Zeolitic imidazolate framework as efficient heterogeneous catalyst for the synthesis of ethyl methyl carbonate

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ABSTRACT

A zeolitic imidazolate framework (ZIF-8) was developed as a novel efficient heterogeneous catalyst for the synthesis of ethyl methyl carbonate from dimethyl carbonate and diethyl carbonate. ZIF-8 was characterized by element analysis, X-ray powder diffraction (XRD), Fourier transform infrared (FT-IR), temperature programmed desorption (TPD), N_2 adsorption–desorption and thermogravimetric analysis. The effects of catalyst amount, temperature and reaction time on the yield of ethyl methyl carbonate were also tested. The results showed that ZIF-8 performed excellent activity, selectivity and reusability under mild reaction conditions.

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1. Introduction

Ethyl methyl carbonate (EMC) can be utilized as a co-solvent in a nonaqueous electrolyte to improve the energy density and discharge capacity of the lithium ion cells. Several methods have been reported for EMC synthesis. Traditionally, EMC is prepared by esterification of chloroformate with ethanol in the presence of basic catalyst [1]. However, this route is not an environmentally benign process since methyl chloroformate is highly toxic. Another method to synthesis EMC is the transesterification of dimethyl carbonate (DMC) with ethanol [2]. This route has the drawback of formation of three binary azeotropes, causing a serious difficulty in separation. EMC can also be prepared by the transesterification of DMC with diethyl carbonate (DEC) [3–8]. Because all the reaction mixtures (DEC, DMC and EMC) can be used as solvent in a nonaqueous electrolyte, the separation step can be avoided in this method. In addition, the composition of the reaction mixture can be adjusted by controlling the raw material ration and the conversion.

For the transesterification of DMC with DEC, $Ti(OBu)_4$ and Bu_2SnO were found to be active homogeneous catalysts [3]. However, the separation of catalysts from product is difficult. Gan et al. [4] reported that lithium diethyl amide and lithiated carbon performed high activity for the reaction. But these catalysts are very expensive, which limits their application. Shen et al. [5] tested the catalytic activity of several metal oxides, and found that MgO is the most active catalyst due to its basic property. Jia et al. [6] reported that carbon-supported MgO (MgO/NC-2) catalysts prepared by a wet impregnation technique are efficient heterogeneous catalysts for the reaction. Palani et al. [7] reported that high yield of EMC can be obtained with Al-MCM-41 or Al-Zn-MCM-41 as catalyst under 175–200 °C. Recently, Jia et al. [8] found that amorphous mesoporous aluminophosphate (AlPO) shows remarkably higher activity than other solid catalysts. 47.7% conversion of DEC was achieved under desired reaction conditions (catalyst 4.8 wt%, 366 K, 0.5 h). Nowadays, it is still important and challenging to develop highly efficient heterogeneous catalyst for the synthesis of EMC from DMC and DEC under mild reaction conditions.

Metal–organic frameworks (MOFs), also known as porous coordination polymers, consist of metallic nodes bonded by organic linkers. In the past decades, MOFs have received much attention due to their special properties, such as ultrahigh surface area combined with a high crystallinity [9–11]. They have been widely used in gas storage and separation [12], magnetism [13], chemical sensing [14], drug delivery [15], and catalysis [16–18]. The use of MOFs as heterogeneous catalyst is interesting, since the pose size and functionality of framework can be easily tuned over a wide range for different catalytic reactions. Recently, Zhou et al. [19] reported that MOF-5 [$Zn_4O(BDC)_3$] (BDC = benzene-1,4-dicarboxylate) is an active catalyst for the transesterification of DMC and DEC. And high EMC yield (50.1%) is obtained. However, MOF-5 is unstable exposing to air [20], which limits its application. Herein, a zeolitic imidazolate framework (ZIF-8) [$Zn(MeIm)_2$]

(MeIm = 2-methylimidazole) which shows high surface area, exceptional chemical and thermal stability was developed as highly efficient heterogeneous catalyst for the synthesis of EMC from DMC and DEC.

2. Experimental

2.1. Catalyst preparation

ZIF-8 was prepared according to the literature reported by Chizallet et al. [21]. A solution consisting of 2-methylimidazole (3.220 g) dissolved in 100 mL of methanol was slowly added (30 min) to a solution of $Zn(OH)_2$ (1.951 g) in aqueous ammonia (25–28% (v/v), 250 mL). The white solid began to produce immediately. Preparation was done under room temperature with gentle steering in 2 days. And the prepared white solid was collected by filtration, then washed 3 times with 100 mL of $H_2O/MeOH$ (1:1, v/v) solution and dried in oven at 100 °C.

2.2. Catalyst characterization

The X-ray diffraction patterns were collected on X-ray diffractometer (XPERT PRO) using a Cu Kα radiation source (λ = 1.54056 Å), operating at 40 kV and 45 mA. FT-IR spectra were obtained by Nicolet 560 in KBr pellets. A continuous mode was used for collecting data at a scanning speed of 0.02°/s. Low temperature nitrogen adsorption and desorption measurements were conducted using a TriStar II 3020 (Micromeritics Instrument Corporation). The content of Zn in filtration was detected by TS IRIS 1000 ICP-AES instrument. Thermogravimetric analysis was conducted on a HCT-2 thermo-analyzer (Beijing Scientific Instrument Factory) with a heating rate of 10 °C/min. The surface acid–base properties of ZIF-8 were characterized by temperature programmed desorption of CO_2 (CO_2-TPD) and NH_3 (NH_3-TPD). The sample was pretreated at 200 °C in argon atmosphere for 1 h, and the desorption temperature was between room temperature and 450 °C with a heating rate of 10 °C/min.

2.3. Catalytic reactions

Typical procedure for the synthesis of EMC: 9.000 g (0.1 mol) DMC, 11.800 g (0.1 mol) DEC and 0.208 g (1 wt%) catalyst were 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 3 h, the mixture was cooled to room temperature. And the product analyzed by GC (Shandong Lunan Ruihong Co. SP-6890). The structure of the product was defined by GC–MS (HP 6890/5973). In the experiment to test the reusability of catalyst, ZIF-8 was separated by filtration, washed using ethanol. After drying in oven, ZIF-8 was reused for the next time.

3. Results and discussion

3.1. Characterization

The catalyst ZIF-8 was characterized by X-ray powder diffraction (XRD), N_2 adsorption–desorption and thermogravimetric analysis. As shown in Fig. 1, the XRD patterns of ZIF-8 in this work were agree well with patterns simulated from single crystal structure in the Cambridge Structural Database. There was a very sharp pattern at 2θ = 7.2° in the XRD pattern of ZIF-8, indicating that the crystallinity of ZIF in this work was relatively high. N_2 adsorption–desorption isotherms and pore size distribution of ZIF-8 were summarized in Fig. 2. The pore structure of ZIF-8 was mainly micropore, and the pore size was about 1.0–1.2 nm. ZIF-8 exhibited a high surface area
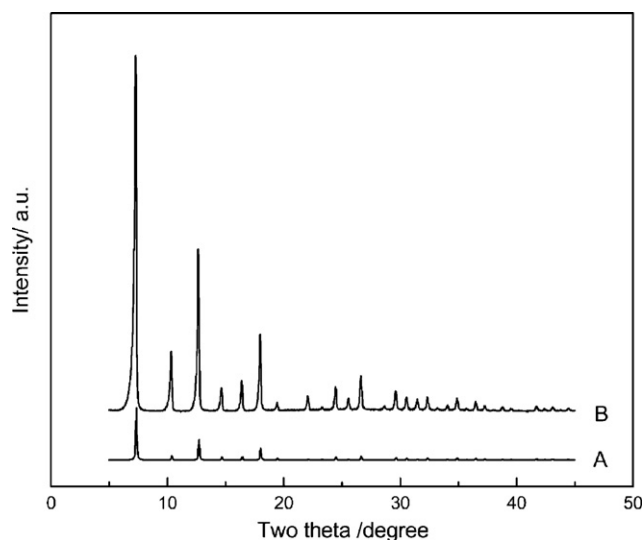

Fig. 1. XRD patterns of ZIF-8: (A) simulated and (B) synthesized in this work.

of 1368 m²/g (calculated by BET), which was similar with that in the previous literature (about 1400 m²/g) [22,23]. In the TG result for ZIF-8, there was little weight loss while the temperature was lower than 400 °C, indicating that ZIF-8 was stable up to 400 °C. It was also verified by the DTA result for ZIF-8 (Fig. 3). The thermal stability of ZIF-8 in this work was agreed well with that reported in the literature [22–24]. According to the results of CO_2-TPD and NH_3-TPD, both acid and base active centers were existed on the surface of ZIF-8 (Figs. 4 and 5).

3.2. Catalytic performance

The activity of different catalysts for the transesterification of DMC with DEC to synthesis EMC was tested, and the results were summarized in Table 1. Obviously, the reaction could not proceed without catalyst (Entry 1), which is in accord with the result reported by literature [8,19]. In the presence of ZIF-8, 50.7% yield of EMC was obtained (Entry 2), which is very close to the equilibrium yield of this reaction [8,19]. It is noteworthy that byproducts were not detected by GC–MS. In order to compare ZIF-8 with other
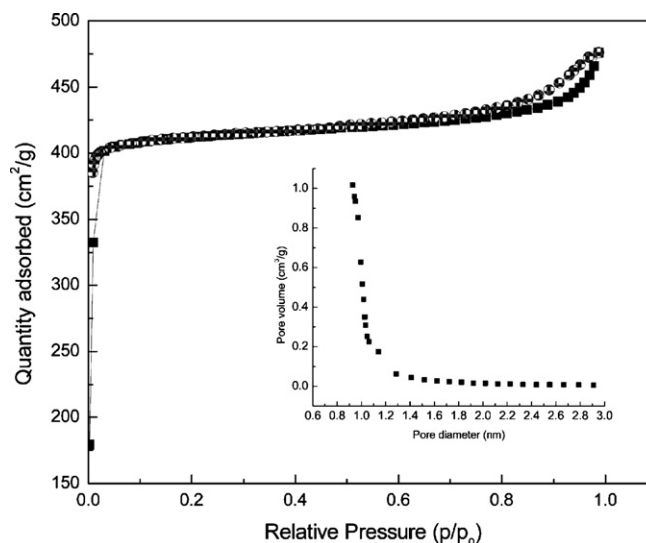

Fig. 2. N_2 adsorption–desorption isotherms and pore size distribution (inset) of ZIF-8.