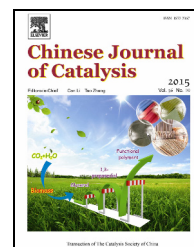


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Article

Transesterification of glycerol with dimethyl carbonate over calcined Ca-Al hydrocalumite

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ABSTRACT

A series of Ca-Al hydrocalumite with different Ca/Al ratios (1–6) were synthesized and used in the transesterification of glycerol with dimethyl carbonate (DMC) to glycerol carbonate (GC) under mild conditions. The calcined Ca-Al hydrocalumites were active with a selectivity toward GC that reached 97% at 93% conversion of glycerol over the sample with Ca/Al = 2 at 70 °C, 3 h, and DMC/glycerol = 3. The glycerol conversion depended mainly on the proportion of strong basic sites in the calcined Ca-Al catalysts. The Ca₁₂Al₁₄O₃₃ phase in the calcined catalysts was stable, but CaO was lost in recycle experiments and thus brought deactivation.

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1. Introduction

Biodiesel is an important renewable biofuel which can be produced from animal fat and vegetable oil via transesterification. The application of biodiesel can help reduce the dependence on fossil energy. Glycerol is a byproduct in the production of biodiesel, and the rapidly rising production of biodiesel leads to a large surplus of glycerol. The catalytic conversion of glycerol to valuable products has become a hot research topic [1–4]. Several products, such as propanediols [5–10], dihydroxyacetone [11–13], acrolein [14–16], and glycerol carbonate (GC) [17–19], can be synthesized from glycerol. Among these products, GC is one of the most attractive derivatives of glycerol because of its high reactivity with alcohols, amines, carboxylic acids, ketones, and isocyanates, which can yield a wide range of valuable products [20]. GC itself can be used as a solvent in NMR analysis and organic synthesis [20]. In addition,

it has been reported that GC is an important alternative solvent in lithium batteries, cosmetics, surfactants, and polymer synthesis [20]. Several routes, such as phosgenation between glycerol and phosgene [21], direct carboxylation of glycerol with CO₂ [22,23], and the glycerolysis of urea [24–28], have been proposed for the production of GC from glycerol. Among these, the direct reaction between glycerol and CO₂ is an attractive route, but it must be performed at high pressure and the yield of GC is low [29,30].

Transesterification of glycerol with dimethyl carbonate (DMC) is also an attractive way to produce GC under mild conditions [17,18]. It was reported that K₂CO₃ [31], CaO [32], K-zeolite derived from coal fly ash [33], Mg/Zr/Sr [34] and Mg/Al/Zr [35] mixed oxides were effective for this reaction. The rate of this reaction depended on the basicity of the catalyst [36], but the selectivity of GC decreased when a strong base (such as NaOH, KOH, and K₂CO₃) was used because of the for-

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mation of glycidol [37]. More recently, Liu et al. [19] disclosed that the activity of transition metal doped hydrotalcites (HT-M) for the transesterification between glycerol and DMC depended on the surface density of basic sites.

Hydrocalumite is a layered double hydroxide (LDH) with a well ordered Ca-Al distribution in the hydroxide layers, while the anions and water are highly ordered in the interlayer spaces [38,39]. The calcined hydrocalumite-like compound mainly contains $\text{Ca}_{12}\text{Al}_{14}\text{O}_{33}$ and CaO, and it shows strong basicity in CO_2 adsorption [40] and in the production of biodiesel via transesterification [41,42]. In this work, a series of Ca-Al hydrocalumite with different Ca/Al ratios (1–6) were synthesized and used in the transesterification of glycerol with DMC to GC under mild conditions. The activity and structure of the calcined hydrocalumite were discussed.

2. Experimental

2.1. Catalyst preparation

Ca-Al hydrocalumite (Ca/Al = 1–6) was prepared by a conventional coprecipitation method. CaCl_2 (12.5–75 mmol) and $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$ (12.5 mmol) were dissolved in 75 mL deionized water (solution A) [43]. Solution B was an aqueous solution of 2 mol/L NaOH. Solutions A and B were simultaneously added to a 250 mL three-necked flask under a purified N_2 flow at 30 °C with the pH of the mixture controlled at 11 during the addition [44]. The resulting suspension was filtered and washed thoroughly with deionized water until the pH of the filtrate reached about 7.0. The precipitate was dried at 110 °C overnight and calcined at 400–1000 °C for 4 h under a purified N_2 flow. The composition of the Ca-Al hydrocalumites was determined using inductively coupled plasma-atomic emission spectroscopy (ICP-AES). The obtained Ca-Al hydrocalumite was denoted as Ca_xAl_y , in which x represented the molar ratio of Ca/Al and y denoted the calcination temperature.

2.2. Catalyst characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX-2500 diffractometer with a 2θ range of 5°–80° using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406$ nm). Thermogravimetric differential scanning (TG-DSC) analysis of the samples from room temperature to 800 °C was carried out on a Netzsch STA409 thermobalance system using a heating rate of 10 °C/min under N_2 nitrogen flow. Scanning electron microscopic (SEM) images were obtained on a Leo Evo Series SEM (VP 1430, Germany). Samples were coated with gold to avoid charging. Analysis was carried out at an accelerating voltage of 15 kV. The N_2 adsorption-desorption isotherm was measured at –196 °C using a TriStar II analyzer after pretreatment of the sample at 150 °C for 10 h. The basicity of the catalyst was determined by temperature-programmed desorption of CO_2 (CO_2 -TPD). In this experiment, the sample was first treated in Ar at 600 °C for 30 min, cooled to 50 °C and exposed to 20% CO_2 (50 mL/min, Ar in balance) for 30 min. It was then purged with Ar for 1 h at 100 °C and heated linearly at 15 °C/min to 800 °C in 50

mL/min Ar. CO_2 ($m/e = 44$) in the effluent was recorded continuously as a function of temperature.

2.3. Catalytic reaction

Measured amounts of DMC (45 mmol) and glycerol (45 mmol) were mixed in a 10 mL round bottomed glass reactor fitted with a magnetic stirrer and a reflux condenser. The mixture was first heated under stirring to 70 °C, and the catalyst (0.15 g) was added to start the reaction. After reacting for 3 h, the solid catalyst was removed by centrifugation, and the supernatant liquid was analyzed using a gas chromatograph (Shimadzu, 14B) equipped with a 30-m capillary column (DB-WAX 52 CB, USA) and a flame ionization detector. All products detected in the liquid were identified by a gas chromatography-mass spectrometry system (GC-MS, Agilent 6890) and quantified by an external calibration method. The product selectivity was calculated on a carbon basis.

3. Results and discussion

3.1. Catalyst characterization

Figure 1 shows the XRD patterns of the Ca-Al samples. All the diffraction peaks of the (002), (004), (010), and (006) planes of hydrocalumite ($\text{Ca}_4\text{Al}_2\text{O}_6\text{Cl}_2 \cdot 10\text{H}_2\text{O}$, JCPDS 00-031-0245) [44,45] were detected. This result indicates that a hydrocalumite-like compound formed and a high degree of crystallinity was detected in all those samples with Ca/Al = 2–6. On the other hand, $\text{Al}(\text{OH})_3$ (JCPDS 00-033-0018) was formed in Ca_1Al due to the high content of Al [40].

Figure 2 shows typical SEM images of the Ca-Al hydrocalumites. Solid Ca-Al lamellas were formed in all samples. A clear image of separated lamellas was detected in Ca_2Al and Ca_3Al . The platelet in Ca_6Al was smaller and an amorphous solid (in white circle) was formed in Ca_1Al . The peony-shaped crystal in Ca_2Al showed the rough outline of hydrocalumite. The high resolution image of this sample is shown in Fig. 2(c). We can also see some “rosette” particles in Ca_3Al (Fig. 2(d)) [46].

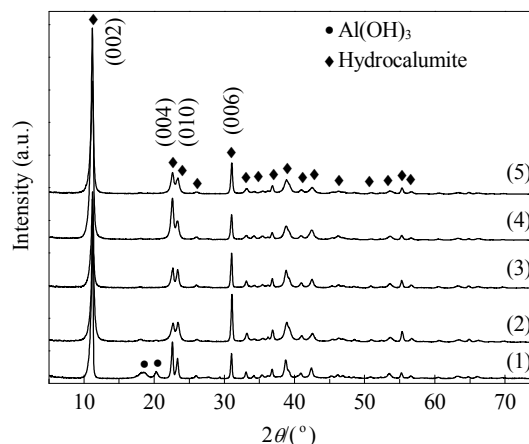


Fig. 1. XRD patterns of fresh Ca-Al hydrocalumite with different Ca/Al ratios. (1) Ca_1Al ; (2) Ca_2Al ; (3) Ca_3Al ; (4) Ca_4Al ; (5) Ca_6Al .

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