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Research article

Influence of Y on the performance of Mg-Al-Y catalysts via hydrotalcite-like precursors for the synthesis of diethyl carbonate from ethyl carbamate and ethanol

Dengfeng Wang [a,*], Xuelan Zhang [a,b,**], Diangen Zhou [a], Shanfang Liu [a], Wei Wei [b]

[a] College of Chemistry, Chemical Engineering and Materials Science, Zaozhuang University, Zaozhuang 277160, PR China
[b] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China

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ABSTRACT

A series of Mg-Al-Y mixed oxides (CHT-Y) with different Y^{3+}:($Al^{3+} + Y^{3+}$) atomic ratios were obtained by thermal decomposition of Y-containing hydrotalcite-like compounds. Then, they were characterized using XRD, TGA, XPS, SEM, ICP, CO_2-TPD and N_2 adsorption-desorption measurement. Meanwhile, all the mixed oxide catalysts were evaluated for the synthesis of diethyl carbonate (DEC) from ethyl carbamate (EC) and ethanol. The results showed that the texture, structure, basic property as well as catalytic activity of CHT-Y were closely associated with the content of Y in the catalyst. Importantly, the role of basic sites was studied in overall reaction and in every comprising reaction path identified in this research. It was found that the reaction of EC and ethanol could be improved by the moderate and strong basic sites of catalyst, while the side-reactions towards undesired products were strongly catalyzed over the catalyst with high basic strength. As a result, the best result was achieved over the catalyst with Y^{3+}:($Al^{3+} + Y^{3+}$) = 0.3. Under the optimal reaction conditions, the yield of EC reached 63.8% with a high DEC selectivity of 81.6%. Furthermore, the reusability test and catalyst characterization indicated that CHT-Y catalyst was heterogeneous and could be reused at least fourth time without obvious loss of reactivity.

1. Introduction

Having negligible toxicity and good biodegradability, diethyl carbonate (DEC) is gaining increasing popularity. It can be applied in ethylation and carbonylation processes to replace the toxic ethyl halides, ethyl sulfate and phosgene. Moreover, DEC also can be used as a raw material in the fields of producing polycarbonates, green solvent, and the electronic chemical for lithium battery [1–6]. Furthermore, due to its higher oxygen content, it could be used as fuel additive, giving rise to less environmental pollution from its decomposition products (CO_2 and ethanol) [7–9]. According to the different carbonyl sources, DEC has been conventionally synthesized via phosgenation of ethanol [10], oxidative carbonylation of ethanol [8,11], ethanolysis of CO_2 [12], carbonylation of ethyl nitrite [13], transesterification of organic carbonate [14], decarbonylation of diethyl oxalate [15], and coupling reaction from CO_2, epoxides and ethanol [16]. Nevertheless, they are all limited by corresponding commercial, technical or environmental drawbacks. As a result, the synthesis of DEC from urea and ethanol is an attractive alternative because it used two cheap, nontoxic raw feedstock [17]. In addition, the co-produced NH_3 could be easily separated, recycled and further reacted with CO_2 to generate urea. Therefore, as a green and economical process, it is drawing considerable interest in fields of catalysis and green chemistry [18–20]. Typically, this reaction could be divided into two steps: ethyl carbamate (EC) is generated first and it further reacts with ethanol to produce DEC. It was well-known that the second step of the reaction, EC to DEC, is the rate-control step for urea ethanolysis [21,22]. Thereby, developing high efficient catalyst towards the reaction of EC and ethanol is the key to the synthesis of DEC from urea and ethanol.

Many catalysts towards the DEC synthesis via urea ethanolysis or EC ethanolysis have been reported in the past [23,24]. Among them, ZnO and zinc-based mixed oxides were highly active to produce DEC. Unfortunately, it was found that the active ZnO phase could dissolve and convert to the homogeneous species of $Zn(NCO)_2(NH_3)_2$ in ethanol [19,22]. Meanwhile, Fujita et al. have proved that zinc-containing solid catalysts homogeneously catalyze glycerol carbonate production from urea and glycerol [25]. Consequently, this was unfavorable for the separation of products with the catalysts. In order to overcome this drawback, basic catalysts including MgO [26], CaO [22], La_2O_3 [18] and slag-derived solid base catalyst [20] were applied to improve DEC synthesis. Very recently, we have discovered the promotion effect of transition metal on the basicity and activity of calcined hydrotalcite catalysts for the DEC synthesis [27]. All these basic catalysts showed high reactivity, but the

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* Corresponding author. ** Correspondence to: X. Zhang, State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, Taiyuan 030001, PR China.

E-mail addresses: bitwdf@163.com (D. Wang), mhszxl@sxicc.ac.cn (X. Zhang).

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DEC selectivity was low due to the side reactions such as *N*-ethylation of EC with DEC. Meanwhile, the previous works stated that for these basic catalysts, the amount and nature of basic sites were important for the DEC synthesis [18,26,27]. However, to the best of our knowledge, the role of basic sites in each reaction step and in the overall reaction performance still remained unknown.

Hydrotalcite-like compounds (HTlcs) with the general chemical formula of $[M^{2+}{}_{1-x}M^{3+}{}_x(OH)_2]^{x+}(A^{n-})_{x/n}\cdot mH_2O$, in which M^{2+} and M^{3+} stand for the divalent and trivalent metal cation, respectively [28], are one of the most investigated catalyst precursors. The mixed oxides formed by thermal decomposition of the corresponding HTlcs possess many merits including high surface area, thermal stability and strongly basic properties [29–33]. In the present work, a series of Mg-Al-Y mixed oxide catalysts derived from Mg-Al-Y hydrotalcite-like (HTl) precursors (Mg^{2+}:(Al^{3+} + Y^{3+}) = 3:1) with Y^{3+}:(Al^{3+} + Y^{3+}) atomic ratios between 0 and 0.7 were tested for the DEC synthesis from EC and ethanol. As part of our continuous research, here, the main focus is to study the role of surface basic sites during the reaction. The reaction system that influenced the DEC selectivity and yield was identified, and every reaction path was separately investigated over these catalysts. Then, the correlation between conversion of reactants, the selectivity and yield of products and basic property of the catalysts was evaluated to examine the role of basic sites on the identified reaction paths. In addition, the reaction parameters were studied to optimize the reaction conditions and the DEC yield could reach 63.8% over the best-performing catalyst. Finally, the recyclability of the catalysts was systematically studied. In a word, the final aim of this article is to give a comprehensive view of the strategies to maximize DEC yield over a heterogeneous catalyst system.

2. Experimental

2.1. Preparation of catalysts

Mg-Al-Y hydrotalcite-like compounds were prepared via co-precipitation method using nitrate salts of the corresponding metals ($Mg(NO_3)_2\cdot 6H_2O$, $Al(NO_3)_3\cdot 9H_2O$ and $Y(NO_3)_3\cdot 6H_2O$) and a mixed solution of NaOH and Na_2CO_3 as the precipitating agent. The stating atomic ratio of Mg^{2+}:(Al^{3+} + Y^{3+}) was kept at 3:1, while that of Y^{3+}:(Al^{3+} + Y^{3+}) = 0:1, 0.1:1, 0.3:1, 0.5:1, 0.7:1, respectively. Typically, the mixed Mg-Al-Y solution and the precipitant were added dropwise with vigorous stirring to 100 mL of deionized water. During this process, the pH was kept at a constant value of 10.0 ± 0.2 by addition of suitable amount of a 2 M NaOH solution. The product was aged at 60 °C for 8 h and then filtered and washed with deionized water until pH = 7. Finally, the filter cakes were dried overnight at 100 °C and further calcined at 500 °C for 5 h in N_2 atmosphere. The as-prepared HTlcs and the corresponding mixed oxide after calcination were named as HT-*n*Y, and HTC-*n*Y, respectively, where the *n* was the Y^{3+}:(Al^{3+} + Y^{3+}) atomic ratio when the precursor were prepared. In addition, Y_2O_3 catalyst was synthesized through the same procedure as for that of HTlc using $Y(NO_3)_3\cdot 5H_2O$ as Y source and NaOH as precipitant, followed by calcination at 500 °C in N_2 atmosphere.

2.2. Characterization

Nitrogen adsorption-desorption isotherms were acquired at −196 °C using static adsorption procedures on a Micromeritics ASAP-2020 instrument (Norcross, GA). Prior to measurement, samples were degassed at 200 °C for 5 h under vacuum. The surface areas and pore volume were determined by the BET isotherm and BJH model, respectively. Power X-ray diffraction (XRD) patterns of the samples were acquired using a Rigaku Miniflex diffractometer equipped a Cu target with a Ni filter over a range of 5–80°. The elemental chemical analysis of samples was measured by an inductively coupled plasma-optical (ICP) emission spectroscopy (Thermo iCAP 6300). Thermogravimetric (TG) analysis of catalyst precursors were characterized using a NETZSCH STA-409 thermal analyzer. The samples were heated at 10 °C/min from 30 to 800 °C under a flow of nitrogen (30 $mL\cdot min^{-1}$). Scanning electron microscopy (SEM) was performed using a Hitachi S4800 microscope with an accelerating voltage of 20.00 kV. X-ray photoelectron spectroscopy (XPS) characterizations were recorded on a Thermo Scientific k-Alpha spectrometer with an Al anode (1486.6 eV) under ultrahigh vacuum (10^{-7} Pa). The binding energies were calibrated internally for surface charging by adventitious carbon deposit C (1s) with $E_b = 284.5$ eV. Carbon dioxide was used as the probe molecule to determine the basic properties of catalysts by CO_2 temperature programmed desorption (CO_2-TPD). Typically, 100 mg samples (40–60 mesh) was heated to 500 °C and held at this temperature for 1 h in flowing Ar. After it was cooled to room temperature, they were saturated with CO_2 (30 L/min) using a six-way valve for 2 h. Then, physical adsorbed CO_2 molecules were eliminated by flushing with Ar flow (40 L/min). Afterward, TPD experiments was carried out from 30 to 700 °C with heating rate of 10 °C/min under Ar flow, and the desorbed CO_2 was detected by Balzers Omnistar Mass spectrometer. CO_2 peak area was quantitatively calibrated by injecting CO_2 pulses.

2.3. Catalytic test

The reaction of EC and ethanol was performed in a 100 mL stainless steel autoclave with a magnetic stirrer and a reflux column. After 0.1 mol EC, 1 mol ethanol and 0.4 g catalyst were put into the reactor, the reactor was heated to 200 °C in a short time and kept for 5 h with magnetic stirring. During the reaction, the temperature error was <2 °C. After the reaction, the autoclave was cooled to room temperature. The product mixture in the autoclave was weighed, clarified and analyzed by a GC with a PEG-20 M capillary column and a flame ionization detector (FID), and a GC–MS (Agilent 7890-7000B) equipped with an HP-5MS capillary column (30 m).

In case of DEC decomposition reaction, a mixture of the DEC (0.1 mol) and 0.4 g of catalyst was set to react for 5 h at 200 °C. Once cooled to room temperature, the reactor was dipped in a cooling bath at −50 °C, and vented. The released gas was analyzed by GC–MS. Then the autoclave was allowed to return gradually to ambient temperature and the liquid reaction mixture was analyzed by GC and GC–MS.

The reaction of EC and DEC was carried out according to the procedure described for the reaction of EC and ethanol. The starting amount of EC, DEC and catalyst were 0.5 mol, 0.1 mol and 0.4 g, respectively, and the liquid products were quantified by means of GC and GC–MS.

3. Results and discussion

3.1. Textural and structural properties of the prepared materials

The powder X-ray diffraction patterns of the precursors with Y^{3+}:(Al^{3+}+Y^{3+}) from 0 to 0.7 shown in Fig. 1(a) illustrate the typical peaks for HTlcs. Apparently, the (003), (006), and (009) crystal planes in the layered structure could be detected at 2*θ* of 12°, 24° and 35°. Besides, the two broad and asymmetric peaks at 38° and 46° were assigned to (015) and (018) crystal planes, respectively. More important, it could be seen that the well-defined (110) and (113) planes appeared at 60° and 61° for HT-*0*Y, HT-*0.1*Y and HT-*0.3*Y samples, and no peaks corresponding to other phases were detected, which implied that all the three cations dispersed in a homogeneous state in the hydroxide layers [28,33]. However, the intensities and sharpness of the peaks at 12° and 24° that were closely related to the precursor crystallinity gradually decreased as the increasing of Y content in samples. Compare to Al^{3+} (0.053 nm), Y^{3+} possessed a much larger ionic radius (0.090 nm) [34]. As a result, a large distortions and co-formation of amorphous precipitates (such as hydroxides and hydroxycarbonates) might occur in the HTl layers upon the incorporation of Y^{3+} into the structure [35,36]. In addition, it was reported that high Al content was