Metal-organic frameworks as an acid catalyst for the synthesis of ethyl methyl carbonate via transesterification

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ABSTRACT

An efficient synthesis of ethyl methyl carbonate using metal-organic frameworks (MOFs) as Lewis acid catalyst has been realized by the transesterification of dimethyl carbonate and diethyl carbonate. The effects of reaction time, temperature, amount of catalyst and the ratios of substrates on the yield of the objective product were examined. It was demonstrated that MOFs can catalyze the reaction smoothly, and that good yield of ethyl methyl carbonate and high selectivity was achieved under optimized conditions. The catalyst leaching test has shown that the reaction takes place heterogeneously. Moreover, the catalyst can be easily recovered simply by centrifugation and reused over three times without obvious loss of its catalytic activity.

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1. Introduction

In electrochemical cells, nonaqueous electrolytes should possess some necessary properties [1]. Ethyl methyl carbonate (EMC) can be used as a cosolvent in a nonaqueous electrolyte, which is able to improve the discharge characteristics of the cells including the energy density and discharge capacity, etc. [2–4]. But the price of EMC is relatively high. Several methods have been developed for the synthesis of EMC. The esterification of methyl chloroformate with ethanol in the presence of basic catalysts is an effective route [5,6]. However, this route is not environmentally benign since the toxicity of the reagent and stoichiometric strong base has to be used to neutralize the acid byproduct. Another route is the transesterification of dimetyl carbonate (DMC) and ethanol. But three binary azeotropes (methanol–DMC, ethanol–DMC, and ethanol–EMC) are formed in the reaction system; as a result the separation in such a process is extremely difficult [7]. In addition, the yield of the target product (EMC) was relatively low. Except for the above two methods, EMC can also be prepared by the transesterification of DMC with diethyl carbonate (DEC). Because all the feedstocks (DMC and DEC) and reaction product (EMC) can be used as solvent in nonaqueous electrolyte, the separation is unnecessary after the reaction, and the reaction mixture can be used directly without separation process. Moreover, the composition of the reaction mixture can be adjusted

through controlling the conversion. But only a limited number of researches have been reported in literature. Transesterification is generally catalyzed by acids or bases, in either homo- or heterogeneous systems [8]. Some homogeneous catalysts are used for this reaction. However, the difficult catalyst–product separation is still an obvious disadvantage. Gan et al. reported that lithium diethyl amide and lithiated carbon could be used as heterogeneous catalysts. But the catalysts are expensive, which therefore limits their application [9]. Solid base catalysts can be used to catalyze this reaction. Jiang and co-workers [10] found that MgO is the most active catalyst among the catalysts examined, and that 44% yield of EMC was obtained at 103 °C. In addition, Palani et al. reported that Al-Zn-MCM-41 is an efficient acid catalyst in the temperature range of 175–200 °C and that the activity of the catalysts followed the order of the acidity of the catalysts [11]. It is important to develop efficient catalysts under mild conditions.

Metal-organic frameworks (MOFs) are a new class of crystalline porous coordination polymers that are formed by copolymerization of multidentate organic ligands with transition metal ions or metal ion clusters, leading in most cases to 3D extended networks with channels and cavities of molecular dimensions [12–16]. Due to their zeolite-like properties, such as high surface areas, microporosity, well-defined structures and the ability to tune pore size on Å scale, recently they have been applied in separation [17], catalysis [18], magnetism [19] and storage of gases [20,21]. Among these applications, the catalytic property of MOFs is most fascinating. Many reactions have been conducted using MOFs as catalysts or carriers such as Knoevenagel condensation reaction [22], Friedel–Crafts

type reaction [23], aldol reaction [24], oxidation [25], asymmetric olefin epoxidation [26], asymmetric hydrogenation [27], transesterification [28], photochemical reaction [29], and so on. However, the chosen catalytic reactions were usually model reactions and/or reactions of little industrial interest [30]. Further studies on the catalytic property of MOFs were required, especially in the important transformation of chemical industry.

It was suggested in a recent research on MOFs, that the dissociation or removal of the terminal coordinated molecules from metal ions could yield more empty frameworks and leave Lewis acid site on the surface, which have potential applications in catalysis [31,32]. In this work, we utilize MOFs as an acid catalyst for the transesterification of DMC with DEC. High yield of ethyl methyl carbonate was achieved under moderate conditions. As a heterogeneous catalyst, MOFs could be easily recovered and reused at least three times with slight decrease in its catalytic activity.

2. Experimental

2.1. Chemicals

Dimethyl carbonate (>99%) was purchased from ACROS ORGANIC. Other solvents and chemicals such as diethyl carbonates, $Zn(NO_3)_2 \cdot 6H_2O$, triethylamine, and 1,4-benzenedicarboxylic acid (H_2BDC), were analytical grades and purchased from Beijing Chemical Reagents Company. All chemicals were used without further purification.

2.2. Catalyst preparation

MOFs, $Zn_4(O)(BDC)_3$, was prepared according to the procedures reported by Huang et al. [33]. $Zn(NO_3)_2 \cdot 6H_2O$ (1.21 g, 4 mmol) and 1,4-benzenedicarboxylic acid (0.32 g, 2 mmol) were dissolved in *N,N*-dimethylformamide (DMF) and MOFs was precipitated by adding the organic base triethylamine (1.6 g, 16 mmol) under vigorous stirring. After 4 h, the precipitate was collected by filtration and washed with DMF. The solid was dried at 90 °C for 12 h under vacuum and then stored in a vacuum desiccator to avoid moisture adsorption. The structure and crystallinity of the sample confirmed by SEM, XRD, IR and TG, are in good agreement with data reported in literature.

MgO was prepared by thermal decomposition of $Mg(OH)_2$ at 500 °C for 10 h in air. ZnO, the commercially available reagent, was activated at 400 °C for 5 h before use. Hydrotalcite (Mg/Al = 3:1) was prepared by coprecipitation according to the procedures in literature [34].

2.3. Characterization

X-ray diffraction (XRD) measurements were conducted on an X-ray diffractometer (D/MAX-RC) operated at 40 kV and 200 mA with Cu Kα (λ = 1.54 Å) radiation. FT-IR spectra were recorded using a Bruker Tensor 27 spectrometer, and the samples were prepared by the KBr pellet method. Thermogravimetric (TG) analysis of MOFs was performed on a Netzsch STA 409 PC/PG thermogravimetric analysis system in N_2 atmosphere at a heating rate of 20 °C min^{-1}. The products were analyzed by a gas chromatograph (GC, Agilent 6820) equipped with a flame-ionized detector. The yield was calculated using the following equation:

$$Yield (\%) = 100 \times \frac{n(EMC)}{2n(DEC)}$$

where $n(EMC)$ is moles of EMC; $n(DEC)$ is moles of DEC.
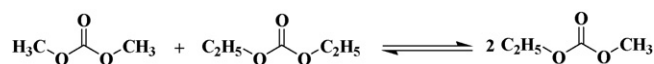
Scheme 1. Transesterification of DMC with DEC to produce EMC.

2.4. Catalytic reactions

Transesterification of DMC with DEC was carried out using MOFs as the catalyst. A typical procedure was as follows: 1.802 g (20 mmol) of DMC, 2.362 g (20 mmol) of DEC, and 2 wt% (based on total mass of reactants) of catalyst were charged into a 10 mL flask, equipped with a magnetic stirring bar and a reflux condenser. Then the mixture was heated up to 100 °C and the stirrer was started. After the reaction was completed, the products were analyzed by GC. The structure of the product obtained under typical experimental conditions was identified by GC–MS (Shimadzu QP2010). The transesterifications above 120 °C was carried out in a 6 mL stainless steel autoclave equipped with a magnetic stirrer. Other procedures are similar to those in a flask.

3. Results and discussion

3.1. Catalysts and reaction conditions

The activity of MOFs and other control catalysts or chemicals was examined for the catalytic transesterification of DMC with DEC (Scheme 1) to produce EMC. The results are summarized in Table 1. The reaction could not proceed in the absence of a catalyst (Table 1, Entry 1). In the presence of MOFs, 50.1% yield of EMC was obtained at 100 °C for 3 h (Table 1, Entry 2). Moreover, it should be noted that no byproducts were detected by GC–MS. In order to compare the catalytic activity of MOFs with the conventional solid base catalysts for transesterification, the catalytic activity of MgO, ZnO, and hydrotalcite (Table 1, Entries 3–5) was also examined. The results indicated that MOFs was the most active catalyst. $Ti(OBu)_4$ is a good homogeneous catalyst for the transesterification [35]. In this reaction, the catalytic activity of $Ti(OBu)_4$ was lower than that of MOFs (Table 1, Entry 6). The decrease in the EMC selectivity is attributed to the exchange of –OBu for –OMe or –OEt.

Because of the better activity of MOFs among all the catalysts used, other experiments were performed with MOFs in the following research. In order to evaluate the effects of different reaction parameters on the yield of EMC, reaction conditions such as time, temperature, amount of catalyst and ratios of substrates were optimized.

As shown in Fig. 1, the yield of EMC increased with reaction time and the reaction reached equilibrium after 2 h. An EMC yield of 50.1% could be achieved with nearly 100% selectivity after 2 h. The selectivity to EMC remained nearly 100% even if the reaction time was prolonged.

Table 1
Reaction of DMC and DEC with different catalysts[a].

Entry	Catalysts	Yields (%)[b]	Selectivity (%)[b]
1	None	–	–
2	MOFs	50.1	100
3	MgO	40.9	100
4	ZnO	0.2	100
5	Hydrotalcite	25.9	100
6	$Ti(OBu)_4$	21.1	98.5
7	$Zn(NO_3)_2 \cdot 6H_2O$	0.2	100
8	MOFs (2nd)	49.7	100
9	MOFs (3rd)	46.7	100
10	MOFs (4th)	48.4	100

[a] Typical reaction conditions: DMC, 1.802 g (20 mmol); DEC, 2.362 g (20 mmol); catalyst, 2 wt%; 100 °C; 3 h.
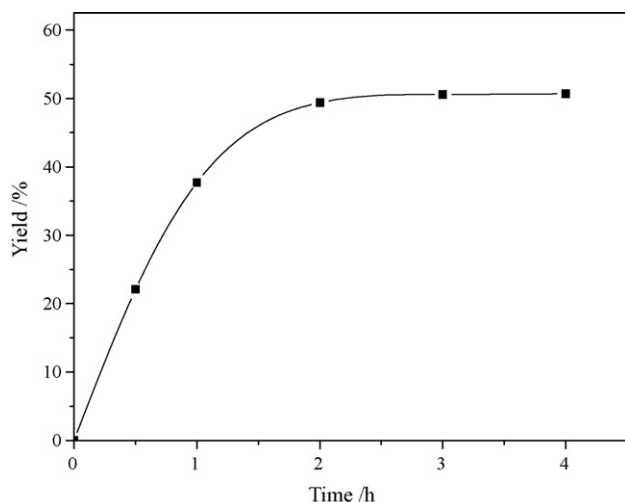
[b] Determined by GC.

Fig. 1. Effect of reaction time on the yield of EMC over MOFs. Other conditions: MOFs (2 wt%), 100 °C, n(DMC)/n(DEC) = 1:1.

Fig. 3. XRD patterns of: (a) MOFs after dried at 90 °C for 12 h under vacuum; (b) MOFs after calcinated at 300 °C for 12 h in air.

The effect of reaction temperature on the performance of EMC synthesis over MOFs is shown in Fig. 2. The yield of EMC increased dramatically with increased temperature from 70 °C to 100 °C. At 100 °C, the yield of EMC reached a maximum of 50.1%. When the temperature was increased from 100 °C to 160 °C, the yield of EMC remained unchanged; however, the selectivity of EMC was decreased slightly. Although nearly 100% selectivity of EMC was obtained over MOFs, trace of methanol and ethanol were also detected. The alcohols were produced via the reaction of DMC or DEC with trace of water, which is the impurity in the reagent used. Conclusively, 100 °C could be the optimal temperature for the reaction.

The reservation of activity at high temperature (160 °C) indicated that MOFs is thermally very stable. This can also be proved by the XRD powder diffraction pattern and IR analysis of MOFs (Figs. 3 and 4). The structure of MOFs remains unaltered when MOFs was heated up to 300 °C for 12 h.

The effect of the amount of catalyst on the yield of EMC over MOFs is shown in Fig. 5. The yield of EMC increased with the increasing amount of catalyst when the catalyst was not enough. In other words, the reaction did not reach equilibrium within 3 h with a very small amount of catalysts. The yield of EMC did not increase further after the amount of catalyst exceeded 2 wt% (based on total mass of the reactants). Therefore, an excess amount of catalyst cannot
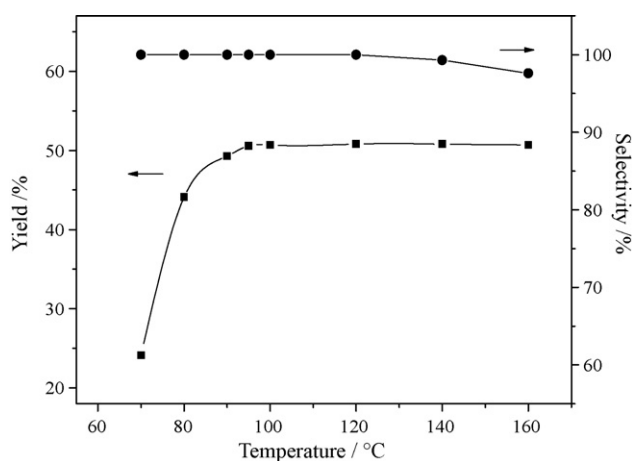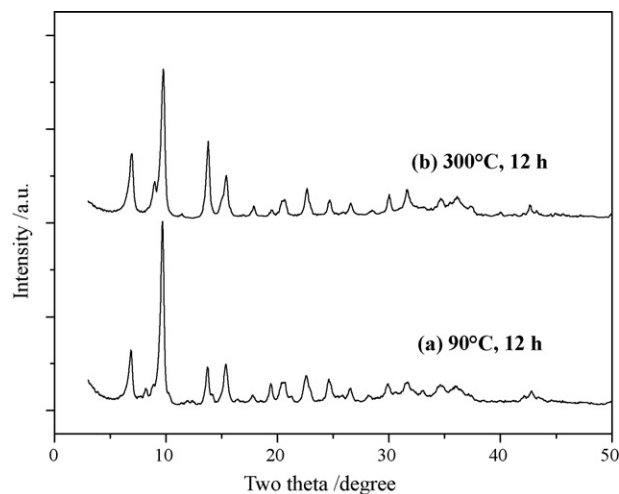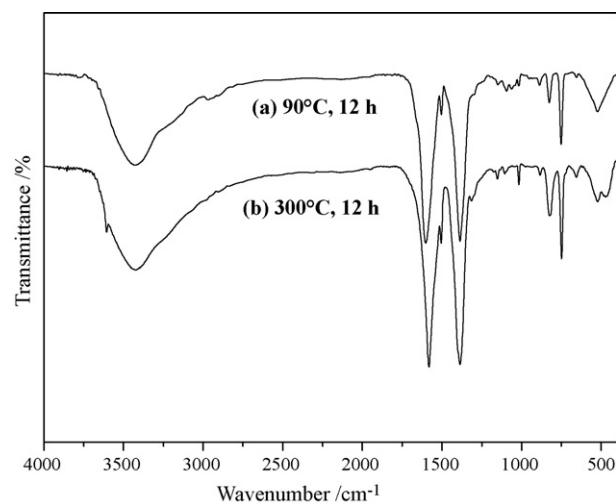

Fig. 4. IR spectra of: (a) MOFs after dried at 90 °C for 12 h under vacuum; (b) MOFs after calcinated at 300 °C for 12 h in air.

Fig. 2. Effect of temperature on the yield of EMC over MOFs. Other conditions: MOFs (2 wt%), 3 h, n(DMC)/n(DEC) = 1:1.

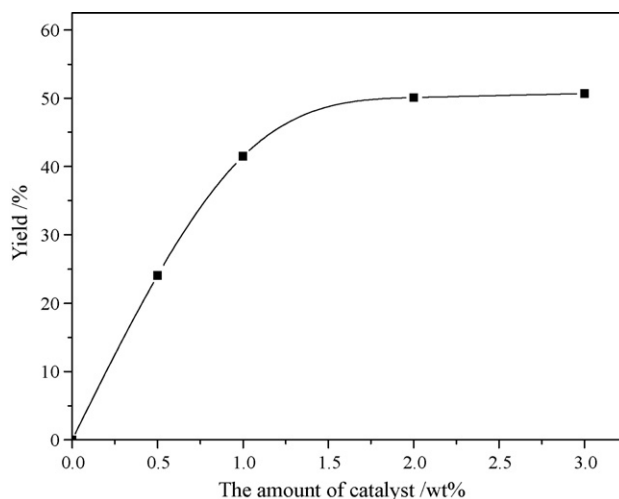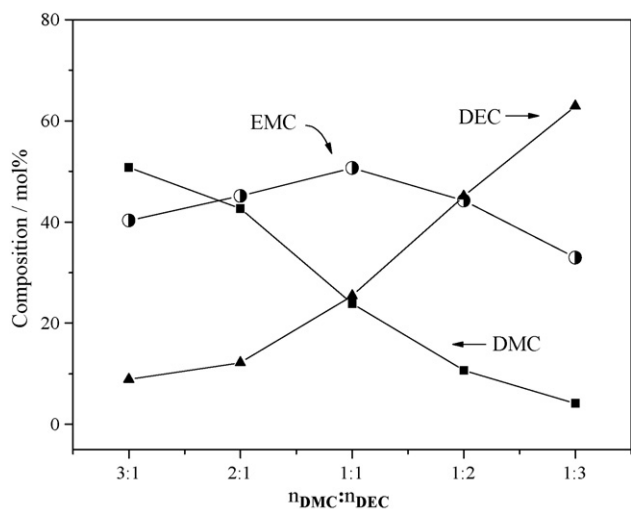**Fig. 5.** Effect of amount of catalyst on the yield of EMC over MOFs. Other conditions: MOFs, 100 °C, 3 h, n(DMC)/n(DEC) = 1:1.

Fig. 6. Influence of ratios of substrates on the composition of reaction mixtures. Other conditions: MOFs (2 wt%), 100 °C, 3 h.

Fig. 8. XRD patterns of fresh and reused (3rd) MOFs.

further promote the reaction to form more product because the reaction has already reached equilibrium.

It is well known that the composition of products can be adjusted through changing the ratio of substrates. When the ratio of DMC to DEC was changed from 1:3 to 3:1, the composition of the reaction mixture was changed dramatically, as shown in Fig. 6. Therefore, many kinds of mixed products with different compositions could be obtained according to the practical requirement. Mixtures of DMC, DEC and EMC are actually used as electrolytes in lithium battery.

3.2. Catalyst leaching test

A leaching experiment was performed to figure out weather the reaction takes place homogeneously or heterogeneously. The possibility of homogeneous catalytic reaction in the present catalytic system was ruled out based on the experimental results. The kinetic plot of the transesterification reaction of DMC with DEC over MOFs at 100 °C for 4 h was compared with that of another reaction where the transesterification reaction was stopped after 0.5 h, and then continued after filtering out the solid catalyst. The results are shown in Fig. 7. There was no further increase in the EMC yield after the solid catalyst was separated out. This observation unambiguously
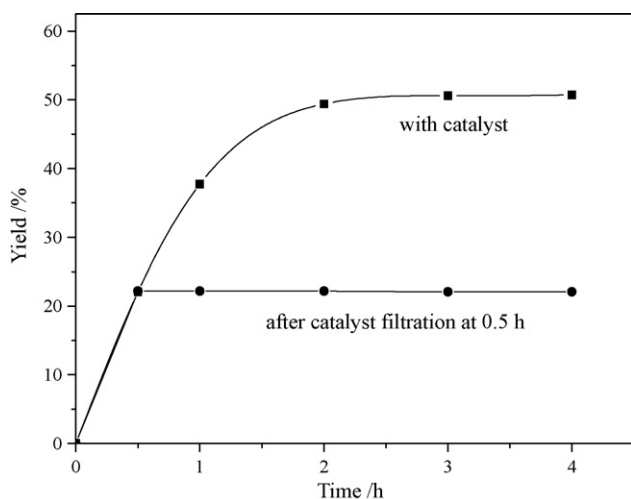
demonstrates that MOFs is a perfect heterogeneous catalyst for the transesterification. Furthermore, $Zn(NO_3)_2 \cdot 6H_2O$ as homogenous catalyst was used for the reaction (Table 1, Entry 7). Only 0.2% yield of EMC was obtained at 100 °C for 3 h. This confirmed indirectly that the active site in MOFs is not soluble in the reaction mixture. Therefore the reaction takes place heterogeneously.

3.3. Catalyst recycling

Apart from the catalytic activity, the deactivation of catalyst is another important issue. After the completion of the reaction, an attempt was made to recover the catalyst and to reuse it for subsequent runs. Accordingly, after 3 h of reaction at 100 °C, the solid catalyst was centrifuged, washed with ether, and dried under vacuum. The recycle was repeated three times and the catalytic performance was similar to that of the fresh catalyst (Table 1, Entries 2, and 8–10). The slight decrease in activity may be due to the loss of catalyst in the course of catalyst recovery.

As shown in Fig. 8, The XRD pattern of the recovered sample matched well that of the fresh one. No significant differences were observed between the two diffractograms, indicating that the crystalline structure of the materials was preserved. IR bands of the recovered catalyst also agreed well with that of the fresh one, as shown in Fig. 9. The above data clearly demonstrated that the struc-

Fig. 7. Kinetic plot of EMC formation from transesterification of DMC with DEC. (i) without filtration of the catalyst and (ii) after filtration of the catalyst at 0.5 h.
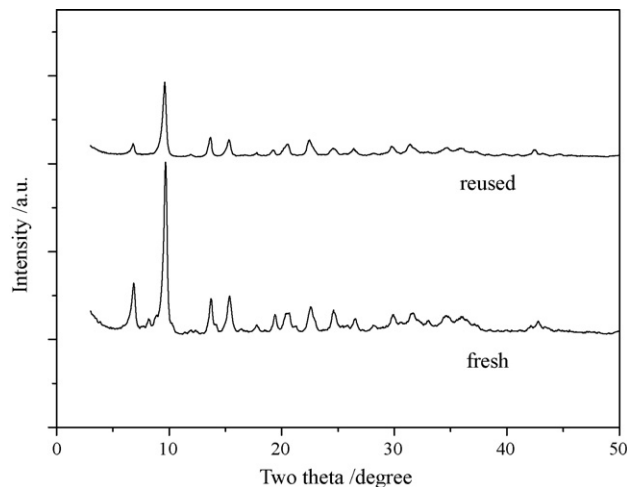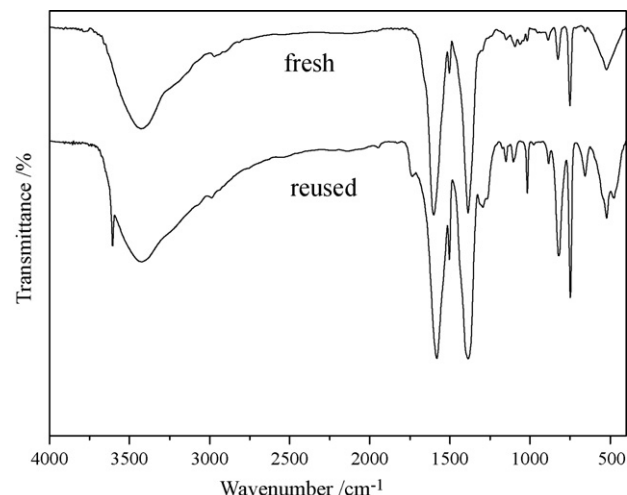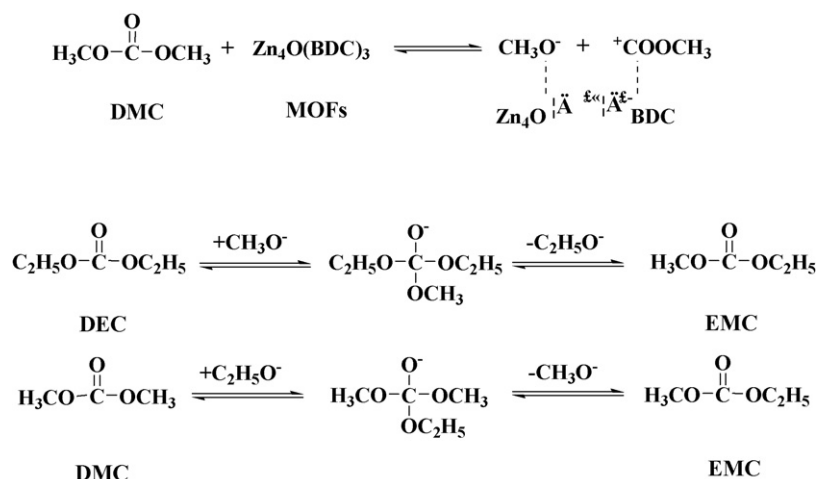

Fig. 9. FT-IR spectra of fresh and reused (3rd) MOFs.

$$H_3CO-\overset{O}{\underset{||}{C}}-OCH_3 \; + \; Zn_4O(BDC)_3 \; \rightleftharpoons \; CH_3O^- \; + \; {}^+COOCH_3$$

DMC　　　　　　　MOFs　　　　　　　　　Zn$_4$O ¦Ä £«¦¦Ä£- BDC

$$C_2H_5O-\overset{O}{\underset{||}{C}}-OC_2H_5 \underset{+CH_3O^-}{\rightleftharpoons} C_2H_5O-\overset{O^-}{\underset{OCH_3}{C}}-OC_2H_5 \underset{-C_2H_5O^-}{\rightleftharpoons} H_3CO-\overset{O}{\underset{||}{C}}-OC_2H_5$$

DEC　　　　　　　　　　　　　　　　　　　　　　EMC

$$H_3CO-\overset{O}{\underset{||}{C}}-OCH_3 \underset{+C_2H_5O^-}{\rightleftharpoons} H_3CO-\overset{O^-}{\underset{OC_2H_5}{C}}-OCH_3 \underset{-CH_3O^-}{\rightleftharpoons} H_3CO-\overset{O}{\underset{||}{C}}-OC_2H_5$$

DMC　　　　　　　　　　　　　　　　　　　　　　EMC

Scheme 2. Possible mechanism of transesterification of DMC with DEC.

ture of the catalyst did not change after being used three times under the present experimental conditions.

3.4. The reaction mechanism

Based on the above results, a plausible mechanism for the transesterification between DMC with DEC is proposed in Scheme 2. It is suggested that DMC is chemisorbed on the Lewis acid site on MOFs to yield the methoxide ion species firstly, which attacks the carbon atom of the carbonyl group subsequently. The ethoxide ion species removed from the intermediate to yield the product EMC. Analogously, the chemisorption of DEC on the surface of MOFs in the first step also gave the same product.

4. Conclusion

In conclusion, MOFs as an acid catalyst is very effective for the transesterification of dimethyl carbonate and diethyl carbonate to form ethyl methyl carbonate. High ethyl methyl carbonate yield (50.1%) and excellent selectivity (100%) was achieved under moderate conditions. As a heterogeneous catalyst, MOFs could be easily separated from the reaction mixture by a simple centrifugation and reused at least three times with slight decrease in its catalytic activity.

Acknowledgements

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