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Short Communication

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

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A B S T R A C T

Zeolitic imidazole framework (ZIF)-67, a novel environmentally benign catalyst, was developed for the 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. NH_3 and CO_2 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.

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 $Ti(OBu)_4$, Bu_2SnO, and $BuSnCl_3$ [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, La_2O_3, and CeO_2 [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.

Metal organic framework (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 framework (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 a 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

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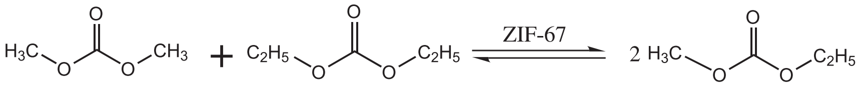

Scheme 1. Transesterification of DMC with DEC to produce EMC.

hexahydrate ($[Co(NO_3)_2]\cdot 6H_2O$, 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 10,000 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 Kα radiation source ($\lambda = 1.54056$ Å) at 40 kV and 45 Ma. A continuous mode was used for collecting data at a scanning speed of 5°/s. N_2 adsorption–desorption isotherm and pore size distribution of materials were measured by ASAP 2020 sorptometer analyzer (Micromeritics 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 thermal analyzer. An 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. The acid-basic property of ZIF catalyst was measured by NH_3-TPD and CO_2-TPD. The measurement was performed using AutoChem II 2920 instrument with helium as carrier gas (20 mL/min). An 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 NH_3 or CO_2. Then the sample was blown with helium (20 mL/min) to move the physical-absorbed CO_2 or NH_3. 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.

2.3.1. 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

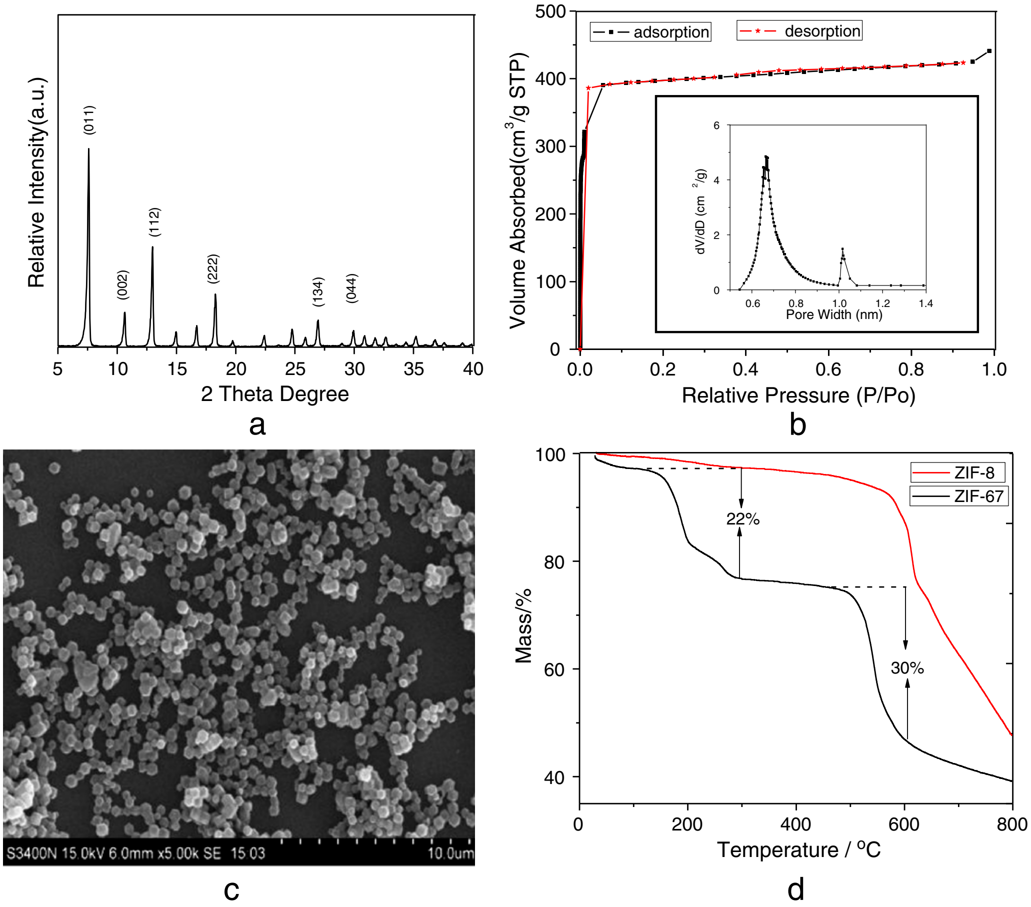

Fig. 1. (a) Powder X-ray diffraction pattern of ZIF-67 catalyst; (b) N_2 adsorption–desorption isotherm of ZIF-67 catalyst at 77 K and pore size distribution curve; (c) Scanning electron microscope image of ZIF-67 catalyst; (d) thermal gravimetric analysis (TGA) curve of ZIF-67 and ZIF-8 catalyst.