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Zeolitic imidazole framework-67 as an efficient heterogeneous catalyst for the synthesis of ethyl

methyl carbonate

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Abstract

Zeolitic imidazole framework (ZIF)-67, a novel environmentally benign catalyst, was developed for preparation of ethyl methyl carbonate (EMC) from dimethyl carbonate and diethyl carbonate. EMC was obtained in 83.39 % yield using ZIF-67 as the catalyst when compared to that obtained using ZIF-8 catalyst. NH₃ and CO₂ temperature-programmed desorption methods were used to evaluate the presence of both acidic and basic sites in ZIF-67 catalyst. The lager surface area of ZIF-67 favors for the adsorption of reactants over the solid surface of the catalyst, facilitating the formation of EMC. Moreover, ZIF-67 catalyst exhibited excellent reusability without significant loss in its catalytic activity.

Keywords: Zeolitic imidazole framework-67; Ethyl methyl carbonate; Heterogeneous catalyst.

1. Introduction

In recent decades, the synthesis of ethyl methyl carbonate (EMC) has attracted much interest because of its use as a co-solvent in the electrolyte of commercial lithium-ion batteries [1-3]. In general, EMC is synthesized by the esterification of methyl chloroformate with alcohol [4] or by the transesterification of dimethyl carbonate (DMC) with ethanol [5]. However, these synthetic routes are not environmentally benign, and the separation of the three binary azeotropes is very difficult. EMC also can be synthesized by the transesterification of DMC with diethyl carbonate (DEC) (Scheme 1) using homogeneous catalysts such as Ti(OBu)₄, Bu₂SnO, and BuSnCl₃ [6]. All the reaction mixtures including DMC, DEC, and EMC, can be used directly as solvent in electrolyte. However, the separation and recovery of homogeneous catalysts remain to be a problem, limiting their practical application. Consequently, a number of heterogeneous catalysts have been investigated [7-9]. The heterogeneous catalyst systems reported include the acids (Al-Zn-MCM-41 and Al-MCM-41 [9]), the bases (MgO, ZnO, La₂O₃, and CeO₂ [8]) and acid-based bifunctional materials (amorphous mesoporous aluminophosphate [7]) for transesterification of DEC and DMC, however, the yield of EMC was still relatively low. A higher EMC yield of 85 % was obtained over Al-Zn-MCM-41 catalyst [9], but the reaction temperature was up to 180 °C. Therefore, it remains a challenge to develop a novel and environmentally benign heterogeneous catalyst which is highly effective for the EMC synthesis under mild conditions.

<Scheme 1>

Metal organic frameworks (MOF)-5 has been studied as an active catalyst for the transesterification of DMC and DEC, and a moderate yield of 50.1 % has been obtained [10]. However, MOF-5 is sensitive to water and air. Zeolitic imidazole frameworks (ZIF), a subclass of MOF, has emerged as a

new kind of porous crystalline materials with excellent properties such as uniform micro-pores, accessible pore volumes, large surface areas as well as exceptional chemical and thermal stabilities [11], making them potentially interesting candidates for gas storage [12], gas separation [13], magnetism [14], and especially catalysis [15-18]. ZIF-8 with sodalite (SOD) topology was reported by Chizallet et al. [19] to have extraordinary activity for the transesterification of vegetable oil and alcohols, and they demonstrated that the presence of both Lewis acid sites (unsaturated coordinative Zn) and Lewis base sites (nitrogen atoms of ligand) located at the external surface played a critical role in the catalytic reaction. Recently, Zhou and coworkers [20] explored the activity of ZIF-8 in the synthesis of EMC from DMC and DEC, but a relatively lower EMC yield of 50.7 % was obtained. Herein, ZIF-67, which was formed via the self-assembly of tetrahedral Co and 2-methylimidazolate linkers (Mim), was developed as a heterogeneous catalyst for the synthesis of EMC from DMC and DEC. Interestingly, a high EMC yield of 83.39 % was obtained over the ZIF-67 catalyst under mild conditions. Besides, ZIF-67 catalyst could be easily recycled at least four times with slight decrease in its catalytic activity. To the best of our knowledge, this is the first report to use ZIF-67 as catalyst for the transesterification reaction of DMC and DEC.

2. Experimental Section

2.1. Catalyst preparation

ZIF-67 was prepared according to a modified procedure described by Qian et al. [21]: a solution of 2-methylimidazole ($C_4H_6N_2$, 6.4×10^{-3} mol) in methanol (1.4 mol) was added to a solution of cobalt nitrate hexahydrate ([$Co(NO_3)_2$]· $6H_2O$, 8×10^{-3} mol) in methanol (1.4 mol), then vigorously stirred for 10 min. Purple polyhedral crystals appeared immediately. Finally, this solution was centrifuged at

10000 rpm and washed 3 times with methanol, then dried overnight at 60 °C. ZIF-8 was prepared according to the procedure described by Moises A. Carreon et al [22].

2.2. Characterization methods

The products were characterized by XRD (Bruker, D8) using Cu K α radiation source (λ =1.54056 Å) at 40 kV and 45 Ma. A continuous mode was used for collecting data at a scanning speed of 5°/s. N2 adsorption-desorption isotherm and pore size distribution of materials were measured by ASAP 2020 sorptometer analyzer (Micrometitics Company) at 77 K using liquid nitrogen as coolant, and the catalyst was degassed at 150 °C for 3 h before the measurement. The morphology of the samples was characterized by scanning electron microscopy (SEM, Hitachi, S-3400N). Thermal analysis technology (TGA) was recorded on a Netzsch STA 409 thermoanalyzer. Approximately 5 mg catalyst was filled into an alumina crucible and heated in a continuous-flow of nitrogen gas with a ramp rate of 10 °C/min from 40 °C up to 800 °C. Acid-basic property of ZIF catalyst was measured by NH₃-TPD and CO₂-TPD. The measurement was performed using AutoChem II 2920 instrument with helium as carrier gas (20 mL/min). Approximately 0.1 g catalyst was filled and pretreated at 250 °C for 3 h, the samples were cooled to room temperature and saturated with dried NH₃ or CO₂. Then the sample was blown with helium (20 mL/min) to move the physical-absorbed CO₂ or NH₃. Finally, the desorption process was started from 50 °C to 500 °C at a heating rate of 10 °C/min and monitored by a thermal conductivity detector.

2.3. Catalyst reactions

DMC and DEC were purchased from Aldrich Chemical Co., Ltd and dehydrated with molecular

sieves 4A overnight. Typical procedure for the synthesis of EMC: a mixture of DMC (9.000 g, 0.1 mol), DEC (11.800 g, 0.1 mol) and catalyst (0.200 g, 2 *wt* %), was charged into a 50 mL flask equipped with a magnetic stirring and a reflux condenser. The reaction mixture was then heated to 100 °C with continuous stirring. After 24 h, the mixture was cooled to room temperature. And the product was filtered and analyzed by a gas chromatograph (GC, Agilent-7890A) equipped with a flame-ionized detector. In the reusability experiment, catalysts were separated by filtration and washed using methanol (10 mL \times 3), then dried in air at 150 °C for the next reaction.

3. Results and discussion

3.1 Catalyst characterization

<Figure.1>

The textural properties of ZIF-67 catalyst were determined by the powder X-ray diffraction (XRD), N_2 adsorption-desorption, scanning electron microscope (SEM), and thermal analysis techniques (TGA). The XRD pattern of ZIF-67 catalyst (Figure.1a) is in good agreement with that reported elsewhere [22-23]. As shown in Figure.1b, ZIF-67 catalyst exhibits an I-type N_2 adsorption-desorption isotherm without hysteresis loop, indicating the microporous nature (diameter<20 Å) of ZIF-67, which is also confirmed by the pore size distribution. The measured BET surface area of ZIF-67 was 912 m²/g, which was higher than that of ZIF-8 (735 m²/g). It must be point out that the measured BET surface area of ZIF-8 is smaller than the data reported, which maybe result from the different preparation conditions including the speed of stirring. The pore size distribution curve was transformed using the Horvath-Kawazoe (HK) method, which further supported the presence of two kinds of microspores. And the result was similar with that of the previous studies [22-23]. Figure.1c exhibits the

morphological feature of ZIF-67 catalyst obtained from SEM, displaying average crystal sizes in the 300-500 nm range. The TGA curves of ZIF-67 and ZIF-8 were shown in Fig.1d. As for ZIF-67, it shows approximately 22 % weight loss at around 400 °C, which relates to the removal of H₂O and CH₃OH molecules (1 H₂O: 8.05 *wt*%, 1 CH₃OH: 14.31 *wt*%). The source of water may be from the crystal water of raw materials $Co(NO_3)_2$]·6H₂O. Thus, ZIF-67 is thermally stable up to 400 °C, which corresponds with the result reported by Omar M. Yaghi [21]. It also can be seen that ZIF-8 is more stable than ZIF-67, and there is only about 5% weight loss (the removal of guest molecules CH₃OH) at around 250°C. ZIF-8 is thermally stable up to 450 °C, which corresponds with the result reported by Lai et al [24].

3.2 Effect of reaction conditions on the yield and selectivity of EMC

In order to evaluate the effect of different reaction parameters on the yield and selectivity of EMC, the reaction conditions such as reaction temperature, catalyst amount, reaction time and ratios of substrates were investigated in details.

<Table 1>

<Figure.2>

Table 1 shows the yield and selectivity of EMC in different ratios of substrates and the control test. Obviously, no EMC is detected in the absence of any catalyst (Entry 1). Moreover, the activity of raw materials of ZIF-67, $[Zn(NO_3)_2]$ ·6H₂O, and 2-methylimidazole, were also tested (Entry 2-Entry 3). The result shows that both of them exhibit no catalytic activity for the reaction. In the presence of ZIF-67 catalyst, the yield of EMC can reach up to 83.39 % (Entry 4). Besides, the ratios of DMC and DEC from 2:1 to 1:2 were also studied (Entry 4-Entry 6), indicating that the EMC yield is the largest with a

ratio of 1:1. ZIF-8 was reported as a novel efficient heterogeneous catalyst for the synthesis of EMC from DMC and DEC in the last year, however, the activity of ZIF-8 is much lower than that of ZIF-67 under the same reaction conditions (Entry 7). In order to study the reasons why the activity of ZIF-67 is higher, we tested the acid-based property of ZIF-67 and ZIF-8 materials using CO₂-TPD and NH₃-TPD technologies (Fig.2). According to the related literature [19], it is known that the acidity of ZIF-67 originates from Co (II) and Co (III) species, and the base sites resulted from nitrogen atoms of MIM ligand. Compared with ZIF-8, it can be seen that ZIF-67 exhibits differing CO₂ and NH₃ desorption behaviors. A desorption peak, accompanied by a shoulder peak, is observed at 330 °C for ZIF-67, while a broad desorption peak is seen at 440 °C for ZIF-8 (Fig.2). In other words, the acid-based sites strength of ZIF-67 is moderate, while ZIF-8 has relatively strong acid-based sites.

The effects of reaction temperature on the yield and selectivity of EMC were investigated in the presence of ZIF-67 (2 *wt*%). The results (see Supplementary Information Fig.1) indicate that the yields of EMC increased from 2.35 % to 83.39 % as the temperature raised from 70 °C to 100 °C. When the temperature is further increased to 110 °C, the yields of EMC almost keep the same level. In addition, although the selectivity of EMC is almost 100 % in the whole temperature range, trace of methanol and ethanol are also detected. The alcohols were produced via the reaction of DMC or DEC with trace of water, which was the impurity in the reagent used. The results reveal that ZIF-67 catalyst shows excellent activity and selectivity at 100 °C.

Besides, we studied the effect of ZIF-67 amount (see Supplementary Information Fig.2) on the EMC yield and selectivity. The EMC yields increase from 59.45 % to 83.39 % with the increasing of ZIF-67 catalyst amount from 0.5 % to 2 %. However, an excess amount of catalyst cannot further promote the reaction but decrease the EMC yield, resulting from the agglomeration of catalysts probably.

Considering that the addition of ZIF-67 catalyst lead to a high yield of EMC, the effect of reaction time was further investigated (see Supplementary Information Fig.3). The yields of EMC steadily increase from 0.28 % to 83.39 % as the reaction time elapse from 1 h to 24 h in the presence of ZIF-67 catalyst at 100 °C. Then the yields keep almost stable even though reaction time is prolonged to 30 h, suggesting that the reaction has reached equilibrium after 24 h (see Supplementary Information Fig.3a). In addition, to prove that ZIF-67 catalyst is stable and the reaction takes place heterogeneously, the leaching test was carried out. In another test run (see Supplementary Information Fig.3b), we moved the catalysts by filtration at 18 h, and found that the yields of EMC remained the same during the last 12 h. Therefore, ZIF-67 catalyst is stable under the reaction conditions and the transesterification belongs to a heterogeneous reaction.

3.3 Reusability test

<Figure.3>

<Figure.4>

Reusability is one of the most important parameters for catalysts, so the reusability of ZIF-67 catalyst was carried out. ZIF-67 catalyst was recovered by filtration, and washed three times with methanol, then dried overnight for the next reaction. As exhibited in Figure.3, the yields of EMC only dropt slightly after four successive runs, indicating that ZIF-67 catalyst shows excellent reusability for the transesterification. Moreover, the XRD pattern of recycled ZIF-67 is almost identical to that of the fresh one (Fig.4), meaning that ZIF-67 shows good stability in the transesterification reaction.

3.4 The reaction mechanism

<Scheme 2>

The mechanism for the transesterification of DMC and DEC has been reported [7-8], in which DMC and DEC were chemisorbed on the Lewis acid sites and base sites of the catalyst to form intermediate. In our case, a possible mechanism concerning the transesterification reaction over ZIF-67 catalyst is depicted in Scheme 2. First, after pretreating for 3 h at 150 °C, the removal of the terminal coordinated CH₃OH and H₂O molecules from metal Co ions could yield more empty frameworks and leave Lewis acid sites on the surface. And the basic site results from the nitrogen atoms of MIM ligand. Then the reagents (DMC and DEC) were chemisorbed on the Lewis acid and Lewis basic sites of ZIF-67 to yield the methoxide ion species and ethoxy group, which could attack the carbon atom of the carbonyl group of DEC or DMC subsequently. Finally, EMC was formed and desorbed easily.

4. Conclusions

An efficient heterogeneous catalyst, ZIF-67, was developed for preparing EMC from DMC and DEC. The textural properties of ZIF-67 were determined by the powder X-ray diffraction, N_2 adsorption-desorption, scanning electron microscope and thermal analysis. The acid-based property of ZIF-67 catalyst was investigated by NH₃ and CO₂ temperature-programmed desorption methods. Several factors associated with the yield including reaction temperature, catalyst amount, reaction time and the ratios of substrates were studied. The results indicated that ZIF-67 displayed excellent activity, selectivity and reusability for the synthesis of ethyl methyl carbonate. Our finding not only proves great potential application of ZIF-67 catalyst but also bring light to new opportunity in the development of high performance catalysts for the synthesis of ethyl methyl carbonate.

Acknowledgments

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Captions for Schemes and Figures

Figure.1. (a) Powder X-ray diffraction pattern of ZIF-67 catalyst; (b) N₂ adsorption- desorption

isotherm of ZIF-67 catalyst at 77K and Pore size distribution curve; (c) Scanning electron microscope

image of ZIF-67 catalyst; (d) Thermal gravimetric analysis (TGA) curve of ZIF-67 and ZIF-8 catalyst.

Figure.2. TPD curves of ZIF-67 and ZIF-8 catalyst: (a) CO₂-TPD analysis; (b) NH₃-TPD analysis.

Figure.3. Reusability of ZIF-67 catalyst for the synthesis of EMC from DMC and DEC. Reaction conditions: ZIF-67 (2 *wt*%), 24 h, 100 °C, n (DMC)/n (DEC) = 1:1.

Figure.4. Powder X-ray diffraction patterns of ZIF-67 catalyst: (a) fresh, (b) recycle 1st, (c) recycle 2nd,

(d) recycle 3^{rd} , (e) recycle 4^{th} .

Table 1 The synthesis of EMC from DMC and DEC with different reaction conditions.

Scheme1. Transesterification of DMC with DEC to produce EMC.

Scheme 2. Possible mechanism of transesterification of DMC with DEC over ZIF-67 catalyst.



Figure.1. (a) Powder X-ray diffraction pattern of ZIF-67 catalyst; (b) N₂ adsorption-desorption

isotherm of ZIF-67 catalyst at 77K and Pore size distribution curve; (c) Scanning electron microscope image of ZIF-67 catalyst; (d) Thermal gravimetric analysis (TGA) curve of ZIF-67 and ZIF-8 catalyst.



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Figure.3. Reusability of ZIF-67 catalyst for the synthesis of EMC from DMC and DEC. Reaction

conditions: ZIF-67 (2 *wt*%), 24 h, 100 °C, n (DMC)/n (DEC) = 1:1.



Figure.4. Powder X-ray diffraction patterns of ZIF-67 catalyst: (a) fresh, (b) recycle 1st, (c) recycle 2nd,

(d) recycle 3rd, (e) recycle 4th.

Entry	Catalyst catalyst	amount (wt%)	n (DMC)/n (DEC)	Yield ^b (%)	Selectivity ^b (%)
1	None	-	-	-	-
2	$[Zn(NO_3)_2] \cdot 6H_2O$	2 %	1:1	-	-
3	2-methylimidazole	2 %	1:1	\mathbf{O}	-
4	ZIF-67	2 %	1:1	83.39	~100 %
5	ZIF-67	2 %	2:1	50.38	~100 %
6	ZIF-67	2 %	1:2	73.91	~100 %
7	ZIF-8	2 %	1:1	50.32	~100 %

Table 1 The synthesis of EMC from DMC and DEC with different reaction conditions.^a

^a Reaction conditions: DMC (0.1 mol), DEC (0.1 mol), 100 °C, 24 h, ^b Determined by GC.

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н₃С .C₂H₅ _____ _CH₃ + C₂H₅ 2 H₃C C_2H_5

Scheme1. The transesterification of DMC with DEC to produce EMC.

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Step 1.



Scheme 2. Possible mechanism of transesterification of DMC with DEC over ZIF-67 catalyst.

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Research Highlights

- ► ZIF-67 catalyst was first used for preparing ethyl methyl carbonate (EMC).
- ► Excellent yield and selectivity of EMC were obtained over ZIF-67 under mild conditions.
- ► ZIF-67 catalyst displayed excellent reusability for the synthesis of EMC.

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