

# Dimethyl carbonate synthesis via transesterification of ethylene carbonate and methanol using ionic liquid catalysts immobilized on mesoporous cellular foams

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**Abstract** Dimethyl carbonate (DMC) was synthesized via transesterification of ethylene carbonate and methanol with ionic liquid catalysts. For this reaction, 1,4-diazobicyclo[2.2.2]octane (DABCO), [Choline]OH, and [BMIM]Cl were used as a homogeneous catalyst, and hydrotalcite, [DABCO]OH@MCF, [DABCO]Cl@MCF, and DABCO/MCF were used as a heterogeneous catalyst. To support the ionic liquids, mesoporous cellular foam (MCF) was prepared and characterized by SEM, TEM and BET surface area analyzer. The average cell and window sizes of the prepared MCF were 34.4 and 21.3 nm, respectively. The prepared MCF had a well structured three-dimensional structure. Among the homogeneous catalysts used, DABCO showed the highest DMC yield about 84 %, and among the heterogeneous catalysts, [DABCO]OH@MCF showed the highest DMC yield about 77 %. In the reusability test of the used catalysts, there was only 8 % point decrease in DMC yield with [DABCO]OH@MCF, whereas 58 percent point decrease in DMC yield with DABCO/MCF after four times recycling tests. The effects of an anion on the catalytic activity were investigated. The optimum reaction condition for DMC synthesis was also investigated with [DABCO]OH@MCF catalyst.

**Keywords** Dimethyl carbonate · Ionic liquids · Mesoporous cellular foam · Ethylene carbonate · Reusability

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## Introduction

It is very attractive to synthesize dimethyl carbonate (DMC) from ethylene carbonate (EC) and methanol (MeOH) in terms of the reuse of carbon dioxide, because ethylene carbonate (EC) is synthesized from carbon dioxide and easily converted to DMC via the transesterification reaction of EC and MeOH. Owing to the high oxygen content, low toxicity, and high chemical stability, DMC is an emerging substitute for phosgene, solvent, and gasoline additives [1–3]. DMC has been produced industrially by the methyl chloroformate reaction of phosgene and methanol. However, this process has a problem of phosgene's toxicity; therefore DMC is produced industrially by a transesterification of ethylene carbonate or propylene carbonate with methanol [4–7].

For the transesterification reaction, homogeneous or heterogeneous, acid or base catalysts have been used. As a heterogeneous catalyst, metal oxides or inorganic materials such as perovskite, hydrotalcite, and ZnO were used [8, 9]. As a homogeneous catalyst, several ionic liquids and 1,4-diazobicyclo[2.2.2] octane (DABCO) were used [10, 11]. The heterogeneous catalysts have some advantages of separation and reusability, while they have a problem of low catalytic activity. On the other hand, the homogeneous catalysts have an advantage of high catalytic activity, while they have a problem of separation after the reaction. To solve these problems, there has been an attempt in which the homogeneous liquid catalysts were supported on some supports such as SBA-15, MCM-41, and mesoporous cellular foams (MCF) [12–14]. The supports with micro-pores can hinder the mass transfer of reactants and products in this reaction, thus mesoporous supports are necessary. There are some kinds of mesoporous materials that have been synthesized such as MCM-41, SBA-15, HMM-33, and FSM-16 [15–18]. MCF has a three dimensional structures in which spherical cells are interconnected. The cell and window sizes can be controlled in the preparation steps.

In the present work, MCF is prepared and characterized, and then several ionic liquids are supported on the MCF to prepare heterogeneous catalysts. We choose MCF as the support because it has three dimensional meso-sized pores and stable structures in this reaction system. DMC is synthesized at various reaction conditions using the prepared catalysts, and the reusability of the used catalysts is tested. The effects of anions of ionic liquids are also investigated.

## Experimental

### Materials

For the preparation of MCF, trimethyl benzene (TMB, 98 %), sodium silicate solution (reagent grade), and Pluronic P123 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol),  $M_n \sim 5800$ ) were purchased from Sigma-Aldrich, and acetic acid (99.5 %) was from Daejung Chemical and Metals Co. For the synthesis of DMC, methanol (99.9 %) and ethylene carbonate

(98 %) were also purchased from Sigma-Aldrich. The purchased reagents were used without further purification. 1,4-diazobicyclo[2.2.2]octane (DABCO), 1-butyl-3-methylimidazolium chloride ([BMIM]Cl, 98 %), and choline hydroxide ([Choline]OH, 45 wt% in methanol) were purchased from Sigma-Aldrich to use as a catalyst. 3-chloropropyl trimethoxy-silane (CPTMS, 97 %), potassium hydroxide (90 %), ethyl ether (98 %), anhydrous toluene (99.8 %), and acetonitrile (99.8 %) were also purchased from Sigma-Aldrich.

### Preparation of the MCF support

For the preparation of MCF, tetraethyl orthosilicate (TEOS) has been used as a silica source; however, in the present work inexpensive sodium silicate was used as the silica source. Pluronic P123 was used as a surfactant. The pore size of MCF was controlled by the weight ratio of TMB to Pluronic P123.

For the preparation of MCF, 9.8 g of Pluronic P123 and 200 mL of deionized water were put into a Duran bottle and the mixture was stirred at room temperature to dissolve. And then, 4.47 mL of acetic acid was added into the prepared Pluronic P123 solution, and the mixture was stirred at room temperature for 30 min. After that, 5.88 g of TMB was added to the prepared solution, and the mixture was vigorously agitated at 60 °C for 2 h. A 200 mL sodium silicate solution in which 16 mL of sodium silicate was dissolved in deionized water was added to the solution, and the mixture was vigorously agitated at 60 °C for 20 h. And then, the prepared emulsion, stored in a capped Duran bottle, was further aged in a convection oven at 100 °C for 24 h. The aged mixture was then filtered and the solid part was washed with 200 mL of deionized water. Finally, the washed solid part was dried in a drying oven at 80 °C for 12 h, and calcined in an air environment at 550 °C for 8 h.

### Preparation of catalysts

Ionic liquids were supported on MCF support by an impregnation and chemical immobilization methods. To distinguish the prepared catalysts, the catalysts prepared by the impregnation method were denoted by ‘/’ like DABCO/MCF, and the catalysts prepared by the chemical immobilization method were denoted by ‘@’ like [DABCO]OH@MCF.

DABCO and [BMIM]Cl that have been used as a homogeneous catalyst were impregnated on MCF. DABCO/MCF stands for “DABCO impregnated on MCF”. For the preparation of the DABCO/MCF catalyst, 2.5 g of MCF, dried in an oven at 100 °C for 12 h, was mixed with 15 mL of anhydrous toluene and DABCO (corresponding to 1 mol% of ethylene carbonate), and the mixture was stirred at room temperature for 20 h. Then, the mixture was filtered, and the solid part was dried in an oven at 60 °C for 12 h.

[DABCO]OH@MCF stands for “[DABCO]OH immobilized on MCF by a chemical bonding”. [DABCO]OH was immobilized on MCF by the anchoring action of CPTMS. For the preparation of [DABCO]OH@MCF, we referred to the work of Moghaddam [19]. For the preparation of [DABCO]OH@MCF, 2.5 g of

MCF, dried in an oven at 100 °C for 12 h, was mixed with 15 mL of anhydrous toluene and CPTMS (corresponding to 1.5 mol% of ethylene carbonate), and the mixture was refluxed at 60 °C for 48 h to prepare chemically bonded CPTMS on MCF. Then, the mixture was filtered, and the solid part was washed with 50 mL of anhydrous toluene and 50 mL of dichloromethane, respectively, and dried in an oven at 60 °C for 12 h. After that, 2 g of the dried solid part was mixed with the solution that was prepared by the dissolving of a predetermined amount of DABCO in 30 mL of anhydrous toluene, and the mixture was stirred for 48 h. In order to exchange chlorine ions for hydroxyl ions, the stirred mixture was mixed with a KOH solution (in which the amount of KOH was corresponding to 2 mol% of ethylene carbonate), and the mixture was stirred for 48 h. Finally, the mixture was filtered, and the solid part was washed with 100 mL of deionized water and dried in an oven at 60 for 8 h. Through this process, the [DABCO]OH@MCF catalyst was prepared. [DABCO]Cl@MCF referred to the catalyst that did not exchange the chlorine ions for hydroxyl ions.

### DMC synthesis reaction

DMC was synthesized by the transesterification of ethylene carbonate and methanol in an autoclave (Parr 4843). The prepared catalyst was mixed with the pre-calculated amounts of ethylene carbonate and methanol, in which the amount of catalyst (ionic liquid) was controlled to be 1 mol% of the limiting reactant, ethylene carbonate. The reaction mixture was stirred in a rate of 450 rpm, and the pressure was maintained at 37–41 psi by their vapor. The reaction was carried out at 70–150 °C for 7 h. The reactants molar ratio (MeOH/EC) was varied from 10 to 25.

To examine the reusability of the used catalysts, the used catalyst was collected by filtration after the reaction, and washed with 100 mL of deionized water, and then dried in an oven at 60 °C for 8 h. The dried used catalyst was reused for the reaction.

The reaction products were analyzed with a gas chromatograph (DS6200) equipped with a FID detector and a capillary column (HP-INNOWAW 30 m, 0.25 mm, 0.25 µm). For the quantitative analysis, we used an internal standard method, in which acetone was used as the internal standard.

### Characterization of catalysts

The specific surface area and pore size distribution of the prepared MCF and supported catalysts were characterized by a surface area analyzer (BELSORP-max). The specific surface area was calculated by the BET method and the pore size distribution was calculated by the Barrett–Joyner–Halenda (BJH) method. The surface and inner structures of MCF were observed by SEM (scanning electron microscope, JSM 6700F) and TEM (transmission electron microscope, JEM 2100F).

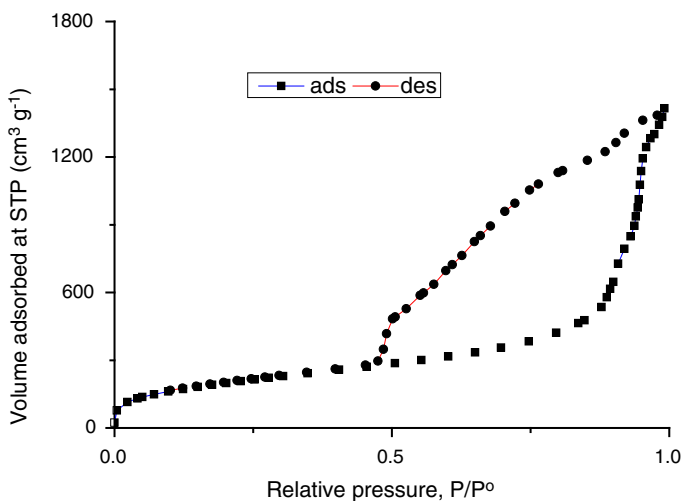
## Results and discussion

### BET surface areas and pore size distribution

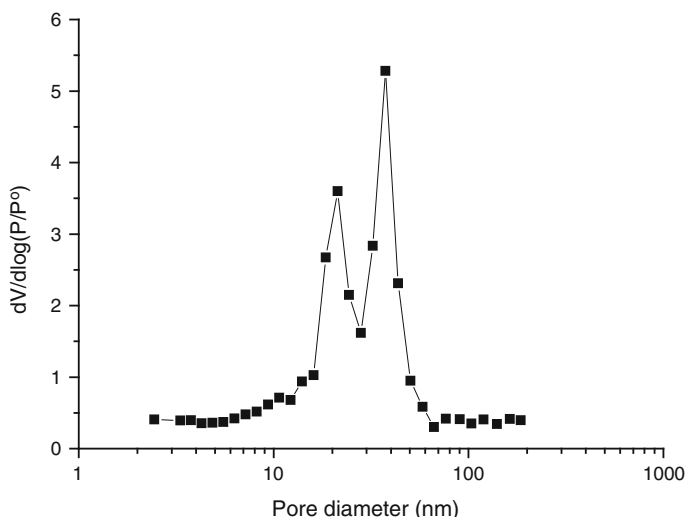
The  $N_2$  adsorption/desorption isotherms of the prepared MCF are depicted in Fig. 1. There is an adsorption–desorption hysteresis observed in the  $P/P^0$  range of 0.9–1, which means that MCF has meso-sized pores [15]. The BET surface area of the prepared MCF was  $733 \text{ m}^2/\text{g}$ . The pore size distribution of the prepared MCF was analyzed by the BJH method and presented in Fig. 2. As shown, the average pore sizes of the cell and window of the MCF are 34.4 and 21.3 nm, respectively. The pore sizes of the cell and window of the MCF are very important, because small pores can hinder the mass transfer of the reactants and products. The prepared MCF shows a proper pore sizes for this reaction. The average surface area, cell size, widow size, and specific volume of the prepared MCF and supported catalysts are summarized in Table 1. The surface area, cell and window pore sizes decrease with the amount of ionic liquids loaded. Especially, DABCO/MCF, prepared by the impregnation method, shows the lowest these values. This can be explained by the reason that DABCO/MCF is a physically supported one, while the others are chemically supported ones, therefore, in the case of DABCO/MCF, the multi-layered ionic liquids may cause the decrease of these values.

### SEM and TEM analysis

The surface structure of the prepared MCF was observed with SEM, and the result was presented in Fig. 3. The low resolution SEM image (Fig. 3a) shows a porous granule-like structure; however, the high resolution image (Fig. 3b) shows relatively



**Fig. 1**  $N_2$  adsorption/desorption isotherms for the prepared MCF



**Fig. 2** Pore size distribution of the prepared MCF; cell size: 37.4 nm, window size: 21.3 nm

**Table 1** Characteristics of the prepared catalysts

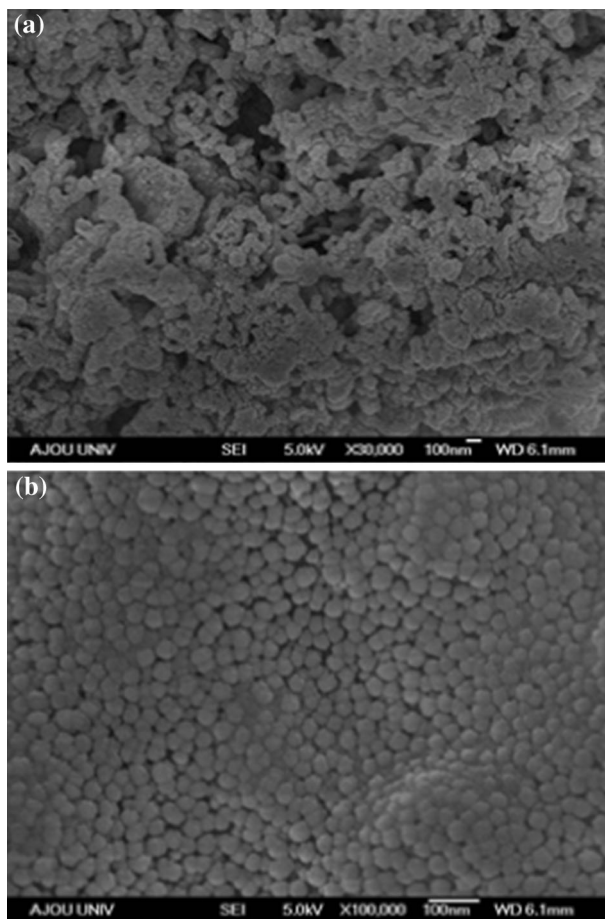
| Catalyst      | $S_{\text{BET}}$ (m <sup>2</sup> /g) | Cell size (nm) | Window size (nm) | $V_{\text{total}}$ (cm <sup>3</sup> /g) |
|---------------|--------------------------------------|----------------|------------------|---|
| MCF           | 732.8                                | 34.4           | 31.3             | 2.2                                     |
| DABCO/MCF     | 477.9                                | 10.4           | 7.0              | 1.4                                     |
| [DABCO]Cl@MCF | 528.2                                | 28.1           | 18.5             | 1.9                                     |
| [DABCO]OH@MCF | 493.9                                | 27.5           | 16.9             | 1.8                                     |

uniform cells with an average size of about 34 nm, that is coincident with the result of BJH analysis.

The structure of the prepared MCF was also observed with TEM, and the result was presented in Fig. 4. From Fig. 4a, it is found that the prepared MCF has a relatively well-developed three dimensional cell structures, and the cells are relatively uniform. From Fig. 4b, a well-developed window structures can be observed. From the TEM images, it is proved that the average sizes of the cells and windows are about 34 and 21 nm, respectively.

### DMC synthesis reaction

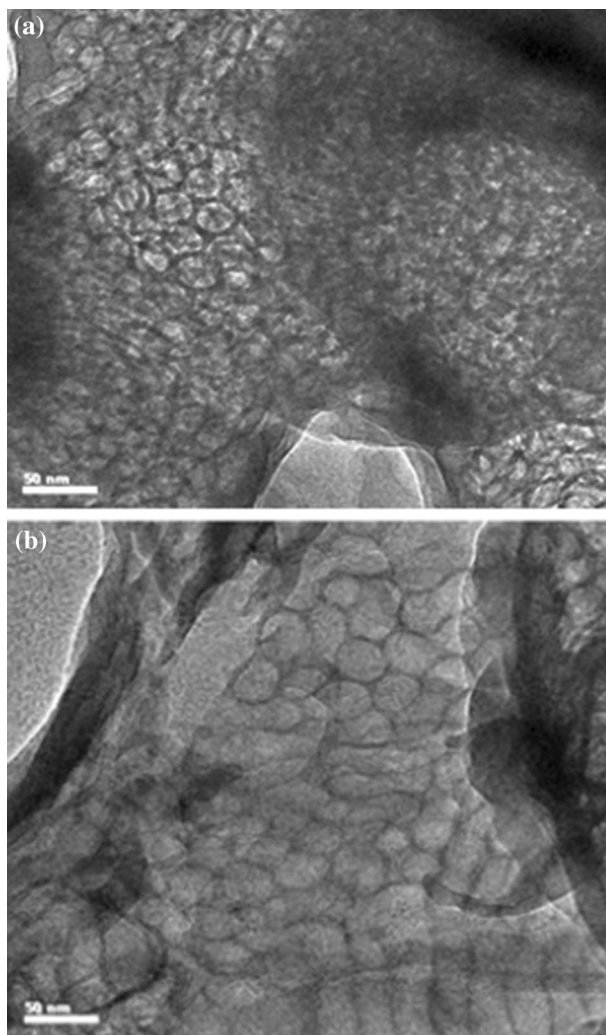
In an autoclave, DMC was synthesized by the transesterification reaction of methanol and ethylene carbonate. For this reaction, DABCO, [Choline]OH, and [BMIM]Cl were used as a homogeneous catalyst, and hydrotalcite, [DABCO]OH@MCF, [DABCO]Cl@MCF, and DABCO/MCF were used as a heterogeneous catalyst.



**Fig. 3** SEM images of the prepared MCF. **a** Low resolution. **b** High resolution

DMC yield was calculated as the percentage of the ratio of the amount of DMC produced to the amount of DMC calculated. EC conversion was also calculated as the percent of the ratio of the amount of EC converted to the amount of EC presented initially.

DMC synthesis results obtained with various catalysts are depicted in Fig. 5. As shown, hydrotalcite, [BMIM]Cl, and [DABCO]Cl@MCF catalysts show a low DMC yield around 10 %. However, DABCO, DABCO/MCF, and [DABCO]OH@MCF show a relatively high DMC yield around 80 %. Among the homogeneous catalysts used, DABCO shows the highest DMC yield of 84 %, and among the heterogeneous catalysts used, [DABCO]OH@MCF shows the highest DMC yield of 77 %.

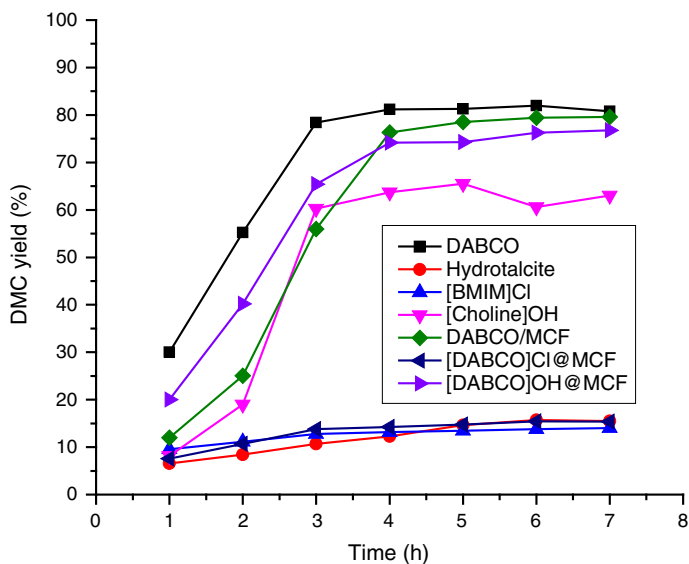


**Fig. 4** TEM images of the prepared MCF

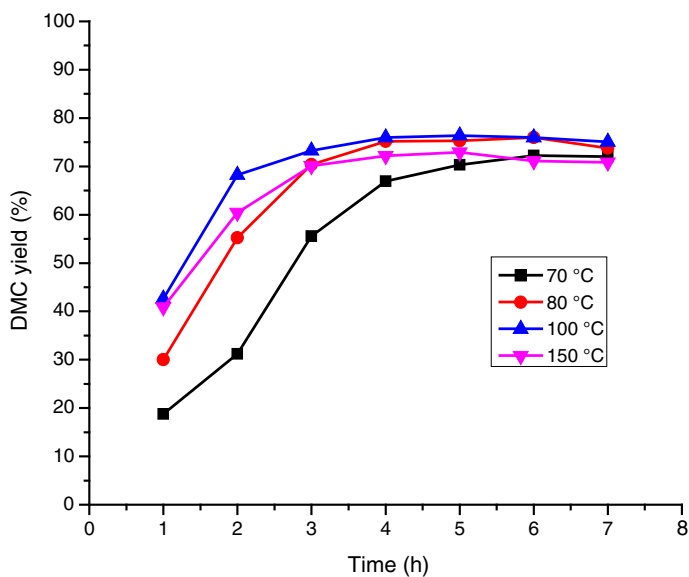
### Effects of temperature and reaction time on DMC yield

In order to examine the effects of temperature and reaction time on DMC yield, the transesterification reaction of ethylene carbonate and methanol was carried out with [DABCO]OH@MCF catalyst, and the result was depicted in Fig. 6. As shown, the time to reach equilibrium decreases with increasing the reaction temperature. The times to reach equilibrium are around 6, 5, 4, and 3 h at 70, 80, 100, and 150 °C, respectively. The highest DMC yield is obtained at 100 °C. The lower DMC yield at 150 °C may be due to the decomposition of ethylene carbonate at higher temperature or the degradation of immobilized species at the higher temperature.





**Fig. 5** DMC yields with various catalysts



**Fig. 6** DMC yields with the reaction time at various temperatures

### Effects of the molar ratio of reactants on DMC yield and EC conversion

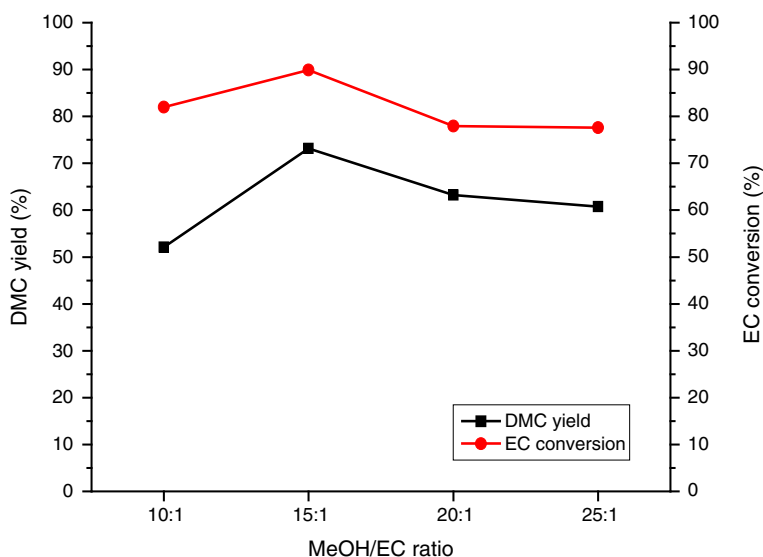
In order to test the effects of the molar ratio of reactants on DMC yield and EC conversion, the transesterification reaction was carried out at a molar ratios of

MeOH/EC = 10–25, and the results were depicted in Fig. 7. Because of the alkoxy group exchange in this reaction system, excess methanol was used. Both the highest DMC yield and the highest EC conversion were obtained at MeOH/EC = 15. From this experiment, it was found that the proper reactants molar ratio (MeOH/EC) was 15.

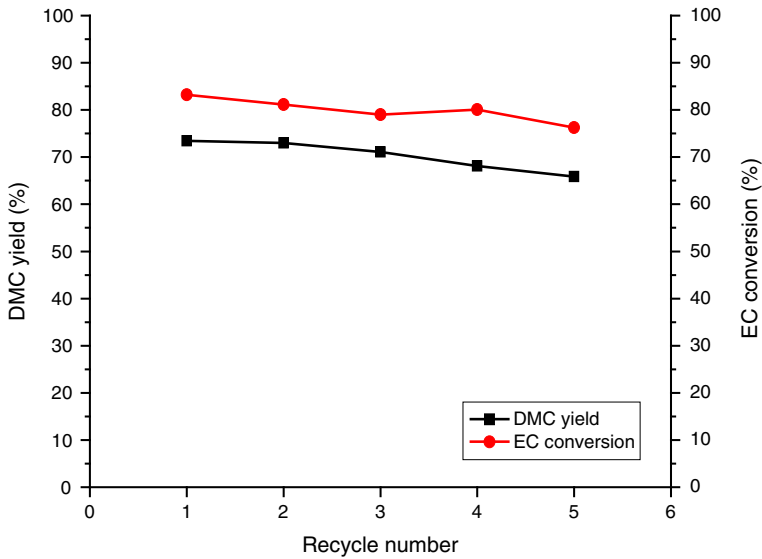
### Reusability test of the used [DABCO]OH@MCF and DABCO/MCF catalysts

Although homogeneous ionic liquid catalysts show a high DMC yield, there is a problem of separation of the catalysts from the products. This problem may be a significant drawback in the industrialization of the process. Therefore, in the present work, ionic liquids were supported on MCF so as to separate the used catalyst easily.

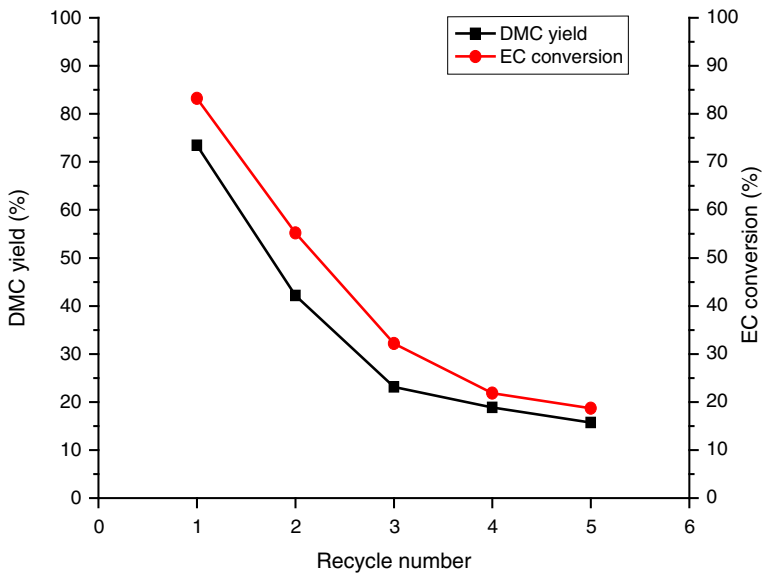
The reusability test of the used [DABCO]OH@MCF and DABCO/MCF catalysts were performed. The changes in DMC yield and EC conversion with the used catalysts were tested and depicted in Figs. 8 and 9. As shown in Fig. 8, there are about 8 percent point decrease in DMC yield and about 7 percent point decrease in EC conversion with the chemically immobilized [DABCO]OH@MCF catalyst after 4 times reuses. On the other hand, the DMC yield and EC conversion decrease by about 58 and 64 percent points, respectively, with the physically impregnated DABCO/MCF catalyst after 4 times reuses, as shown in Fig. 9. From these results, it is proved that the chemically immobilized [DABCO]OH@MCF catalyst is much more stable than the physically impregnated DABCO/MCF catalyst. [DABCO]OH@MCF catalyst shows a possibility for the industrial application of the chemically immobilized ionic liquid catalysts.



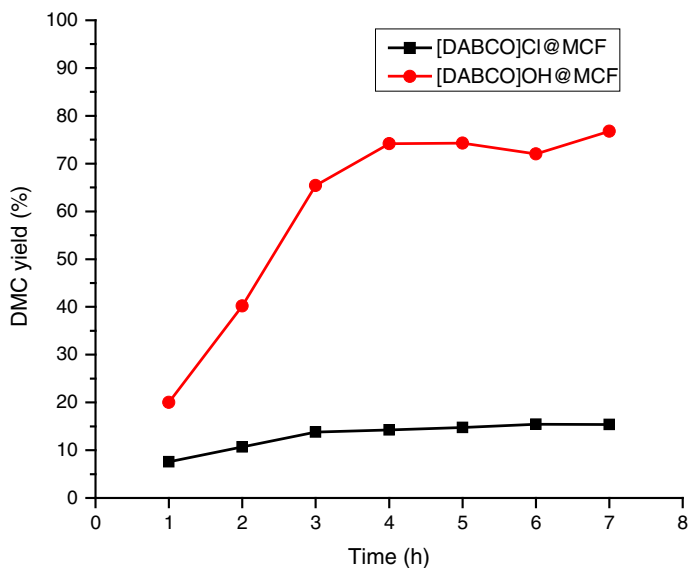
**Fig. 7** DMC yield and EC conversion with various molar ratios of methanol and ethylene carbonate



**Fig. 8** Changes in DMC yield and EC conversion as a function of the recycle number of used [DABCO]OH@MCF



**Fig. 9** Changes in DMC yield and EC conversion as a function of the recycle number of used DABCO/MCF



**Fig. 10** Changes in DMC yield with different anion-bearing catalysts

### Effects of the anions of ionic liquids on DMC yield

The effects of the anions of ionic liquids on DMC yield were examined with [DABCO]OH@MCF and [DABCO]Cl@MCF catalysts, and the result was depicted in Fig. 10. The [DABCO]OH@MCF catalyst shows approximately 60 percent point higher DMC yield than [DABCO]Cl@MCF catalyst. In other words, the catalyst containing  $\text{OH}^-$  anion shows higher DMC yield than the one containing  $\text{Cl}^-$  anion. The reaction mechanism proposed for the transesterification of ethylene carbonate and methanol is as follows: first, a hydrogen bond between the cation of ionic liquids and methanol is formed, then the methanol is converted to a methoxy group ( $\text{CH}_3\text{O}^-$ ) by the anion ( $\text{OH}^-$  or  $\text{Cl}^-$ ) of the ionic liquids, finally the produced methoxy group reacts with ethylene carbonate, producing DMC and ethylene glycol [7, 20]. The  $\text{OH}^-$  anion facilitates the formation of  $\text{CH}_3\text{O}^-$  through the hydrogen bond with methanol, whereas the  $\text{Cl}^-$  anion does not form the hydrogen bond with methanol. As a result, catalysts with  $\text{OH}^-$  anion show a higher activity than the one with  $\text{Cl}^-$  anion [21]. Therefore, the [DABCO]OH@MCF catalyst showed a higher DMC yield than [DABCO]Cl@MCF catalyst.

### Conclusions

In order to prepare a supported ionic liquid catalyst, MCF was prepared as a support. The MCF, whose average cell and window sizes are 34.4 and 21.3 nm respectively, was prepared successfully. Furthermore, the MCF was verified to have a well-structured three-dimensional structure by SEM and TEM analyses. Among the

homogeneous catalysts used, DABCO showed the highest DMC yield of 84 %, and among the heterogeneous catalysts, [DABCO]OH@MCF showed the highest DMC yield of 77 %. In the reusability test of the used catalysts, there was about 8 percent point decrease in DMC yield with the chemically immobilized [DABCO]OH@MCF catalyst after four times recycling tests, whereas there was about 58 % point decrease in DMC yield with the physically impregnated DABCO/MCF catalyst after four times recycling tests. The chemically immobilized [DABCO]OH@MCF catalyst was much more stable than the physically impregnated DABCO/MCF catalyst. The anions contained in the ionic liquids played an important role in the DMC synthesis reaction. The optimum reaction conditions for the DMC synthesis with [DABCO]OH@MCF catalyst were 100 °C, MeOH : EC = 15 : 1 and 4 h.

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