Cu-Au/HT, (f) 0.5Cu-Au/HT, (g) 1Cu-Au/HT, and (h) 2Cu-Au/HT sample

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average pore diameter decreased from ~7.6 nm in HT and Au/HT to ~3.6 nm in the Cu modified Au/HT samples. Some mesopores of the support might be destroyed and converted to smaller mesopores during the extra impregnation, drying and calcination of the Cu modified catalysts, thus resulted in the increase of the surface area and decrease of the average pore diameter.^{29, 30} In addition, the diffusion of substrate, intermediates and products is not hindered in the mesoporous structure.

Catalytic performance for 1,2-propanediol oxidation into lactate acid. The catalytic performance of 1,2-propanediol to lactic acid over Au/HT catalysts with different copper loading are shown in Table 3. All Au catalysts with different copper loadings are active for 1,2-propanediol oxidation. The 1,2propanediol conversion at all Au catalysts tested were above 92.8 %, indicating that the activity of these catalysts were high and not influenced by various copper content for 1,2propanediol oxidation at the reaction conditions. Differently, the selectivity of lactic acid increased sharply from 75.7 % over Au/HT to 89.9 % over Cu-Au/HT catalyst modified with 0.25 wt% copper, and then decreases gradually to 85.7 % with further improving copper loading to 2.0 wt%, indicating that moderate amount of copper was in favor of the production of lactic acid from 1,2-propandiol oxidation. The acetic acid selectivity decreased from 16.2 % over Au/HT to the minimum of 6.8 % over 0.25Cu-Au/HT, and then increased to 9.5 % with further increasing copper loading to 2.0 wt%. Additionally, the formic acid selectivity decreased continuously from 6.8 % to 0.1 % over



Fig. 4 (a) HAADF-STEM image of 0.5Cu-Au/HT catalyst; elemental mapping of (b) Au, (c) Cu and (d) Au & Cu for the area in image (a); (e) line-scan profiles of Au and Cu for the position marked by yellow line in image (a).

Samples	Content of Au ^a	Content of Cu ^a	SBET	D _{pore} (nm)	Particle size ^b (nm)
	(wt%)	(wt%)	(m² g ⁻¹)		
HT	-	-	225	7.8	-
Au/HT	0.62	-	225	7.4	8.0
0.05Cu-Au/HT	0.58	0.04	288	3.4	5.6
0.1Cu-Au/HT	0.59	0.09	276	3.3	6.1
0.25Cu-Au/HT	0.60	0.23	276	3.4	6.3
0.5Cu-Au/HT	0.61	0.46	294	3.6	6.8
1Cu-Au/HT	0.63	0.88	270	3.6	6.7
2Cu-Au/HT	0.64	1.80	279	3.9	6.5

^a Obtained from ICP measurement. ^b Measured from the TEM micrographs.

Table 2 The textural properties of HT support and catalysts

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Au/HT catalysts with increasing copp loading to 2.0 wt%. These findings indicated that the ge ation of main sideproducts, including acetic acid and form acid, was suppressed by adding copper promoter into Au/HT alysts. Furthermore, the catalytic activity of 0.5Cu/HT was to ed, and a conversion of merely 28.5 % and a selectivity of 1 % were obtained. These results indicated that Au is imp ant for the catalytic activity and the addition of Cu is favor of creasing lactate acid. Therefore, the higher catalytic perform ce achieved over Cu-Au/HT catalysts probably ascribes to ne synergistic effect between Cu and Au. In addition, total lectivity of detected products was less than 100%, indicating nat there were other undetected products in the reaction. O of them was CO₃²⁻ in ause some gas was the alkaline reaction environment, b generated in the acidification process products and the gas was proved to be CO₂ via the reaction w limewater. However, the amount of CO₂ was difficult to be of ined.

Effects of the reaction parameters, including the reaction temperature, O_2 pressure and reaction time, were investigated to obtain high yields of lactic acid over the Cu modified Au/HT catalysts. The 0.5Cu-Au/HT, which was one of the most activecatalysts, was selected as a model for the investigations, and the results are shown in Fig. 5. The 1,2-propanediol conversion continually increased from 62.8 % to approach 100%

with increasing reaction temperature from 60 to 80 °C and kept constant with further increasing temperature to 90 °C. The lactic acid selectivity monotonically decreased from 95.2 % to 70.1 %, while the acetic acid selectivity significantly increased from 3.4% to 19.9% with increasing the temperature from 60 to 90 °C. The selectivity for another side-product of formic acid maintained below 1.0% in the reaction temperature range we tested, probably due to the different pathways into formic and acetic acid. Higher reaction temperature is favorable of the formation of acetic acid in the 1,2-propanediol oxidation, which is responsible for the decreasing lactic acid selectivity.

As shown in the Fig. 5b, 1,2-propanediol conversion rapidly increased from 83.6 % to 98.5 % when increasing O_2 pressure from 0.5 to 1.0 MPa, and then kept constant with further increasing pressure to 2.0 MPa. However, the lactic acid selectivity decreased sharply from 91.6 % to 60.3 %, while the selectivity to acetic acid and formic acid always increased form 5.6 % and 0.4 % to 26.5 % and 5.1 % with increasing O_2 pressure from 0.5 to 2.0 MPa, respectively. These findings indicate that the side reactions are promoted by high O_2 pressure.

The conversions and selectivity of 0.5Cu-Au/HT in 1,2propanediol oxidation as a function of reaction time at 1.0 MPa O_2 and 80 °C are shown in Fig. 5c. The conversion of 1,2propanediol increased drastically to 90.3 % in the first 4 h, and

Catalanta	Conversion (%) –		Selectivity (%)	
Catalysts		lactic acid	acetic acid	formic acid
Au/HT	94.2	75.7	16.2	6.8
D.05Cu-Au/HT	92.8	85.0	10.0	4.8
0.1Cu-Au/HT	98.2	87.8	8.1	0.3
0.25Cu-Au/HT	98.2	89.9	6.8	0.1
0.5Cu-Au/HT	98.5	88.5	7.6	Not detected
1Cu-Au/HT	99.0	87.6	8.3	0.1
2Cu-Au/HT	97.1	85.7	9.5	0.1

Reaction condition: 30 mL 10 wt% 1,2-propanediol aqueous solution, 3.15 g NaOH, 1.0 g Catalyst, 80 °C, 1.0 MPa O_2 , 6.0 h.



Fig. 5 Effect of reaction temperature (a), reaction pressure (b) and reaction time (c) on the catalytic conversion and selectivity over 0.5Cu-Au/HT catalyst. (Reaction condition: 30 g 10 wt% 1,2-propanediol aqueous solution, 3.15 g NaOH, 1.0 g 0.5Cu-Au/HT, (a): 6.0 h, 1.0 MPa O₂; (b): 6.0 h, 80 °C; (c): 1.0 MPa O₂, 80 °C.

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then increased gradually to 98.9 % with a further increasing the reaction time to 8 h. The selectivity to lactic acid decreased slightly from 91.3 to 84.6 % with the increasing reaction time from 2 to 8 h, which shows the stability of the lactic acid in the oxidation reaction. Besides, the selectivity to acetic acid increased from 5.8 to 10.3 %, whereas the selectivity to formic acid remained almost constant with the increasing reaction time from 2 to 8 h.

The effects of the reaction parameters mentioned above show the possibility for improving the catalytic performance of 1,2-propanediol oxidation into lactic acid. For example, at the appropriate reaction conditions (80 °C and 1.0 MPa O₂), a complete transformation of 1,2-propanediol and selectivity of 88.5 % to lactic acid were achieved on 0.5Cu-Au/HT catalyst in the presence of sufficient NaOH, which is comparable with those on the other supported Au catalysts.

To investigate the recyclability of 0.5Cu-Au/HT catalyst, the used catalyst was filtrated, washed with deionized water for three times and reduced at 350 °C in a H2 flow for 3 h after every 1,2propanediol oxidation reaction. Afterward, the catalyst was recharged into the autoclave together with fresh reactant and NaOH additive. The conversion and lactic acid selectivity decreased slightly from 98.5 % and 88.5 % to 96.5 % and 82.5 % respectively after 5 recycles (Fig. 6a). This result shows an acceptable stability of the 0.5Cu-Au/HT in the 1,2-propanediol oxidation. Furthermore, the reason for the decrease of the catalytic performance was studied. It can be discovered from the XRD patterns of fresh and used 0.5Cu-Au/HT catalysts (Fig. 6b), the peak intensity of HT support change to be a little weaker in the hot basic solution of the reaction process. Moreover, no obvious change of morphology can be observed in the SEM image (Fig. 6c) of used catalyst. These results indicated that the stability of the HT support was passable in the reaction process. In addition, from the TEM image of used catalyst (Fig. 6d), the average particle size of active metals was about 8.3 nm, which was a little bigger than fresh catalyst. To sum up, the growth of metal particles might be the main reason for catalyst deactivation.



Fig. 6 (a) Recycling performance of 0.5Cu-Au/HT catalyst for the catalytic oxidation of 1,2-propanediol (reaction condition: 30 g 10 wt% 1,2-propanediol aqueous solution, 3.15 g NaOH, 1.0 g 0.5Cu-Au/HT, 80 °C, 1.0 MPa O₂, 6.0 h); (b) XRD patterns of fresh and used catalysts; (c) SEM image of used catalyst; (d) TEM image of used catalyst



Scheme 2 Reaction pathways for catalytic oxidation of 1,2-propanediol ¹⁻⁶ and functional mechanism of Cu promoter

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Table 4 Oxidation of lactic acid and hydroxyacetone catalyzed by Au/HT and 0.5Cu-Au/HT catalysts

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Substrate	Catalysts	Conversion (%) -	Selectivity (%)		
			Lactic acid	Formic acid	Acetic acid
Lactic acid	Au/HT	21.8	-	1.8	62.8
Lactic acid	0.5Cu-Au/HT	8.4	-	0	66.7
Hydroxyacetone	Au/HT	95.1	42.6	10.7	16.8
Hydroxyacetone	0.5Cu-Au/HT	96.2	37.4	10.2	21.3

Functional mechanism of Cu promoter. In the oxidation reaction of 1,2-propanediol into lactic acid, formic acid and acetic acid were usually generated as by-products. In the previous works ^{11-15, 31}, it was reported that 1,2-propanediol was oxidized to lactate through two possible parallel pathways (Scheme 2). In the pathway 1, oxidation of the primary hydroxyl group in 1,2-propanediol occurred firstly to form lactaldehyde. The resultant lactaldehyde can be oxidized to lactic acid rapidly, so that the lactaldehyde wasn't detected in our experiment. In the pathway 2, oxidation of the secondary hydroxyl group of 1,2-propanediol occurred firstly and hydroxyacetone was generated. The resultant hydroxyacetone can be oxidized into lactate acid via another intermediate of pyruvaldehyde. Moreover, the reason for generation of formic acid and acetic acid was investigated. Dimitratos et al.11 and Feng et al.15 revealed that the pyruvaldehyde, which was an intermediate in the pathway 2, could converted to formate and acetate in the alkaline solution (Side reaction 1). Besides, this work discovered that the lactic acid selectivity decreased and the acetic acid selectivity increased, when the reaction time was prolonged (Fig. 4c). So it was possible that the lactate could convert to CO_3^{2-} and acetate in the alkaline environment by the oxidative decarboxylation reaction (Side reaction 2).

In order to verify the formation mechanism of formate and acetate, and investigate the functional mechanism of Cu, catalytic oxidation reactions of lactic acid and hydroxyacetone over Au/HT and 0.5Cu-Au/HT were tested, and the results were shown in Table 4. When the reaction substrate was lactic acid, its conversion over Au/HT catalyst and 0.5Cu-Au/HT catalyst were 21.8 % and 8.4 %, respectively. And the main products were acetic acid over both the catalysts. This results proved that the lactate could be further oxidized to acetate in the reaction conditions, and 0.5Cu-Au/HT catalyst had lower activity for this side reaction than Au/HT catalyst. When the substrate was hydroxyacetone, its conversion exceeded 95 % and formic acid selectivity over both catalysts were nearly 10%, indicating that the formate was formed in pathway 2, which was consistent with the conclusion of previous works^{1, 2}. Moreover, the formic acid selectivity over the two catalysts were similar, which revealed that the Cu promoter couldn't reduce the C-C cleavage of pyruvaldehyde to form the formate. However, it was notable that over 0.5Cu-Au/HT catalyst, the selectivity of formic acid was 10.2 % when the substrate was hydroxyacetone, while the selectivity of formic acid was 0.1 % when the substrate was 1,2propanediol (Table 1). These results pointed out that the oxidation of 1,2-propanediol to lactic acid was almost through the pathway 1 over the Cu modified Au/HT catalysts, and

oxidation of secondary hydroxyl of 1,2-propanediol hardly occurred over these catalysts. So that, the pyruvaldhyde wasn't obtained over Cu modified Au/HT catalysts, thus the formation of formate was inhibited. The reason for this effect may be that the oxidation activity for primary hydroxyl group of 1,2propanediol was improved due to synergistic effect between the Au and Cu. It has been reported that there was synergistic effect between Au and Cu which arose most probably from the electronic interaction in the Au-Cu alloy catalyst supported on SiO₂, and this interaction promoted oxidation of various alcohols to the corresponding aldehydes.⁷

Conclusion

A series of Cu modified Au/HT catalysts were prepared for catalytic oxidation of 1,2-propanediol to lactic acid. The Cu was proved as an excellent promoter to increase conversion of 1,2propanediol and selectivity of lactic acid. The 1,2-propanediol conversion and lactic acid selectivity could exceed 98 % and 88 % respectively over optimized 0.5Cu-Au/HT catalyst at reaction conditions of 80 oC and 1.0 MPa O2, and the 0.5Cu-Au/HT catalyst exhibited good recycling performance. According to the corresponding results of structure characterization and reactions, the functions of copper addition for promoting catalytic performance were proposed in two ways. On the one hand, oxidation of secondary hydroxyl of 1,2-propanediol didn't occurred over Cu modified Au/HT catalysts, thus sharply decreased the selectivity formic acid and acetic acid generated from pyruvaldehyde. On the other hand, Cu promoted catalysts had lower activity for oxidative decarboxylation of lactate than Au/HT catalyst, thus had lower acetic acid selectivity and higher lactic acid selectivity. The higher catalytic performance achieved over Cu-Au/HT catalysts probably ascribes to the synergistic effect between Cu and Au.

Conflicts of interest

There are no conflicts to declare.

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1,2-propanediol was converted to lactic acid over Cu modified Au/hydrotalcite catalysts with high conversion and selectivity.