PREPARATION OF MgO-CeO$_2$ MIXED OXIDE WITH IONIC LIQUID AS CATALYST FOR DIMETHYL CARBONATE SYNTHESIS VIA TRANSESTERIFICATION

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ABSTRACT

The synthesis and application of dimethyl carbonate (DMC) are achieving increasing importance due to its low toxicity and versatile reactivity. The phosgenation-route has been losing attraction recently due to the use of virulent phosgene. In transesterification process, DMC is co-generated with ethylene glycol (EG). In this study, various ionic liquids were used as template in coprecipitation methods to prepare mesoporous MgO–CeO$_2$ mixed oxides particles. Among the ionic liquids, [Bmim][BF$_6$] displayed the best performance in terms of activity, while [Omim][PF$_6$] 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 depend 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.

Keyword: preparation, MgO-CeO$_2$, ionic liquid, dimethyl carbonate, coprecipitati

INTISARI

Sintesa dan aplikasi dimetil karbonat (DMC) semakin bertambah penting dikarenakan rendahnya sifat racun dan reaktifitas yang sangat banyak. Saat ini, pembuatan melalui rute phosgene telah kehilangan daya tariknya dikarenakan penggunaan senyawa yang bersifat racun. Pada proses transesterifikasi, DMC dibuat bersamaan dengan etilen glikol (EG). Dalam kajian ini, beberapa cairan ionik (ionic liquid/IL) telah digunakan sebagai 'cetakan' dalam metoda kopresipitasi untuk preparasi partikel oksida campuran MgO-CeO$_2$ yang bersifat mesopori. Diantara cairan ionik tersebut, [Bmim][PF$_4$] telah memperlihatkan kemampuan yang paling baik dalam hal aktifitas, sementara itu [Omim][PF$_6$] telah menghasilkan selektifitas yang paling baik untuk reaksi ini. Penambahan IL dalam metode kopresipitasi meningkatkan luas permukaan dan volume pori dari katalis-katalis itu. Sementara itu, ukuran kristalit dari katalis-katalis itu berkurang beberapa kali. Akan tetapi, tidak ada pengaruh dari luas permukaan dan ukuran partikel terhadap aktifitas katalitik dari katalis tersebut dalam reaksi ini. Aktifitas dan selektifitas dari katalis tergantung pada distribusi kekuatan basa. Permukaan basa moderat bertanggung jawab terhadap aktifitas katalitik, sedangkan selektifitas lebih bergantung kepada permukaan basa kuat.

Kata Kunci: preparasi, MgO-CeO$_2$, cairan ionik, dimetil karbonat, kopresipitasi

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[1,2,3]. 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 methylnitrite 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 ^{0}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[12,13,14], and hydrotalcite[15] were used for the transesterification.

In our previous work, MgO–CeO$_2$ 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 ^{0}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–CeO$_2$ 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. MgCl$_2$ 6H$_2$O (98%, Kanto) and Ce(NO$_3$)$_3$ 6H$_2$O (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 (CH$_3$CN) and filtrated. The obtained solid was dried at 110^0 C for 12 h and then calcined at 500^{0}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 *(see Table 2)* according to literature[19].

Table 1. List of room temperature ionic liquids

Symbol*	Full name
BPF$_6$	1-Butyl-3-methylimidazolium hexafluorophosphate
HPF$_6$	1-Hexyl-3-methylimidazolium hexafluorophosphate
OPF$_6$	1-Octyl-3-methylimidazolium hexafluorophosphate
BCF$_3$	1-Butyl-3-methylimidazolium trifluoromethanesulfonate
HCF$_3$	1-Hexyl-3-methylimidazolium trifluoromethanesulfonate
BBF$_4$	1-Butyl-3-methylimidazolium tetrafluoroborate
HBF$_4$	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 flowrate of 1.08 ml/min, corresponding to liquid hourly space velocity (LHSV) of 18 h^{-1}. The reaction temperature was fixed at 150 $^{\circ}$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 μm × 25.0 m, HP-FFAP Polyethylene Glycol TPA).

Table 2. Hammett indicators used for the benzoic acid titration

Indicator	Base strength (H_)
Phenolphthaleine	8.2 – 9.8
Thymolphthaleine	9.3 - 10.5
2,4 Dinitroaniline	15.0
4-Chloro-2-nitroaniline	17.2
p-4-Nitroaniline	18.4
4-Chloroaniline	26.5

RESULTS AND DISCUSSION

Figure 1 illustrates XRD patterns of MgO–CeO$_2$ catalysts. *Fig. 1(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 coprecipitaion 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–CeO$_2$ 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 3*. 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. HPF$_6$ catalyst has the smallest crystallites, while BPF$_6$ has the greatest particles among the catalysts prepared with IL's addition.
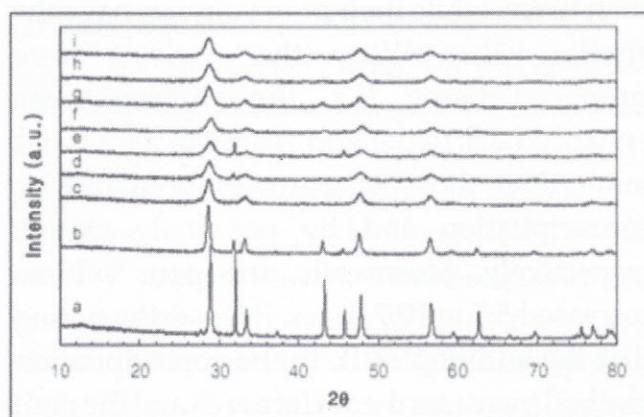

Figure 1. The XRD patterns of the catalysts: (a) Phys, (b) MC41, (c) BPF$_6$, (d) HPF$_6$, (e) OPF$_6$, (f) BCF$_3$, (g) HCF$_3$, (h) BBF$_3$, (I) HBF$_4$.

Table 3. Crystallite size of mixed oxide catalysts calculated from XRD data.

Catalyst	2θ (^{0})	FWHM (^{0})	Crystallite size (nm)
Phys^a	28.87	0.25	108.78
MC41$_b$	28.77	0.46	69.93
BPF$_6$	28.71	0.88	41.55
HPF$_6$	28.86	1.24	21.76
OPF$_6$	28.81	1.2	22.37
BCF$_3$	28.89	1.12	23.21
HCF$_3$	28.79	1.10	28.20
BBF$_4$	28.73	1.29	27.17
HBF$_4$	28.77	1.25	25.66

*Physically mixed; *Coprecipitation without IL; FWHM: Full Width at Half Maximum

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 4*. 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 OPF_6 has the greatest surface area of 64.57 m^2/g, while BPF_6 has the smallest with 26.75 m^2/g among the catalysts prepared with IL's.

Table 4. BET surface area, pore volume and pore size of catalysts ($MgO/CeO_2 = 4/1$) 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
BPF$_6$	26.75	0.22	33.22
HPF$_6$	48.43	0.34	27.90
OPF$_6$	64.57	0.42	25.74
BCF$_3$	37.85	0.29	30.24
HCF$_3$	48.98	0.39	32.26
BBF$_4$	55.41	0.43	30.87
HBF$_4$	48.54	0.26	21.74

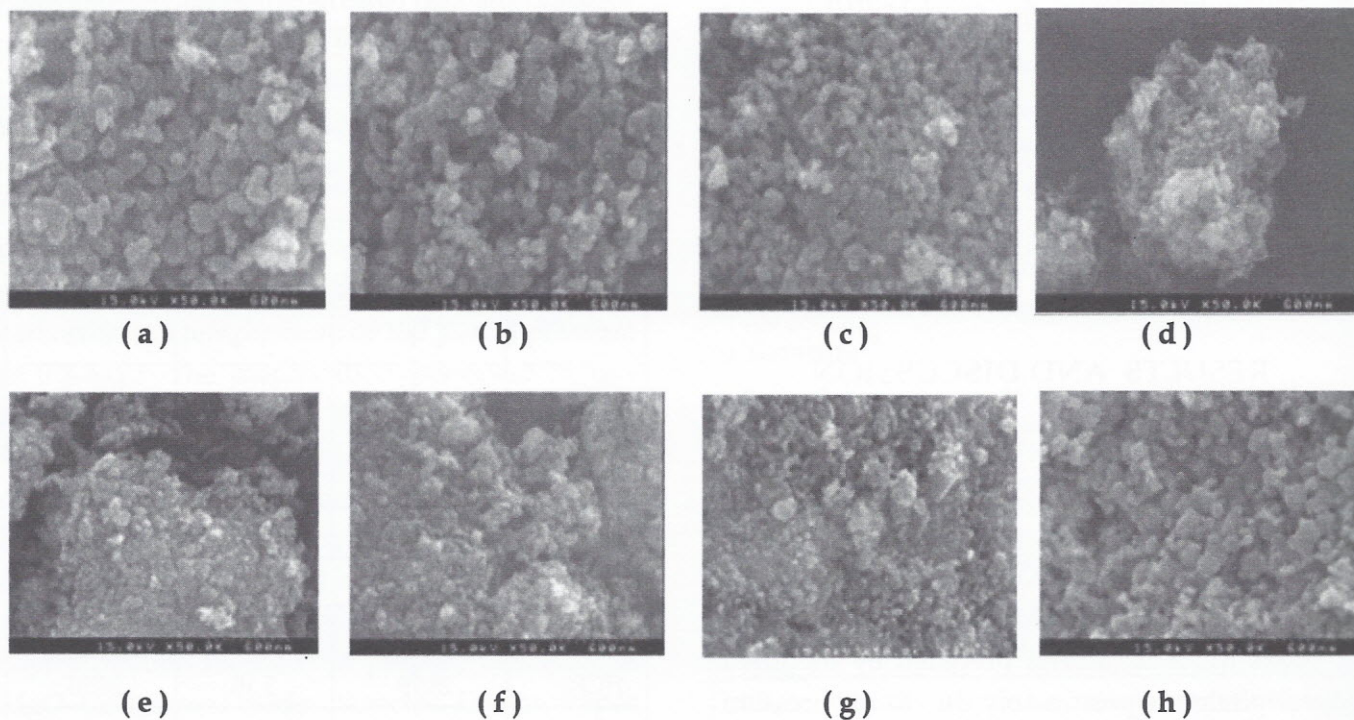[a]Physically mixed; [b]Coprecipitation without I

Figure 2. FE-SEM images of catalyst prepared by (a) coprecipitation without IL, and with IL's, (b) BPF$_6$, (c) HPF$_6$, (d) OPF$_6$, (e) BCF$_3$, (f) HCF$_3$, (g) BBF$_4$ and (h) HBF$_4$.

Fig. 2 shows the SEM images of MgO–CeO$_2$ prepared with and without IL's. We observed as expected that XRD (Fig. 1) and SEM (*Fig.* 2) analysis show that crystallite size is remarkably decreased with addition of IL's in the coprecipitation method. In particular, *Fig.* 2 (d)–(g) shows the agglomerate of the particles.

The catalytic activity measurements of the catalysts with correlation of surface area are presented in *Fig.* 3. Among the catalysts, the catalyst BBF$_4$ prepared with ionic liquid [Bmim][BF$_4$] produced the highest EC conversion (65.3%) and the highest DMC yield (56.6%), as well. Although its surface area was the biggest, the catalyst OPF$_6$ obtained the lowest EC conversion and DMC yield of 46.4% and 42.1%, respectively. In the group of catalysts prepared with IL containing the same anion part ([PF$_6$]), the catalytic performance reduced with the surface area. BPF$_6$ with surface area 26.8 m^2/g could convert 52.8% of EC to generate 49.0% of DMC. Meanwhile, OPF$_6$ seized the biggest surface area 64.6 m^2/g, but it generated a lowest DMC and converted the lowest EC, as well. On the other hand, the catalysts prepared using ionic liquids with the same cation part ([Bmim]$^+$) show relatively correlation of surface area to the catalytic activity. The surface area tends to increase significantly from BPF$_6$ (26.8 m^2/g) to BCF$_3$ (37.9 m^2/g) and to BBF$_4$ (55.4 m^2/g), but the catalytic activity shows a slightly increase with EC conversion of 52.8, 58.0 and 65.3%, respectively.

In fact, there is no relation between catalytic activity and the surface area or crystallite size of the MgO-CeO$_2$ mixed oxide catalysts. The phenomena, that OPF$_6$ produced the best DMC selectivity and BBF$_4$ gave the best catalytic activity in term of EC conversion and DMC yield, could be explained by the base strength distribution (H_) of the catalysts illustrated in *Table* 5. BBF$_4$ could obtain the best activity due to the greatest moderate base strength in the range 10.5 ≤ H_ ≤ 17.2, while the catalyst OPF$_6$ attained the best DMC selectivity because of the less strong basic sites (17.2 ≤H_ ≤26.5).

In our previous work[22], it was observed that the strong base increases the EC conversion but not the DMC yield, so it produces more by-products in the reaction. Meanwhile, the moderate base is esponsible to produce more DMC in this reaction[15]. *Table* 5 illustrates DMC selectivity and base strength distribution (H_) of the mixed oxides. OPF6 has higher DMC selectivity than HPF$_6$. This is possibly caused by a highest moderate base strength (10.5 ≤ H_ ≤ 15.0) dominated on the surface of OPF$_6$ particles, while HPF$_6$ has the lowest among the catalysts containing anion [PF$_6$]. Despite of the highest strong base strength (17.2 ≤ H_ ≤26.5), BCF$_3$ has DMC selectivity similar with BBF$_4$ due to a higher moderate base strength dominated on the surface of BCF$_3$ particles. However, BBF$_4$ has a better activity than BCF$_3$ with higher values of EC
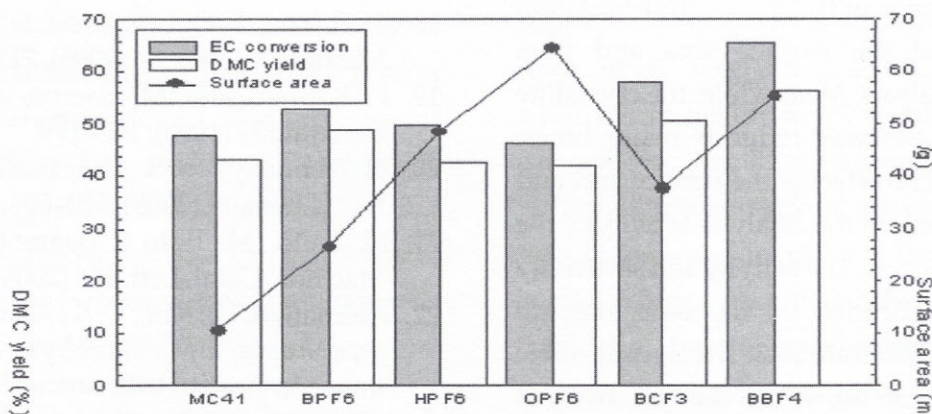

Figure 3. The catalytic activity of catalysts (DMC yield and EC Conversion) correlate to surface area.

conversion and DMC yield. The base strength distribution contributes also in the catalytic activity, whereas the strong base strength stimulates the EC conversion and the moderate base strength gives an influence to DMC yield.

Table 5. DMC selectivity and base strength distribution (H_) of MgO-CeO_2 mixed oxides.

Catalysts	DMC Selectivity (%)	Base strength distribution (H_) (%)[a]				
		8.2-10.5	10.5-15.0	15.0-17.2	17.2-18.4	18.4+
MC41	90.33	26.4	27.0	29.3	11.4	5.9
BPF$_6$	92.99	30.3	35.7	18.8	8.9	6.1
HPF$_6$	85.61	29.5	34.8	21.0	8.7	6.0
OPF$_6$	90.67	21.1	44.5	17.6	8.8	8.0
BCF$_3$	87.03	9.6	33.8	29.7	14.1	12.9
BBF$_4$	87.00	19.3	32.5	31.7	8.6	7.8

CONCLUSIONS

Transesterification of ethylene carbonate with methanol over MgO-CeO_2 mixed oxide catalysts has been successfully demonstrated. Among the ionic liquids, [Bmim][BF$_4$] displayed the best performance in terms of activity, while [Omim][PF$_6$] 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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