

Effects of ionic liquid in the catalyst preparation of MgO-CeO₂ mixed oxide for dimethyl carbonate synthesis via transesterification

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Introduction

The synthesis and application of dimethyl carbonate (DMC) are achieving increasing importance due to its low toxicity and versatile reactivity. DMC can be used as environment-friendly intermediate and starting material for organic synthesis via carbonylation and it can replace methylating agents such as dimethyl sulphate and methyl halides [1–3]. DMC is also being considered as a component for replacing methyl *tert*-butyl ether (MTBE) as an oxygen-containing additive for gasoline, owing to its high oxygen content, good blending octane and quick biodegradation [4]. Moreover, DMC can be used in lithium batteries as an electrolyte due to its high dielectric constant [5].

With the exception of phosgenation-route, there are three main production technologies for DMC synthesis, methanol oxy-carbonylation, carbonylation of methyl nitrite and transesterification of ethylene carbonate (EC) or urea [2,5,6]. The phosgenation-route has been losing attraction recently due to the use of virulent phosgene [5]. In transesterification process, DMC is co-generated with ethylene glycol (EG). This reaction takes place in the presence of a catalyst at about 100–150 °C at moderate pressure [7]. Numerous homogeneous and heterogeneous, acid or base catalysts have been reported as being useful for this reaction. However, the base catalyzed reaction appears generally to be the most effective for the synthesis of DMC [8,9]. Various heterogeneous catalysts such as alkali-treated zeolite [10,11], basic metal oxides [12–14], and hydrotalcite [15] were used for the transesterification.

In our previous work, MgO–CeO₂ catalyst systems, which were prepared via co-precipitation of magnesium chloride and cerium (III) nitrate, were found to have attractive catalytic performance without decay of activity and had excellent selectivity to the sum of dimethyl carbonate at a temperature of 150 °C and pressure of 0.2 MPa. The modification presented in this study is to apply ionic liquid as a templating material. Ionic liquids (ILs) are an exceptional type of solvent consisting virtually only of ions. They have practically no vapor pressure and possess tunable solvent properties [16,17]. In this study, various ionic liquids

were used as template in coprecipitation methods to prepare mesoporous MgO–CeO₂ mixed oxides particles. The low vapor pressure of ionic liquid could assist in reducing the problem of gel shrinkage during sol ageing and gel drying, which could prevent reduction of surface area. An anion part of ionic liquid was crucial factor due to its various strength of hydrogen bond with water. A cation part of ionic liquid gave an influence on determining the pore size and volume of particles [18].

Experimental

Mixture of Mg(OH)₂-Ce(OH)₄ hydroxide gels were prepared from their salt solutions as precursors by co-precipitation method. MgCl₂·6H₂O (98%, Kanto) and Ce(NO₃)₃·6H₂O (98.5%, Kanto) at molar ratio (Mg/Ce) of 4 were first dissolved with distilled water. One of ILs (delivered by TOYOCOLOR) presented in Table 1 was added into the mixed solution with an IL/mixed-oxide molar ratio of 3 at room temperature. 1 M NaOH aqueous solution was slowly added to the mixture until the pH value reached 10 with stirring. The precipitates were further aged at room temperature for 5 h in the mother liquid. After filtration and washing with distilled water, the excess IL was extracted using acetone nitril (CH₃CN) and filtrated. The obtained solid was dried at 110 °C for 12 h and then calcinated at 500 °C for 5 h in air. The catalysts were further characterized by BET, XRD, FE-SEM for morphology of the catalysts. For basicity and base strength distribution of the catalysts were measured respectively by retroaldolisation of diacetone alcohol and by benzoic acid titration using Hammett indicators according to literature [19].

Table 1. List of room temperature ionic liquids

Symbol*	Full name
BPF6	1-Butyl-3-methylimidazolium hexafluorophosphate
HPF6	1-Hexyl-3-methylimidazolium hexafluorophosphate
OPF6	1-Octyl-3-methylimidazolium hexafluorophosphate
BCF3	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
HCF3	1-Hexyl-3-methylimidazolium trifluoromethanesulfonate
BBF4	1-Butyl-3-methylimidazolium tetrafluoroborate
HBF4	1-Hexyl-3-methylimidazolium tetrafluoroborate

* used in this study

The transesterification of ethylene carbonate with methanol for catalytic activity measurements was carried out according to [20] with 3 grams of catalyst powder, molar ratio (MeOH/EC) = 8.0 and a flow rate of 1.08 ml/min, corresponding to liquid hourly space velocity

(LHSV) of 18 h^{-1} . The reaction temperature was fixed at $150 \text{ }^\circ\text{C}$ and the reaction pressure was maintained to be constant by BPR (Back Pressure Regulator) at 3.5 psig (0.2 MPa). The output products were analyzed using a gas chromatograph system (HP 6890 series) equipped with a FID detector and a capillary column ($200 \text{ } \mu\text{m} \times 25.0 \text{ m}$, HP-FFAP Polyethylene Glycol TPA).

Results and Discussion

The catalytic activity measurements of the catalysts are presented in Fig. 1. It can be seen that the catalyst OPF6 is the best in the category of DMC selectivity with more than 82%, while for the conversion of ethylene carbonate ($> 68\%$) and DMC yield ($\sim 53\%$) the catalyst BBF4 is the most active catalyst. Generally, the modified coprecipitation method with ionic liquids increased the activity of the catalyst and selectivity compare to the physically mixed. However, the addition of some ionic liquids to the coprecipitation of MgO-CeO₂ catalyst did not increased the activity.

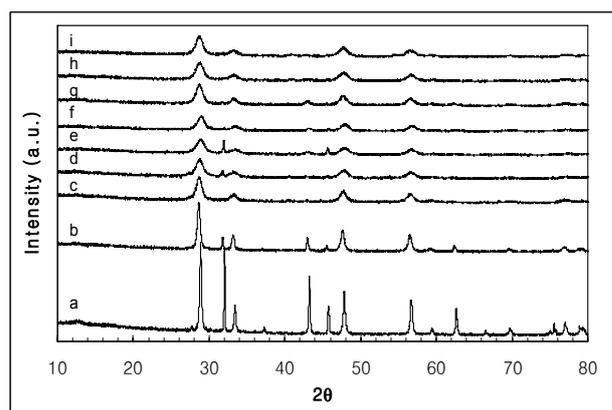
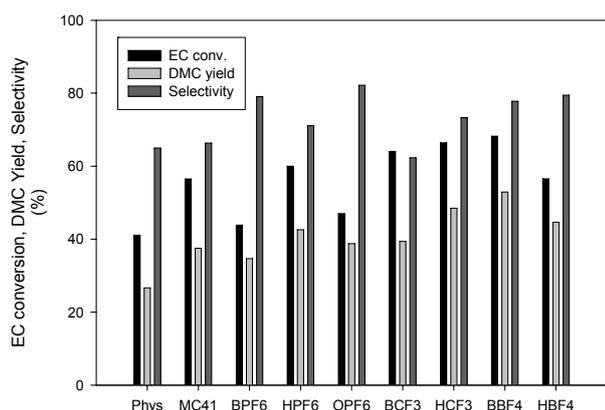


Figure 1. The catalytic activity of catalysts prepared by physically mixing, coprecipitation and modified coprecipitation with ionic liquids.

Figure 2. The XRD patterns of the catalysts: (a) Phys, (b) MC41, (c) BPF6, (d) HPF6, (e) OPF6, (f) BCF3, (g) HCF3, (h) BBF4, (i) HBF4.

Figure 2 illustrates XRD patterns of MgO-CeO₂ catalysts. Fig. 2(c)–(i) are respectively XRD patterns of catalysts prepared with addition of ionic liquids. In these XRD profiles some peaks are faded out, especially MgO peaks. The absence of peaks MgO at catalyst prepared by modified coprecipitation is presumably due to suppression of crystal growth. This fact is supported by the suggestion of Saito et al. [21] that the MgO component is in amorphous or fine particle. The width of peaks of MgO-CeO₂ in the X-ray diffraction curve reflects the

average grain size and it can be calculated using Scherrer's formula. The average crystallite sizes of the catalysts were calculated and illustrated in Table 2. It can obviously be seen that the particle size of the catalysts prepared with addition of IL's is much smaller than the catalyst prepared without IL. HPF6 catalyst has the smallest crystallites, while BPF6 has the greatest particles among the catalysts prepared with IL's addition.

Table 2. Crystallite size of mixed oxide catalysts calculated from XRD data.

Catalyst	2θ (°)	FWHM (°)	Crystallite size (nm)
Phys ^a	28.87	0.25	108.78
MC41 ^b	28.77	0.46	69.93
BPF6	28.71	0.88	41.55
HPF6	28.86	1.24	21.76
OPF6	28.81	1.32	22.37
BCF3	28.89	1.12	23.21
HCF3	28.79	1.10	28.20
BBF4	28.73	1.29	27.17
HBF4	28.77	1.25	25.66

^a Physically mixed; ^b Coprecipitation without IL

Surface areas, pore volumes and pore diameters of the magnesium-cerium mixed oxides prepared with ILs together with the physically mixed and conventional coprecipitation are summarized in Table 3. It can be seen that the surface area and pore volume of mixed oxides prepared by modified sol-gel method are obviously greater than those of the catalysts prepared without IL. The surface area of mixed oxide by coprecipitation is greater than physically mixed catalyst more than twice, while their pore volumes have the similar value. When the catalysts were prepared using ILs, the surface areas enhanced 2.5 to 6.0 and by 5.9 to 14.3 times more than those of particles prepared by coprecipitation and by physically mixed, respectively. Meanwhile, the pore volume increased 5.5 to 10.7 times. It is worthy noting that the addition of IL in the coprecipitation method increases the surface area and the pore volume of catalysts dramatically. This indicates that IL could prevent the reduction of surface area and pore volume of particles. The catalyst OPF6 has the greatest surface area of 64.57 m²/g, while BPF6 has the smallest with 26.75 m²/g among the catalysts prepared with IL's.

Figure 3 shows the SEM images of MgO–CeO₂ prepared with and without IL's. We observed as expected that XRD (Fig. 2) and SEM (Fig. 3) analysis show that crystallite size is remarkably decreased with addition of IL's in the coprecipitation method. In particular, Fig. 3(d)–(g) shows the agglomerate of the particles.

Table 3. BET surface area, pore volume and pore size of catalysts (MgO/CeO₂ = 4/1) prepared with and without ionic liquid

Catalyst	Surface area (m ² /g)	Pore volume (cm ³ /g)	Pore size (nm)
Phys ^a	4.52	0.04	36.50
MC41 ^b	10.70	0.04	24.72
BPF6	26.75	0.22	33.22
HPF6	48.43	0.34	27.90
OPF6	64.57	0.42	25.74
BCF3	37.85	0.29	30.24
HCF3	48.98	0.39	32.26
BBF4	55.41	0.43	30.87
HBF4	48.54	0.26	21.74

^a Physically mixed; ^b Coprecipitation without IL

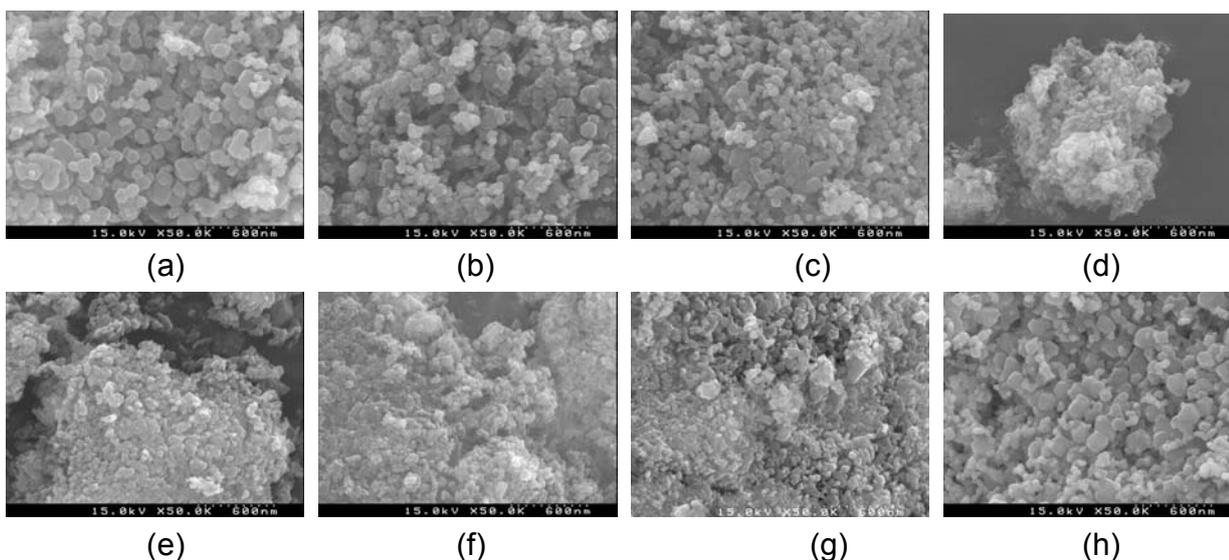


Figure 3. FE-SEM images of catalyst prepared by (a) coprecipitation without IL, and with IL's: (b) BPF6, (c) HPF6, (d) OPF6, (e) BCF3, (f) HCF3, (g) BBF4 and (h) HBF4.

In fact, there is no relation between catalytic activity and the surface area or crystallite size of the MgO-CeO₂ mixed oxide catalysts. The phenomena, that OPF6 produced the best DMC selectivity and BBF4 gave the best catalytic activity in term of EC conversion and DMC yield (see Fig. 1), could be explained by the base strength distribution (H_{-}) of the catalysts illustrated in Table 4. BBF4 could obtain the best activity due to the greatest moderate base strength in the range $10.5 \leq H_{-} \leq 17.2$, while the catalyst OPF6 attained the best DMC selectivity because of the less strong basic sites ($17.2 \leq H_{-} \leq 26.5$).

Table 4. Base strength distribution (H₊) obtained from color changes of Hammett indicators by benzoic acid titration.

Catalysts	Base strength distribution (H ₊) (%)				
	8.2-10.5	10.5-15.0	15.0-17.2	17.2-18.4	18.4-26.5
Phys	9.3	12.1	16.4	22.2	6.1
MC41	26.4	27.0	29.3	11.4	5.9
BPF6	30.3	35.7	18.8	8.9	6.1
HPF6	21.1	44.5	17.6	8.8	8.0
OPF6	29.5	34.8	21.0	8.7	6.0
BCF3	9.6	33.8	29.7	14.1	12.9
HCF3	19.0	41.2	22.9	8.5	8.3
BBF4	19.3	32.5	31.7	8.6	7.8
HBF4	28.9	36.5	19.3	7.1	8.1

Conclusion

Transesterification of ethylene carbonate with methanol over MgO-CeO₂ mixed oxide catalysts has been successfully demonstrated. Among the ionic liquids, [Bmim][BF₄] displayed the best performance in terms of activity, while [Omim][PF₆] obtained the best selectivity for this reaction. The addition of IL's in the coprecipitation method increased the surface area and pore volume of the catalysts. Meanwhile, the crystallite size of the catalysts was reduced many times. However, there is no effect of the surface area and particle size as well on the catalytic activity of the catalyst in this reaction. The activity and selectivity of the catalyst depended on the base strength distribution. The moderate basic site is responsible for the catalytic activity, while the selectivity is more dependable on the strong basic site.

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