available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article (Special Issue in Memory of the 80th Birthday of Professor Jingfa Deng)

Trivalent metal ions M^{3+} in $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ layered double hydroxide as catalyst precursors for the hydrogenolysis of glycerol

XIA Shuixin, ZHENG Liping, NIE Renfeng, CHEN Ping, LOU Hui, HOU Zhaoyin*

Institute of Catalysis, Department of Chemistry, Zhejiang University, Hangzhou, 310028, Zhejiang, China

ARTICLE INFO

Article history:

Received 31 October 2012

Accepted 3 December 2012

Published 20 May 2013

Keywords:

Layered double hydroxide

Bimetallic

Solid base

Glycerol

Hydrogenolysis

Propanediol

ABSTRACT

Trivalent metal ions M^{3+} in $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ ($M = Ru, Re$) layered double hydroxides (LDHs) were successfully synthesized by coprecipitation. Bimetallic M-Cu/solid base catalysts with high metal dispersion were obtained after calcination and H_2 reduction of these LDH precursors. These catalysts exhibited excellent performances for the hydrogenolysis of biomass-derived glycerol under mild conditions. The catalysts were stable when recycled five times. Characterizations indicated that the addition of Ru or Re enhanced the adsorption and activation of hydrogen on the surface of catalysts, which contributed to the high conversion of glycerol.

© 2013, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Heterogeneous catalysts containing more than one metal are widely employed in the chemistry industry. Usually, these kinds of catalysts are prepared by coprecipitation, impregnation, sol-gel, or ion-exchange methods on different supports [1]. However, these methods usually resulted in some inhomogeneous agglomeration of the active metals and thus affect the efficiency of the catalysts. Achieving a homogeneous dispersion of the functionalized metals would of great interest in the catalysis community, especially if those catalysts contained two or more active metals.

Layered double hydroxides (LDHs) have received considerable attention due to their unique structure and their application as catalysts and catalyst precursors in recent years [2–4]. The properties of the LDHs can be easily tailored by se-

lecting the appropriate metals with the desired properties, and homogeneously dispersed mixed oxides with acidic-basic and redox properties can be synthesized via the controlled calcination and reduction of LDH precursors. In particular, the preparation of homogeneously dispersed metal catalysts, with two and more active metals from LDH precursors has been widely reported [5–10].

Recently, with the rapid growth of the biodiesel industry, glycerol has become widely produced as it is a major by-product (10% by weight). This large surplus of glycerol is widely regarded as a waste [8,11]. It is therefore important to find new ways of converting this glycerol into value-added products, such as the catalytic oxidation of glycerol to glyceric acid and dihydroxyacetone [12–17], dehydration of glycerol to acrolein [18–21], and hydrogenolysis of glycerol to propanediols [11,22–34]. Amongst them, the selective dehydroxylation of

* Corresponding author. Tel/Fax: +86-571-88273283; E-mail: zyhou@zju.edu.cn

This work was supported by the National Natural Science Foundation of China (21273198, 21075139) and Zhejiang Provincial Natural Science Foundation (LZ12B03001).

DOI: 10.1016/S1872-2067(11)60505-6 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 34, No. 5, May 2013

glycerol to 1,2-propanediol (1,2-PDO) is a promising route.

Many catalysts have been reported for the hydrogenolysis of glycerol to 1,2-PDO. One group is based on noble metal catalysts, such as Ru [22–25], Pt [26,27], Re [23,28,29], and Ag [30]. Cu [31–36], Ni [37,38] and Co [37] have also been shown to be active in the hydrogenolysis of glycerol. The activities of these metals are generally lower than the noble metals, but lower prices and higher resistance to poisoning by trace impurities make them more competitive. Among these non-noble metals, Cu is superior to Ni and Co in terms of the selectivity for PDOs due to its lower activity for C–C bond cleavage.

In our previous work, we have successfully prepared Cu/solid-base catalysts via LDH precursors and found that the activity of the Cu/solid-base increased with the dispersion of Cu and the base strength of the support [3], and the selectivity could be improved by the addition of a small amount of Pd [39]. Bimetallic Pd–Fe, Pd–Ni, Pd–Co, and Pd–Zn have been recently shown to be active for this reaction [40]. These results directed us to use a small amount of noble metal in a Cu/solid-base to improve the catalyst.

Herein, we report the efficient synthesis for a Ru- or Re-doped Cu/solid base catalyst with highly disperse copper and Ru or Re through the thermal decomposition of $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ ($M = Ru, Re$) LDHs compounds, and their application in the hydrogenolysis of glycerol.

2. Experimental

2.1. Catalyst preparation

Trivalent metal ions (Ru^{3+} , Re^{3+}) in $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ ($M = Ru, Re$) LDH precursors with $M:Cu:Mg:Al$ molar ratios of 0.02:0.4:5.6:1.98 were prepared by coprecipitation. The calculated amounts of MCl_3 , $Cu(NO_3)_2 \cdot 3H_2O$, $Al(NO_3)_3 \cdot 9H_2O$, and $Mg(NO_3)_2 \cdot 6H_2O$ (AR, Shanghai Chemicals, China) were dissolved together in 400 ml of deionized water to make solution A. Solution B comprised a mixture of 0.25 mol/L Na_2CO_3 and 0.8 mol/L $NaOH$ (AR, Shanghai Chemicals, China). Solution A and B were simultaneously added to a glass reactor with vigorous stirring at room temperature and at a pH of 9.5. The slurry was aged at 120 °C for 20 h, filtered, and washed thoroughly with distilled water until free of Cl^- . The precipitate was then dried at 80 °C overnight and identified as $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$. The LDH precursors were then calcined at 300 °C in stationary air for 4 h, before being identified by X-ray diffraction (XRD) as $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}O_9$. Further reduction with H_2 at 300 °C for 1 h yielded the bimetallic M-Cu/solid base catalysts.

2.2. Characterizations

XRD patterns of the synthesized $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ LDH precursors and its decomposition product, the mixed oxides $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}O_9$, were detected at room temperature on a Rigaku D/WAX-2500 diffractometer using $Cu K\alpha$ radiation ($\lambda = 0.15406$ nm) with a 2θ step of 0.02°.

The pore structure and surface area of the decomposed

mixed oxides $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}O_9$ were measured by N_2 adsorption at its normal boiling point using Micromeritics ASAP 2010 analyzer after being pretreated at 250 °C for 4 h in vacuum. The BET surface area and BJH pore size distribution were calculated using their desorption isotherms.

The outline and fine structure of the fresh $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ precursors were detected by scanning electron microscopy (SEM) on a microscope (Leo Series VP 1430, Germany) with a silicon detector equipped with an energy-dispersive X-ray (EDX) facility (Oxford instruments). Samples were coated with gold using sputter coating to avoid charging. Analysis was carried out at an accelerating voltage of 15 kV. Transmission electron microscopy (TEM) images of the hydrogen reduced Ru- or Re-doped Cu/solid base catalysts were obtained using an accelerating voltage of 200 kV (TEM, JEOL-2010F).

The reducibility of the decomposed mixed oxides $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}O_9$ was performed via temperature-programmed reduction (H_2 -TPR). These characterizations were carried out in a quartz reactor. Samples were first pretreated at 400 °C for 1 h under N_2 at a flow rate of 30 ml/min and cooled to room temperature. A reduction agent (10% H_2 -90% N_2 mixture, 30 ml/min) was shifted and the reactor was heated to 450 °C at a rate of 10 °C/min. The effluent gas was dried by powdered KOH and the consumption of hydrogen were recorded by thermal conductivity detector (TCD). Calibration of the instrument was carried out with a known amount of CuO .

The H_2 activation activity of the reduced catalysts was carried out via temperature-programmed desorption of H_2 (H_2 -TPD). The sample was first reduced at 300 °C in a H_2 flow of 30 ml/min for 1 h, purged with purified Ar and further treated at 450 °C for 0.5 h in Ar. The reactor was then cooled to 50 °C in Ar, exposed to 10% H_2 -90% Ar for 30 min, purged with Ar for 5 h at 50 °C in order to eliminate the physical adsorbed H_2 . Temperature-programmed desorption was conducted by ramping to 450 °C at 10 °C/min and H_2 ($m/e = 2$) in the effluent was detected and recorded as a function of temperature by a quadrupole mass spectrometer (OmniStar™, GSD301, Switzerland).

2.3. Catalytic reactions

Hydrogenolysis of glycerol was performed in a custom-designed 100 ml stainless steel autoclave equipped with a Teflon inner layer. Before the reaction, the catalyst was pretreated in a stream of H_2 at 300 °C for 1 h. The reaction mixture included an 8.0 g solution of glycerol (75 wt%) in different solvents and a controlled amount of catalyst. Then the autoclave was charged with H_2 to 2.0 MPa and placed in an oil bath preheated to required temperature with vigorous stirring (MAG-NEO, RV-06 M, Japan). After the reaction, the reactor was cooled to room temperature. The vapor phase was collected and analyzed, the liquid phase was centrifuged to remove the solid catalyst powder and analyzed using an FID gas chromatograph (Shimadzu, 14 B) equipped with a 30 m capillary column (DB-WAX 52 CB, USA). All products detected in the liquid phase were verified by a GC-MS system (Agilent 6890).

and quantified via external calibration method. The selectivity for product was calculated on carbon basis.

3. Results and discussion

3.1. Chemical and physical properties

Figure 1 shows the XRD patterns of the fresh $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ precursors. Sharp and symmetrical reflections lines assign as diffraction from the (003), (006), (012), (015), (110), and (113) planes were observed, which reflected the characteristic structure of LDHs. The intensity of the (003) reflection decreased with the addition of M, which means that the orderliness of layered double hydroxide crystallite declined.

The well developed layered structure of the solid lamella in the $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ precursors were also directly identified in their SEM images. Figure 2 shows the SEM images of the as synthesized $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$ and $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ precursors. The LDH precursors appeared to be ball/flower particles sized from 1.8–2.0 μm in diameter (shown in the insert images in Fig. 2). Under higher resolution, well developed layered structures of the solid lamella could be identified in each particle. The average thickness of a solid lamella was about 20 nm in $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$ (Fig. 2(a)). This thickness decreased to 15–16 nm in both $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ samples (see Fig. 2). This decrease in thickness of the solid lamella could be attributed to that the decrease in orderliness in the LDH crystallite caused by the addition of the noble metals, and these results fit well with the XRD analysis (see Fig. 1). Inter-particle spaces and slit pores were detected in all the samples, which could be ascribed to the accumulation of these layered solid lamellae. These can be regarded as the source of the mesopores. These mesopores are a great enhancement as they enhance the accessibility of reactants to the active sites and improve the diffusion of products.

After calcination at 300 °C for 4 h, the characteristic diffraction peaks of lamellar structure still could be detected, which means that the gallery structure of hydrotalcite remained, however, the intensity and the sharpness of the peaks decreased, which indicates that the orderliness of solid lamellar decreased during thermal decomposition owing to partial loss

Fig. 1. XRD patterns of fresh LDHs. (1) $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$; (2) $Ru_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$; (3) $Re_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$.

of carbonate and water in the gallery of the hydrotalcite during the calcinations. No separated peaks from the oxides of Cu, Ru, or Re were detected, which means the amount of these metals was sufficiently low and remained highly dispersed in the solid lamellae (see Fig. 3).

Figure 4 shows TEM images of the cross-sections of the hydrogen reduced Ru- or Re-doped Cu/solid base catalysts, in which the gallery structure of hydrotalcite can be seen, which agrees with the XRD analysis (see Fig. 3). The solid lamellae in these reduced catalysts, with thicknesses of about 16–17 nm and being 450–480 nm in length, can be seen, agreeing with

Fig. 3. XRD patterns of the calcined materials. (1) $Cu_{0.4}Mg_{5.6}Al_2O_9$; (2) $Ru_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}O_9$; (3) $Re_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}O_9$.

Fig. 2. SEM images of the fresh LDHs. (a) $Cu_{0.4}Mg_{5.6}Al_2(OH)_{16}CO_3$; (b) $Ru_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$; (c) $Re_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$. Inset images show the same image at lower magnification.

Fig. 4. TEM images of the reduced samples. (a) $\text{Ru}_{0.02}\text{Cu}_{0.4}/\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_{8.57}$; (b) $\text{Re}_{0.02}\text{Cu}_{0.4}/\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_{8.57}$.

previous reports [3,41]. These lamellae are arranged in parallel with a gap of about 70–80 nm. High resolution TEM images of the solid lamellae disclosed that the d spacing of the reduced sample is around 0.8 nm, which fits well with the calculated structure of LDH [42]. No separate Cu particles can be identified, which confirms the Cu and Ru or Re to be dispersed homogeneously in the matrix of the hydrotalcite.

The nitrogen adsorption-desorption isotherms of the calcined $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ and $\text{M}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ are shown in Fig. 5. All of the isotherms are type IV according to the IUPAC classification. All the samples therefore have mesoporous structures, which is in accordance with their SEM and TEM images (Fig. 4). And these mesopores should enhance the accessibility of reactants to the active sites and improve the outward diffusion of products. The closure point of hysteresis loop of $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ is located at a relative pressure of 0.6. However, the hysteresis loop of $\text{Ru}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ closed at 0.5, which suggests that the pore diameter has decreased. $\text{Re}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ has a closure point of hysteresis loop at about 0.6, inferring a similar pore diameter to $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ (see Table 1). The calculated BET surface area of $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ is 204.6 m^2/g . A slight increase was observed in

Fig. 5. N_2 adsorption-desorption isotherms of the calcined samples. (1) $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$; (2) $\text{Ru}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$; (3) $\text{Re}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$.

$\text{Ru}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$, and a slight decrease in BET surface area in $\text{Re}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ (see Table 1).

Figure 6 illustrates the H_2 -TPR profiles of the calcined $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ and $\text{M}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$. Only one broader peak from 250 to 340 $^{\circ}\text{C}$ was detected in $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$. This hydrogen consumption could be designated to the reduction of Cu^{2+} ions in lamellar structure of $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$ [3]. This same reduction peak of copper drops to 210–305 $^{\circ}\text{C}$ in $\text{Ru}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ and to 230–310 $^{\circ}\text{C}$ for $\text{Re}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$. These results mean that the reducibility of Cu^{2+} ions in lamellar structure of $\text{M}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ was improved by the addition of the noble metals. This improvement could be ascribed to superior dissociation of H_2 on noble metals before moving to the Cu^{2+} ions [39,43–44]. That is, the addition of Ru or Re in $\text{M}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ improves the concentration of active hydrogen available for use in the reduction of Cu^{2+} ions. At the same time, no peaks relating to the reduction of the M^{3+} ions were observed, which was most likely due to the small amount of the noble metal present.

The hydrogen activation and the spillover ability of the $\text{M}_{0.02}\text{Cu}_{0.4}/\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_{8.57}$ catalysts were tested by H_2 -TPD and shown in Fig. 7. It can be found that no desorption peak was observed over the whole temperature range for $\text{Cu}_{0.4}/\text{Mg}_{5.6}\text{Al}_2\text{O}_{8.6}$. However, three obvious H_2 desorption peaks (at 90–140, 240–300, and 300–360 $^{\circ}\text{C}$) were detected in both

Fig. 6. H_2 -TPR profiles of the calcined samples. (1) $\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$; (2) $\text{Ru}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$; (3) $\text{Re}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$.

Table 1

The structure of the calcined $\text{M}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$ precursors.

Catalyst*	$A_{\text{BET}}/(\text{m}^2/\text{g})$	Pore diameter (nm)	Pore volume (cm^3/g)
$\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_2\text{O}_9$	204.6	16.8	0.860
$\text{Ru}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$	235.2	11.1	0.653
$\text{Re}_{0.02}\text{Cu}_{0.4}\text{Mg}_{5.6}\text{Al}_{1.98}\text{O}_9$	162.9	15.9	0.648

*All of the catalysts are calcined at 300 $^{\circ}\text{C}$ for 4 h.

Fig. 7. H_2 -TPD profiles of the reduced catalysts. (1) $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$; (2) $Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$; (3) $Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$.

$M_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$. These results indicated that the addition of Ru or Re significantly enhanced the ability to adsorbing hydrogen. According to the published works in this area, the resolved peak at low temperature (90–140 °C) could be ascribed to the decomposition of MH_x or hydrogen adsorbed on M. While a much broader signal in the range of 240–300 °C monitors the desorption of hydrogen from the Cu particles, and the shoulder peak at 300–360 °C would arise from splitting H–H on the surface of the Mg–Al–O oxides [45–48]. These results suggested that hydrogen activation and spillover phenomena driven by the added Ru or Re markedly influence the adsorption of H_2 . The addition of Ru or Re enhanced both the hydrogen storage capacity and H_2 activation ability over the surface of the catalysts. These enhanced H_2 activation abilities would improve its activity for glycerol hydrogenolysis.

3.2. Glycerol hydrogenolysis

Table 2 summarized the activity of the hydrogen reduced Ru- or Re-doped Cu/solid base catalysts which were prepared from the $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ (M = Ru, Re) LDH precursors for glycerol hydrogenolysis. On the surface of the $Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$ catalyst, the conversion of glycerol and the

Hydrogenolysis of glycerol on $M_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$.

Catalyst	Solvent	Conversion (%)	Selectivity (%)		
			1,2-PDO	Ethylene glycol	Others*
$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$	H_2O	56.7	97.1	1.1	1.8
$Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	H_2O	70.6	96.1	3.3	0.6
$Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	H_2O	71.6	96.7	2.8	0.5
$Ru_{0.02}/Mg_{5.6}Al_{1.98}O_{8.57}$	H_2O	1.5	78.5	1.5	20.0
$Re_{0.02}/Mg_{5.6}Al_{1.98}O_{8.57}$	H_2O	1.2	72.3	2.6	25.1
$Cu_{0.4}/Mg_{5.6}Al_2O_{8.6}$	C_2H_5OH	71.3	97.9	1.1	1.0
$Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	C_2H_5OH	90.2	98.5	1.0	0.5
$Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	C_2H_5OH	91.0	98.7	1.1	0.2
$Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	CH_3OH	91.2	98.6	0.9	0.5
$Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	CH_3OH	91.5	98.5	1.0	0.5
$Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	C_3H_7OH	89.4	98.3	1.1	0.6
$Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	C_3H_7OH	90.5	98.6	0.9	0.5

Reaction conditions: 75 wt% solutions of glycerol 8.0 g, 2.0 MPa H_2 , 180 °C, 10 h. The catalysts have been reduced under H_2 for 1 h.

* Methanol and 1-propanol.

Table 3

Hydrogenolysis of glycerol on recycled $M_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$.

Catalyst	Cycle	Conversion (%)	Selectivity (%)		
			1,2-PDO	Ethylene glycol	Others*
$Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	1	90.2	98.5	1.0	0.5
	2	86.3	98.3	1.1	0.6
	3	81.5	98.7	0.8	0.5
	4	77.4	98.0	0.9	1.1
	5	74.8	98.4	0.9	0.7
$Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$	1	91.0	98.7	1.1	0.2
	2	88.6	98.5	0.9	0.6
	3	83.9	98.6	1.0	0.4
	4	78.1	98.5	0.8	0.7
	5	76.0	98.7	0.9	0.4

Reaction conditions: glycerol ethanol solution (75 wt%) 8.0 g, 2.0 MPa H_2 , 1.0 g reduced catalyst, 10 h.

* Methanol and 1-propanol.

selectivity for 1,2-PDO in aqueous solution were 56.7% and 97.1%, respectively, at low hydrogen pressure (2.0 MPa) and short time (10 h). With the addition of M, a remarkable increase in the conversion of glycerol could be observed. The conversion of glycerol over $Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ and $Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ were 70.6% and 71.6%, respectively. In order to investigate the reason for this improved activity, $M_{0.02}/Mg_{5.6}Al_{1.98}O_{8.57}$ were also prepared and tested in the glycerol hydrogenolysis reaction. However, almost no conversion of glycerol was observed. All the results indicated that the enhanced activity of $M_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ was not due to additional M sites, but to a synergistic effect of M on the active Cu sites, which enhanced the hydrogen activation ability over just M [39,43,44].

Glycerol hydrogenolysis in different solvents was also performed. The use of alcohols clearly favored the conversion of glycerol. This can be attributed to the stronger adsorption of water onto the catalyst than methanol, ethanol, and C_3H_7OH , which hinders the accessibility of glycerol [49].

Table 3 shows the activity of recycled $M_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ catalyst in ethanol solution. The detected conversion of glycerol over $Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ decreased from 90.2% (the fresh catalyst) to 86.3% (for the second cycle) and similar phenomena could be detected in the following recycles. The decrease of the glycerol conversion could be attributed to the loss of catalyst associated with separation and transfer of the catalyst in recycling process. Overall, the amount of catalyst decreased from 1.0 g to 0.65 g in the fifth cycle. The trend of glycerol hydrogenolysis on $Re_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ is similar to that of $Ru_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$. All the results indicated $M_{0.02}Cu_{0.4}/Mg_{5.6}Al_{1.98}O_{8.57}$ was stable for the consecutive reactions.

4. Conclusions

Ru- or Re-doped Cu/solid base catalysts have been successfully synthesized via calcination of the $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ (M = Ru or Re) precursors prepared by co-precipitation. These catalysts exhibited excellent performance for the hydrogenolysis of glycerol under mild conditions. Char-

Graphical Abstract

Chin. J. Catal., 2013, 34: 986–992 doi: 10.1016/S1872-2067(11)60505-6

Trivalent metal ions M^{3+} in $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ layered double hydroxide as catalyst precursors for the hydrogenolysis of glycerol

XIA Shuixin, ZHENG Liping, NIE Renfeng, CHEN Ping, LOU Hui, HOU Zhaoyin*
Zhejiang University

Trivalent metal ions M^{3+} in $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ ($M = Ru, Re$) layered double hydroxides (LDHs) derived M-Cu/solid base catalysts show excellent performance for the hydrogenolysis of biomass-derived glycerol under mild conditions.

acterization indicated that the addition of M enhanced the adsorption and activation ability of hydrogen in the Cu/solid base catalyst, which contributed to its higher activity in the hydrogenolysis of glycerol.

References

- [1] Marceau E, Carrier X, Che M, Clause O, Marcilly C. In: Ertl G, Knözinger H, Schüth F, Weitkamp J eds. Handbook of Heterogeneous Catalysis. 2nd Ed. Vol II. Weinheim: Wiley-VCH, 2008. 467
- [2] Liu H B, Jiao Q Z, Zhao Y, Li H S, Sun C B, Li X F. *J Alloys Compd*, 2010, 496: 317
- [3] Yuan Z L, Wang L N, Wang J H, Xia S X, Chen P, Hou Z Y, Zheng X M. *Appl Catal B*, 2011, 101: 431
- [4] Shao M F, Ning F Y, Zhao J W, Wei M, Evans D G, Duan X. *J Am Chem Soc*, 2012, 134: 1071
- [5] Meher L C, Gopinath R, Naik S N, Dalai A K. *Ind Eng Chem Res*, 2009, 48: 1840
- [6] Valente J S, Hernandez-Cortez J, Cantu M S, Ferrat G, López-Salinas E. *Catal Today*, 2010, 150: 340
- [7] Guo X H, Li Y, Song W, Shen W J. *Catal Lett*, 2011, 141: 1458
- [8] Takehira K, Shishido T, Wang P, Kosaka T, Takaki K. *J Catal*, 2004, 221: 43
- [9] Tsyganok A I, Tsunoda T, Hamakawa S, Suzuki K, Takehira K, Hayakawa T. *J Catal*, 2003, 213: 191
- [10] Morioka H, Shimizu Y, Sukenobu M, Ito K, Tanabe E, Shishido T, Takehira K. *Appl Catal A*, 2001, 215: 11
- [11] Huang J H, Chen J X. *Chin J Catal* (黄金花, 陈吉祥. 催化学报), 2012, 33: 790
- [12] Zope B N, Hibbitts D D, Neurock M, Davis R J. *Science*, 2010, 330: 74
- [13] Villa A, Veith G M, Prati L. *Angew Chem, Int Ed*, 2010, 49: 4499
- [14] Villa A, Gaiassi A, Rossetti I, Bianchi C L, Benthem K, Veith G M, Prati L. *J Catal*, 2010, 275: 108
- [15] Liang D, Gao J, Wang J H, Chen P, Hou Z Y, Zheng X M. *Catal Commun*, 2009, 10: 1586
- [16] Liang D, Cui S Y, Gao J, Wang J H, Chen P, Hou Z Y. *Chin J Catal* (梁丹, 崔世玉, 高静, 王军华, 陈平, 侯昭胤. 催化学报), 2011, 32: 1831
- [17] Zhang M Y, Liang D, Nie R F, Lu X Y, Chen P, Hou Z Y. *Chin J Catal* (张梦媛, 梁丹, 聂仁峰, 吕秀阳, 陈平, 侯昭胤. 催化学报), 2012, 33: 1340
- [18] Chai S H, Wang H P, Liang Y, Xu B Q. *Green Chem*, 2007, 9: 1130
- [19] Cavani F, Guidetti S, Marinelli L, Piccinini M, Ghedini E, Signoretto M. *Appl Catal B*, 2010, 100: 197
- [20] Wang F, Dubois J L, Ueda W. *J Catal*, 2009, 268: 260
- [21] Katryniok B, Paul S, Capron M, Lancelot C, Bellière-Baca V, Rey P, Dumeignil F. *Green Chem*, 2010, 12: 1922
- [22] Ma L, Li Y M, He D H. *Chin J Catal* (马兰, 李宇明, 贺德华. 催化学报), 2011, 32: 872
- [23] Ma L, He D H. *Catal Today*, 2010, 149: 148.
- [24] Miyazawa T, Koso S, Kunimori K, Tomishige K. *Appl Catal A*, 2007, 318: 244
- [25] Maris E P, Davis R J. *J Catal*, 2007, 249: 328
- [26] Oh J, Dash S, Lee H. *Green Chem*, 2011, 13: 2004
- [27] Maris E P, Ketchie W C, Murayama M, Davis R J. *J Catal*, 2007, 251: 281
- [28] Daniel O M, DeLaRiva A, Kunkes E L, Datye A K, Dumesic J A, Davis R J. *ChemCatChem*, 2010, 2: 1107
- [29] Amada Y, Shinmi Y, Koso S, Kubotac T, Nakagawa Y, Tomishige K. *Appl Catal B*, 2011, 105: 117
- [30] Zhou J, Zhang J, Guo X, Mao J, Zhang S. *Green Chem*, 2012, 14: 156
- [31] Xia S X, Nie R F, Lu X Y, Wang L N, Chen P, Hou Z Y. *J Catal*, 2012, 296: 1
- [32] Yuan Z L, Wu P, Gao J, Lu X Y, Hou Z Y, Zheng X M. *Catal Lett*, 2009, 130: 261
- [33] Yuan Z L, Wang J H, Wang L N, Xie W H, Chen P, Hou Z Y, Zheng X M. *Bioresour Technol*, 2010, 101: 7088
- [34] Wu Z, Mao Y, Wang X, Zhang M. *Green Chem*, 2011, 13: 1311
- [35] Bienholz A, Schwab F, Claus P. *Green Chem*, 2010, 12: 290
- [36] Bienholz A, Blume R, Knop-Gericke A, Girgsdies F, Behrens M, Claus P. *J Phys Chem C*, 2011, 115: 999
- [37] Guo X H, Li Y, Liu Q Y, Shen W J. *Chin J Catal* (郭小惠, 李勇, 刘琪英, 申文杰. 催化学报), 2012, 33: 645
- [38] Hu J Y, Liu X Y, Wang B, Pei Y, Qiao M H, Fan K N. *Chin J Catal* (胡基业, 刘晓钰, 王彬, 裴燕, 乔明华, 范康年. 催化学报), 2012, 33: 1266
- [39] Xia S X, Yuan Z L, Wang L N, Chen P, Hou Z Y. *Appl Catal A*, 2011, 403: 173
- [40] Musolino M G, Scarpino L A, Mauriello F, Pietropaolo R. *ChemSusChem*, 2011, 4: 1143
- [41] Labajos F M, Rives V, Ulibarri M A. *J Mater Sci*, 1992, 27: 1546
- [42] Liang J, Ma R, Iyi N, Ebina Y, Takada K, Sasaki T. *Chem Mater*, 2010, 22: 371
- [43] Xia S X, Yuan Z L, Wang L N, Chen P, Hou Z Y. *Bioresour Technol*,

- 2012, 104: 814
- [44] Li B D, Wang J, Yuan Y Z, Ariga H, Takakusagi S, Asakura K. *ACS Catal*, 2011, 1: 1521
- [45] Genger T, Hinrichsen O, Muhker M. *Catal Lett*, 1999, 59: 137
- [46] Wilmer H, Genger T, Hinrichsen O. *J Catal*, 2003, 215: 188
- [47] Ahlers J A, Grasser J A, Loveless B T, Muggli D S. *Catal Lett*, 2007, 114: 185
- [48] Arena F, Italiano G, Barbera K, Bordiga S, Bonura G, Spadaro L, Frusteri F. *Appl Catal A*, 2008, 350: 16
- [49] Bienholz A, Schwab F, Claus P. *Green Chem*, 2010, 12: 290

由 $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ (M = Ru, Re)水滑石为前驱体制备的双金属固体碱催化甘油氢解

夏水鑫, 郑丽萍, 聂仁峰, 陈 平, 楼 辉, 侯昭胤*

浙江大学化学系催化研究所, 浙江杭州310028

摘要: 采用共沉淀法合成了 $M_{0.02}Cu_{0.4}Mg_{5.6}Al_{1.98}(OH)_{16}CO_3$ (M = Ru, Re)水滑石前驱体, 然后经焙烧和还原制备了铜分散度较高的双功能M-Cu/固体碱催化剂. 这些双功能催化剂在粗甘油氢解制备丙二醇反应中表现出了很好的催化活性. 表征结果证明, M的加入增强了催化剂表面氢的吸附和活化, 进而促进了甘油的转化.

关键词: 水滑石; 双金属; 固体碱; 甘油; 氢解; 丙二醇

收稿日期: 2012-10-31. 接受日期: 2012-12-03. 出版日期: 2013-05-20.

*通讯联系人. 电话/传真: (0571)88273283; 电子信箱: zyhou@zju.edu.cn

基金来源: 国家自然科学基金(21273198, 21073159); 浙江省自然科学基金(LZ12B030001).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).