Hydrogenolysis of glycerol over Cu-substituted hydrocalumite mediated catalysts

Liping Zheng, Shuixin Xia, Zhaoyin Hou *

Key Lab of Applied Chemistry of Zhejiang Province, Department of Chemistry, Zhejiang University, Hangzhou 310028, China

ABSTRACT

A series of Cu-substituted hydrocalumite with different content of Cu^{2+} were synthesized and used as the precursor of bifunctional Cu/solid base catalysts ($Cu_x/Ca_yAlO_{y + 1.5}$) in this work. It was found that mainly hydrocalumite formed when the content of Cu^{2+} was lower (x < 1.5 in $[Cu_xCa_yAl(OH)_{2x + 2y + 2}]NO_3 \cdot nH_2O$). After controlled calcination and hydrogen reduction, Cu dispersed highly in the matrix of $Ca_yAlO_{y + 1.5}$ and the total amount of basic sites reached its maximum in $Cu_{1.5}/Ca_{2.0}AlO_{3.5}$. These catalysts were active and selective for the hydrogenolysis of glycerol under mild conditions. The calculated specific activity of surface Cu increased with the basicity of catalysts. The detected conversion of glycerol on $Cu_{1.5}/Ca_{2.0}AlO_{3.5}$ reached 75.3% with a 98.1% selectivity towards 1,2-PDO at 180 °C, 2.0 MPa H_2 and 21 h.

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1. Introduction

Biodiesel is a renewable fuel produced from vegetable oils such as rape seed oil, sunflower seed oil, soybean oil and also used frying oils or animal fats, it can be used both in blended with fossil diesel fuel and in pure form. Biodiesel has been demonstrated to have significant environmental benefits in terms of decreased global warming impacts, reduced CO_2 emissions, and a positive impact on agriculture (Dodds and Gross, 2007; Bozell, 2010; Bozell and Petersen, 2010). But the rapidly rising production of biodiesel has lead to a serious surplus of glycerol (Tan et al., 2013). Glycerol is nontoxic, edible, and biodegradable, and it can be used as a building block for value-added chemicals (Pagliaro et al., 2007; Zhou et al., 2008; Katryniok et al., 2011). A number of potential products can be obtained by the selective dehydration, oxidation and hydrogenolysis of glycerol (Chaminand et al., 2004; Maris and Davis, 2007; Kurosaka et al., 2008; Nakagawa et al., 2010). Among of which, hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) instead of the expensive hydration of petro-based propylene oxide has attracted much attention in the past decade (Chaminand et al., 2004; Shinmi et al., 2010; Gandarias et al., 2011).

Significant efforts have been made for the production of 1,2-PDO from glycerol over noble-metal catalysts, such as Ru (Maris and Davis, 2007; Miyazawa et al., 2007a, 2007b; Ma et al., 2008; Vasiliadou et al., 2009; Bolado et al., 2010; Ma and He, 2010; Salazar et al., 2014), Pt (Maris and Davis, 2007; Yuan et al., 2009; Oberhauser et al., 2015), Pd (Li et al., 2014a; Mauriello et al., 2015), Rh (Shinmi et al., 2010; Li et al., 2015), and Ag (Yadav et al., 2012; Sun et al., 2014). At the same time, Cu (Huang et al., 2009; Rode et al., 2010; Wang et al., 2010; Yuan et al., 2010; Xia et al., 2013; Vasiliadou et al., 2014; Vasiliadou et al., 2015; Zhu et al., 2015), Ni (Miranda et al., 2014; Yun et al., 2014), and Co (Guo et al., 2009; Cao et al., 2011) were also reported for this reaction. In published works, it is suggested that glycerol hydrogenolysis perform in a consecutive dehydration (to acetol) and hydrogenation (of acetol) mechanism under acidic condition, but acid catalysts also catalyze the cleavage of C–C bond in glycerol (Li et al., 2014b). On the other hand, 1,2-PDO could be synthesized in a tandem dehydrogenation–dehydration–hydrogenation reaction in basic solutions (Yuan et al., 2011). In our laboratory, a series of solid base supported Pt (Yuan et al., 2009), Cu (Yuan et al., 2011), Pd–Cu (Xia et al., 2011), ZnO-Cu (Xia et al., 2012) catalysts were synthesized and tested in the hydrogenolysis of glycerol to 1,2-PDO. It was found that the conversion of glycerol depended strongly on the basicity of these catalysts, enhancing the basicity of these catalysts can accelerate the formation of 1,2-PDO.

In this work, a series of $Cu_x/Ca_yAlO_{y + 1.5}$ catalysts with different content of Cu were prepared via controlled calcination and reduction of Cu-substituted hydrocalumite and used in the hydrogenolysis of glycerol. The activity of these $Cu_x/Ca_yAlO_{y + 1.5}$ catalysts were discussed with their structure and basicity.

2. Experimental

2.1. Catalyst preparation

$[Cu_xCa_yAl(OH)_{2x + 2y + 2}]NO_3 \cdot nH_2O$ hydrocalumite was prepared according to reference (Dékány et al., 1997). De-ionized and decarbonated water, N_2 atmosphere protection were used throughout

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* Corresponding author.
E-mail address: zyhou@zju.edu.cn (Z. Hou).

the precipitation and washing processes. NaOH (150 mmol) and NaNO$_3$ (130 mmol) were first dissolved in 150 mL purified water. A solution of mixed Cu(NO$_3$)$_2$·3H$_2$O (0.5–25 mmol), Ca(NO$_3$)$_2$·4H$_2$O (37–12.5 mmol) and Al(NO$_3$)$_3$·9H$_2$O (12.5 mmol) in 75 mL water was then added slowly to above mixture under stirring in N$_2$ atmosphere. The obtained solid was separated by centrifugation, washed with purified water and dried in vacuum at 60 °C overnight to form [Cu$_x$Ca$_y$Al(OH)$_{2x + 2y + 2}$]NO$_3$·nH$_2$O, where x and y represent the amount of Cu and Ca in the final products, respectively. The composition of prepared [Cu$_x$Ca$_y$Al(OH)$_{2x + 2y + 2}$]NO$_3$·nH$_2$O was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES) and summarized in Table 1. After calcination at 500 °C for 4 h, [Cu$_x$Ca$_y$Al(OH)$_{2x + 2y + 2}$]NO$_3$·nH$_2$O changed into Cu$_x$Ca$_y$AlO$_{x + y + 1.5}$ because water and NO$_3$ were removed during calcinations. Before catalytic reaction, Cu$_x$Ca$_y$AlO$_{x + y + 1.5}$ was reduced in hydrogen flow (30 mL/min) at 450 °C for 1 h, and the reduced catalyst was denoted as Cu$_x$/Ca$_y$AlO$_{y + 1.5}$ because Cu^{2+} species was reduced to Cu^0. The notation of these catalysts was summarized in Table S1 (in supplementary data).

2.2. Catalyst characterization

N$_2$ adsorption of Cu$_x$Ca$_y$AlO$_{x + y + 1.5}$ was measured at its normal boiling point using an ASAP 2010 analyzer (Micromeritics) after pretreated at 250 °C for 4 h in vacuum. Specific surface area and pore size distribution were calculated using their adsorption isotherms. Powder X-ray diffraction (XRD) patterns of fresh and calcined hydrocalumites were detected at room temperature on a Rigaku D/WAX-2500 diffractometer using CuKα radiation (λ = 1.5406 Å) with a 2θ step of 0.02°, and 1°/min from 5 to 80°. FULLPROF program was used for the Rietveld refinement analysis (Rodriguez-Carvajal, 1990). Scanning electronic images (SEM) were detected on Leo Evo Series SEM (VP 1430, Germany). Samples were coated with gold using sputter coating to avoid charging. Analysis was carried out at an accelerating voltage of 15 kV. Differential scanning calorimetry- thermogravimetric analysis (DSC-TGA) of the prepared samples from room temperature to 600 °C was carried out on a Netzsch STA409 thermobalance system using a heating rate of 10 °C/min in purified N$_2$. Temperature-programmed reduction of calcined Cu$_x$Ca$_y$AlO$_{x + y + 1.5}$ was performed in the following procedures: samples (0.1 g) were first pretreated at 500 °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$_2$/N$_2$ mixture, 30 mL/min) was shifted and the reactor was heated to 450 °C at a ramp of 10 °C/min. Effluent gas was dried by powder KOH and the consumption of hydrogen was recorded by thermal conductivity detector. The amount of reduced Cu in these samples was calibrated with pure CuO (AR, Sinopharm Chemical Reagent Co., Ltd., China) of known amount.

The number of surface metallic copper was determined by N$_2$O oxidation and followed H$_2$ titration using the procedure described by Van Der Grift et al. (Van Der Grift et al., 1991). Catalysts were first reduced in the procedure described above, and the amount of hydrogen consumption was denoted as X. And then the reactor was purged with

He to 50 °C. 20% N$_2$O/N$_2$ (30 mL/min) was shifted to oxidize surface copper atoms to Cu$_2$O at 50 °C for 0.5 h. The reactor was flushed with He to remove the oxidant. Finally, another reduction experiment was performed in 10% H$_2$/N$_2$ at a flow rate of 30 mL/min. Hydrogen consumption in the second reduction was denoted as Y. The dispersion of surface Cu was calculated according to the following equation:

Reduction of all copper atoms:
CuO + H$_2$ → Cu + H$_2$O, hydrogen consumption in the first TPR = X.
Reduction of surface copper atoms only:
Cu$_2$O + H$_2$ → 2Cu + H$_2$O, hydrogen consumption in this TPR = Y.
And the dispersion of the surface Cu was calculated as:

$$D = (2 \times Y/X) \times 100\%.$$

The amounts of hydrogen consumption of these catalysts were summarized in Table S2 (in Supplementary data).

The basicity of catalyst was determined via temperature-programmed desorption (TPD) of CO$_2$ (CO$_2$-TPD). The calcined sample (Cu$_x$Ca$_y$AlO$_{x + y + 1.5}$) was first reduced at 450 °C in H$_2$ flow of 30 mL/min for 1 h, and then the reactor was cooled to 50 °C in Ar, purged by purified Ar and further treated at 700 °C for 0.5 h in Ar. Then the reactor was cooled to 50 °C in Ar, exposed to 20% CO$_2$/Ar for 30 min, purged by Ar for 5 h at 100 °C in order to eliminate the physically adsorbed CO$_2$. CO$_2$-TPD was conducted by ramping to 700 °C at 10 °C/min and CO$_2$ (m/e = 44) in effluent was detected and recorded as a function of temperature on a quadrupole mass spectrometer (Omni Star TM, GSD301, Switzerland).

2.3. Catalytic reaction

Hydrogenolysis of glycerol was performed in a custom-designed stainless steel autoclave. The reaction mixture contains 1.6 g H$_2$O, 0.8 g glycerol and 0.1 g reduced catalyst. Then the autoclave was purged with H$_2$ for several times, pressurized to 2.0 MPa and placed in an oil bath preheated to required temperature and maintained at that temperature under vigorous stirring (MAGNEO, RV-06 M, Japan). After reaction, the reactor was cooled to the room temperature; vapor phase was collected by a gas-bag and analyzed with a gas chromatograph (Shimadzu, 8A) with thermal conductivity detector. Solid catalyst powder in liquid phase was separated via centrifugation and washed with deionized water (5 × 5 mL). The eluent and reaction mixture were collected and charged into a 50 mL volumetric flask and analyzed using a flame ionization detector gas chromatograph (Shimadzu, 14B) equipped with a 30 m capillary column (DB-WAX 52 CB, USA). All products detected in liquid were verified by a gas chromatography and mass spectrometry system (GC–MS, Agilent 6890) and quantified via external calibration method. The selectivity of product was calculated on carbon basis.

3. Results and discussion

3.1. Catalyst characterization

Fig. 1 showed the XRD patterns of fresh synthesized [Cu$_x$Ca$_y$Al(OH)$_{2x + 2y + 2}$]NO$_3$·nH$_2$O hydrocalumite. The classical reflections of (002), (004), and (008) planes of a typical hydrocalumite (JCPDS 00-050-0652) could be detected in those samples with lower Cu^{2+} content (x < 2.8) (Rousselot et al., 2002; Segni et al., 2006; Kim et al., 2012). And the small reflection at 12.1° in [Ca$_{2.3}$Al(OH)$_{6.6}$]NO$_3$·nH$_2$O could be attributed to the formation of another hydrocalumite phase (Ca$_8$Al$_4$O$_{13}$CO$_3$·24H$_2$O) due to the adsorption of CO$_2$. However, the intensity of these reflections decreased when the content of Cu^{2+} was high (x > 2.8). The decline of intensity of these hydrocalumite crystals could be ascribed to the decrease of relative content of Ca^{2+} and it was hard to synthesizing perfect hydrocalumite crystal due to the Jahn-Teller effect in Cu^{2+} ion

Table 1
Composition and lattice parameter of synthesized hydrocalumite[a].

Samples	x(Cu/Al)	y(Ca/Al)	a/Å[b]	c/Å[b]
[Ca$_{2.3}$Al(OH)$_{6.6}$]NO$_3$·nH$_2$O	0	2.3	5.756	17.355
[Cu$_{0.1}$Ca$_{1.7}$Al(OH)$_{5.6}$]NO$_3$·nH$_2$O	0.1	1.7	5.711	17.133
[Cu$_{0.4}$Ca$_{1.8}$Al(OH)$_{6.4}$]NO$_3$·nH$_2$O	0.4	1.8	5.736	17.259
[Cu$_{1.5}$Ca$_{2.0}$Al(OH)$_9$]NO$_3$·nH$_2$O	1.5	2.0	5.755	17.333
[Cu$_{2.8}$Ca$_{2.2}$Al(OH)$_{12}$]NO$_3$·nH$_2$O	2.8	2.2	5.7633	17.468

[a] All these lattice parameter were calculated on the basis of modified Ca$_4$Al$_2$(OH)$_{12}$(NO$_3$)$_2$(H$_2$O)$_4$ (ICSD No. 280,171) in Rietveld Refinement analysis (see Fig. S1 in the supplementary data).
[b] c = average value calculated from (002), (004), and (008) reflections and a = 2d(110), according to the method in reference (Zhao et al., 2002).