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The double component catalyst for the direct synthesis of dimethyl carbonate from carbon dioxide, propylene oxide and methanol

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Dimethyl carbonate (DMC) can be directly synthesized from carbon dioxide, methanol and propylene oxide in the presence of double component catalyst consisted of metal halide and inorganic alkali. The active components of catalyst are loaded on the surface of inorganic oxide by wet-impregnation. The results of experiment indicate that metal ion of halide attacks C– O bond of propylene oxide to form M– O bond. The insertion of carbon dioxide into this M– O bond is the key step of its activation. The alkality of catalyst effectively affects the yield of dimethyl carbonate. The catalytic activity can be enhanced by the introduction of strong base site which is formed in the calcination procedure of catalyst under air atmosphere.

KEY WORDS: double component catalyst; synthesis; dimethyl carbonate.

1. Introduction

Dimethyl carbonate (DMC) is a green chemical. With one carbonyl group and two methoxyl groups, DMC can be used as a starting material for organic synthesis via carbonylation and methylation, replacing high-risk and environment-harmful compounds such as phosgene, dimethyl sulfate and halogen methane. It is also a new and clean fuel additive that can increase octane value and oxygen content of fuel and decrease pollution effectively [1].

DMC can be prepared by the phosgenation of methanol, the oxidative carbonylation of methanol or the transesterification between cyclic carbonate and methanol. The phosgenation method is the earliest industrial procedure for DMC synthesis, but it is losing attraction because of the use of phosgene [2]. Oxidative carbonylation of methanol is commonly carried out with copper or palladium compound catalysts, and there is a possibility of explosions in this case [3–4]. DMC can also be synthesized by the transesterification between methanol and cyclic carbonate which is prepared by the cycloadditions of carbon dioxide and epoxide compounds such as ethylene oxide or propylene oxide [5,6].

Carbon dioxide is the main greenhouse gas and a potential carbon resource [7–8]. The synthesis of DMC from carbon dioxide is of great benefit both to protect environment and develop new carbon resource. Since Kizlink reported the direct synthesis of DMC from carbon dioxide and methanol in the presence of organometallic compounds [9], this route has been widely investigated. The effects of super critical carbon dioxide, iodide, orthoesters and acetals on the promotions of direct synthesis have also been noted [10–14]. However, the activation of carbon dioxide is difficult so that the yield of DMC is far from satisfactory. The direct synthesis reactions are generally carried out in homogeneous systems, so the catalyst is not easily separated from the reaction system. These disadvantages limit the industrialization for the route.

Carbon dioxide is activated by its insertion into M– O bond of organometallic compound in direct synthesis route [10,12]. The yield of DMC is very low due to the difficulty for carbon dioxide activation. However, carbon dioxide can be readily activated by its cycloaddition with epoxides. Thus, DMC can be produced easily in the transesterification between cyclic carbonate and methanol. We believe that epoxides can be adopted to improve the activation of carbon dioxide and enhance DMC yield in the direct synthesis of DMC from carbon dioxide.

Cycloaddition and transesterification reactions are generally carried out in the presence of metal salt and alkali catalysts, respectively. In this paper, metal halide and inorganic alkali are chosen for the preparation of double component catalyst used in the direct synthesis of DMC from carbon dioxide, propylene oxide and methanol and the yield of DMC can be enhanced significantly. The heterogeneous catalyst is prepared by wet impregnation in order to separate catalyst and product. The introduction of strong base site into catalyst also increases the yield of DMC efficiently. Good results in the conversion of carbon dioxide and DMC yield have been obtained.

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2. Experimental

2.1. Preparation of catalyst supports

2.1.1. MgO

Aqueous solution of NaOH (1 M) was added dropwise to an aqueous solution of $MgCl_2$ (1 M) at room temperature with vigorous stirring until a final pH of 7.0 was obtained. The solid product was separated by filtration, washed thoroughly with deionized water, and spray-dried at 110 °C , calcined at 600 °C for 3 h, crushed to 80–100 mesh. The BET surface area is 120 m^2/g (N_2 sorption).

2.1.2. SiO_2

Aqueous solution of sulfuric acid (1 M) was added dropwise to an aqueous solution of sodium silicate (1 M) at room temperature with vigorous stirring until a final pH of 3.0 was obtained. The solid product was separated by filtration, washed thoroughly with deionized water, and dried under air atmosphere at 110 °C, crushed to 80–100 mesh. The BET surface area is 200 m^2/g (N_2 sorption).

Other catalyst supports are commercial reagents. The BET surface areas determined by N_2 sorption are listed as follows. Acidic Al_2O_3: 165 m^2/g, alkaline Al_2O_3: 180 m^2/g, TiO_2: 100 m^2/g, ZnO: 120 m^2/g.

2.2. Preparation of supported catalysts

The supported catalysts were prepared by wet impregnation. Metal halide and inorganic alkali of certain quantity were dissolved in deionized water to form a mixed solution. The inorganic oxide supports mentioned above were dispersed in this aqueous solution with vigorous stirring. Then the slurry was sprayed into 110 °C air atmosphere, and dried powder was collected. The water content was less than 0.5% (wt%). Finally the catalyst powder was crushed to 1–5 μm with an air-jet mill.

Table 1
Reactions of carbon dioxide, propylene oxide and methanol in the presence of homogeneous two component catalysts

Catalyst	PO conversion (%)	Selectivity (%)				DMC yield (%)
		DMC	PM	PG	PC	
LiCl–Na_2CO_3	82.4	22.4	10.7	24.9	42.0	18.4
NaCl–Na_2CO_3	83.3	21.5	8.68	26.8	43.0	17.9
KCl–Na_2CO_3	83.7	21.7	11.3	27.2	39.9	18.1
LiCl–$NaHCO_3$	84.4	19.8	12.6	29.9	37.7	16.7
NaCl–$NaHCO_3$	83.7	18.2	9.04	26.5	46.2	15.2
KCl–$NaHCO_3$	84.2	20.0	7.56	21.1	51.4	16.8
LiCl–NH_4HCO_3	82.3	18.1	8.31	23.8	49.9	14.9
NaC–NH_4HCO_3	83.4	16.2	7.98	26.9	48.9	13.5
KCl–NH_4HCO_3	83.8	17.4	8.12	25.7	48.8	14.6

Reaction conditions: propylene oxide/methanol = 1/4(mol/mol),CO_2 2.5 MPa, 160 °C for 5 h, catalyst content: 5% (wt%), chloride/alkali = 1(wt/wt). PO: propylene oxide, PC: propylene carbonate, PG: propylene glycol, PM: propylene glycol methyl ether.

Table 2
Reactions of carbon dioxide, propylene oxide and methanol over supported catalysts

Catalyst (surface area: m^2/g)	PO conversion (%)	Selectivity (%)				DMC yield (%)
		DMC	PM	PG	PC	
Na_2CO_3–KCl/Al_2O_3[a](178)	85.7	20.1	7.85	36.7	35.4	17.2
Na_2CO_3–KCl/Al_2O_3[b](160)	83.2	16.3	8.43	35.9	39.3	13.6
Na_2CO_3–KCl/ZnO(117)	85.8	21.6	8.29	36.1	34.0	18.7
Na_2CO_3–KCl/MgO(114)	84.9	21.4	5.47	40.0	32.3	18.2
Na_2CO_3–KCl/SiO_2(196)	82.3	16.2	6.06	37.5	40.2	13.3
Na_2CO_3–KCl/TiO_2(94)	83.7	15.5	7.54	38.4	38.6	13.0
Al_2O_3[a]	DMC cannot be detected					
Al_2O_3[b]	DMC cannot be detected					
ZnO	DMC cannot be detected					
MgO	DMC cannot be detected					
SiO_2	DMC cannot be detected					
TiO_2	DMC cannot be detected					

Other reaction conditions: see table 1.

[a] Alkaline Al_2O_3.

[b] Acidic Al_2O_3 loading content: 30%, halide/alkali = 1 (wt/wt).

Table 3
Reactions of carbon dioxide, propylene oxide and methanol over supported catalysts with strong base sites

Catalyst	P^K	PO conversion (%)	Selectivity (%)				DMC yield (%)
			DMC	PM	PG	PC	
K_2CO_3–KCl/MgO[a]	≥27	100	46.2	2.47	50.1	1.23	46.2
K_2CO_3–KCl/MgO[b]	<15	88.4	23.6	6.72	27.1	42.6	20.8
K_2CO_3–KCl/MgO[c]	15—27	92.7	35.2	2.65	46.9	15.2	32.6
K_2CO_3–KCl /Al_2O_3[a]	15—27	100	35.4	5.94	40.1	18.6	35.4
K_2CO_3–KCl /Al_2O_3[b]	<15	86.3	22.2	5.25	29.3	38.4	19.1
K_2CO_3–KCl /Al_2O_3[c]	15—27	91.2	34.8	6.72	38.6	19.9	31.7
K_2CO_3–KCl /SiO_2[a]	15—27	95.7	27.9	8.06	31.5	32.5	26.7
K_2CO_3–KCl /SiO_2[b]	<15	83.2	17.1	11.2	24.4	47.3	14.2
K_2CO_3–KCl /SiO_2[c]	<15	91.3	24.2	8.87	26.8	40.1	22.1

Reaction conditions: see table 2.

[a] Calcined at 600 °C.

[b] Non-calcined.

[c] Regenerate catalyst.

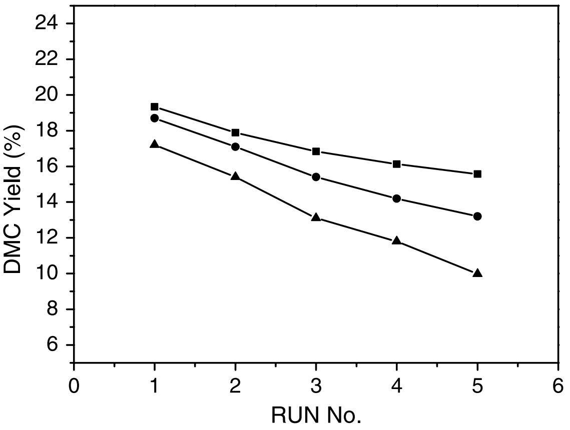

Figure 1. The reuse of catalyst after regeneration. ■, Na_2CO_3–KCl/ZnO; ●, Na_2CO_3–KCl/MgO; ▲, Na_2CO_3–KCl/Al_2O_3.

2.3. Catalytic runs

Catalytic reactions were carried out in a stainless steel autoclave equipped with a magnetic stirring and a temperature controlling system. Methanol, propylene oxide and catalyst were charged into this reactor. Then the container was sealed. After the introduction of nitrogen for eliminating oxygen, liquid carbon dioxide stored in a cylinder was added into the reactor through a stainless tube and compressed to desired pressures with a pump. Measurement of its amount was achieved by the weigh of the reactor. The reactor was heated to desired temperature under stirring. After reaction, the autoclave was cooled to −5 °C by ice-salt water and vented slowly. The reaction mixture was analyzed by GC equipped with TCD and Porapak Q column. The selectivity of products was defined as the mole proportions of products/the conversion of propylene oxide.

2.4. Regeneration of supported catalysts

The spent supported catalysts were filtered and washed with methanol and dried under air atmosphere at 100 °C for 2 h.

2.5. Determination of strong base site

Strong base site of fresh and regenerated catalysts were determined by Hammett indicator method [15].

2.6. DRIFT research

The supported catalyst was separated from post-reaction system by filtration under a nitrogen atmosphere. Then it was washed with acetone and dried in vacuum. DRIFT tests of separated catalyst sample were carried out with a Bruker EQUINO55.

3. Results and discussion

As the key step of DMC direct synthesis, the activation of carbon dioxide is not easy. The equilibrium conversion of carbon dioxide is not more than 8% in the direct reaction of carbon dioxide and methanol even under the pressure of 10 MPa [16]. Some researchers believe that metal methoxyl compound was exhausted in this reaction system [9]. Isaacs and other researchers reported the method to enhance DMC yield in which iodomethane was added into this reaction system [10,14]. In fact, iodomethane plays a role of methylating agent. The reaction intermediate formed during the insertion of carbon dioxide into M–O bond of metal methoxyl compound reacts with iodomethane to form DMC. Super critical carbon dioxide improves the dissolving and dispersing properties of reactants in the reaction system, but the reaction route is not changed [12].

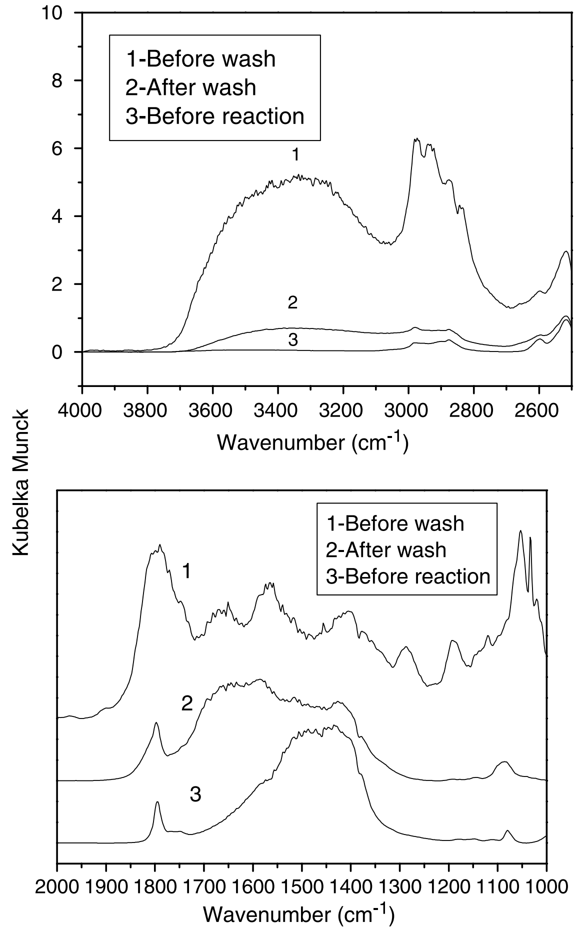

Figure 2. DRIFT patterns of catalysts before and after reactions.

The introduction of epoxide can promote the activation of carbon dioxide and play a key role in the process of the direct synthesis of DMC. The path and thermodynamic functions of reaction can be changed by the introduction of epoxide. In this paper alkali metal halide and inorganic alkali catalysts are used for the direct synthesis from carbon dioxide, epoxide and methanol. The results are listed in table 1.

Table 1 shows that the catalysis activities are not very different while inorganic alkali keeps unchanged. But the alkalinity of inorganic alkali affects the selectivity and DMC yield effectively. The conversion of propylene oxide keeps high in presence of every two component catalyst. This indicates that carbon dioxide is easier to be activated in presence of propylene oxide. The yield of DMC is affected mainly by the transesterification between cyclic carbonate and methanol. The alkalinity of inorganic alkali used as the catalyst for transesterification plays an important role in the enhancement of DMC yield.

We prepared supported two component catalysts by loading alkali metal halide and inorganic alkali on the surface of inorganic oxides. The results of catalytic runs are listed in table 2.

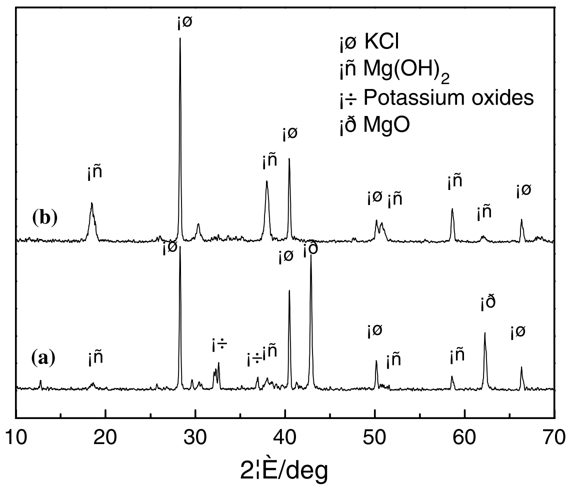

Figure 3. XRD patterns of KCl–K_2CO_3/MgO before and after calcinations (b is the pattern of catalyst without calcination, a is the pattern of catalyst calcined at 600 °C for 3 h).

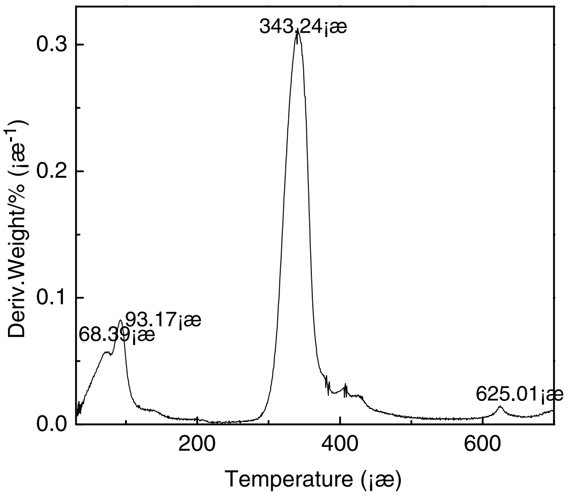

Figure 4. TGA for the calcinations of K_2CO_3–KCl/ Al_2O_3.

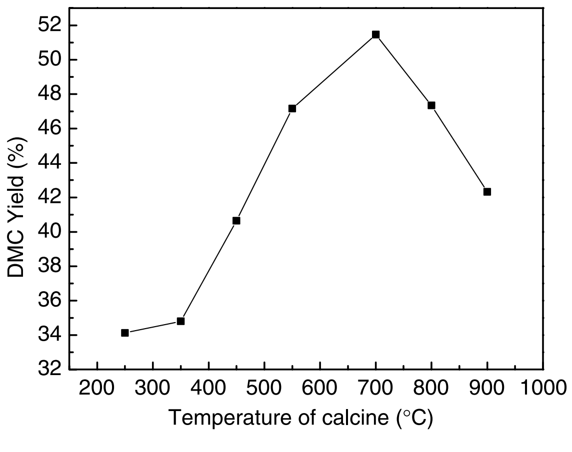

Figure 5. The relationship between calcining temperature and catalytic activity. Catalyst: K_2CO_3–KCl/Al_2O_3.

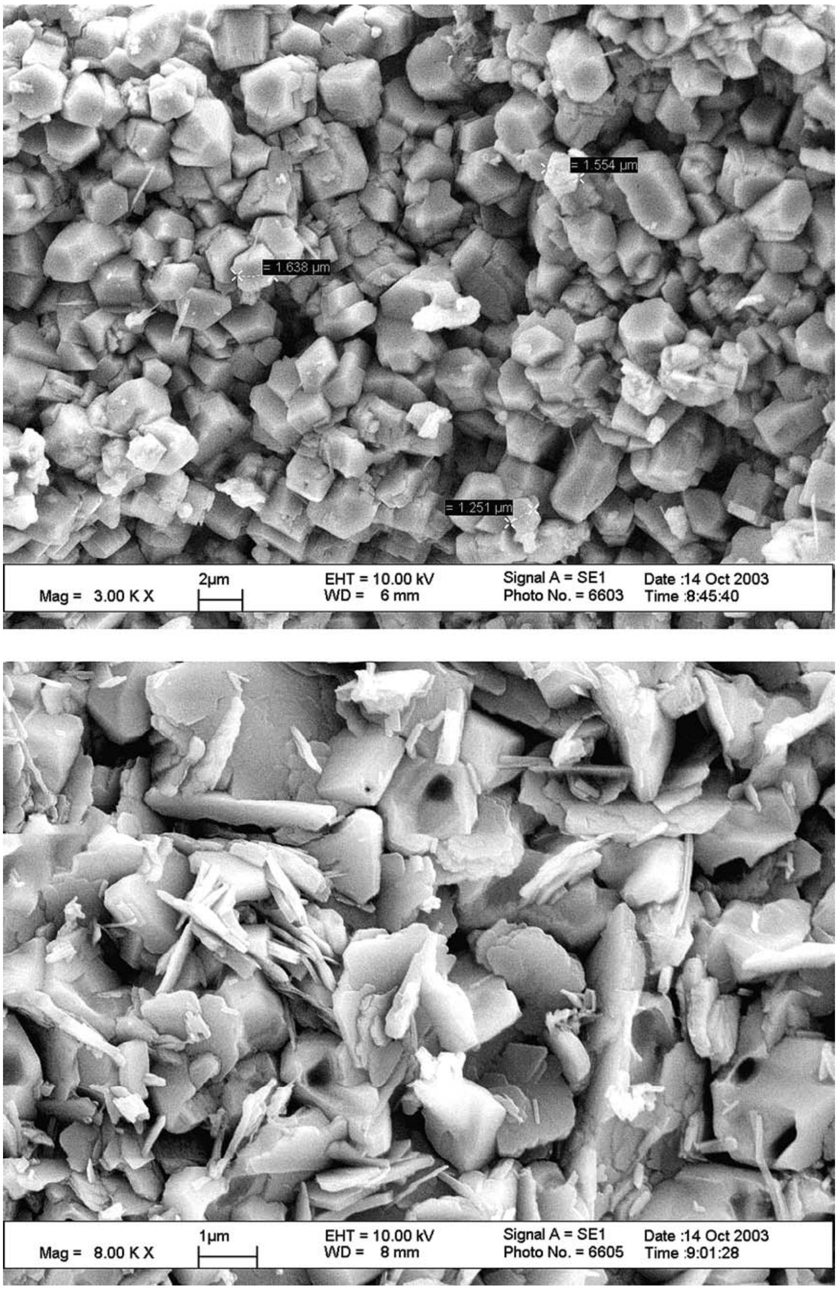

Figure 6. SEM of K_2CO_3–KCl/Al_2O_3 Top. Calcined at 600 °C for 3 h/Bottom. Calcined at 900 °C for 3 h.

As listed in table 2, the synthesis reaction of DMC can also be carried out assisted by heterogeneous catalyst supported on inorganic oxides. However DMC cannot be detected in the reaction system assisted by inorganic oxide alone. The catalysts supported over different inorganic oxides give different activities. The catalysts loaded on zinc oxide, magnesium oxide and alkaline aluminum oxide give high activities compared with those loaded on silica and titania.

The catalytic runs of regenerated catalysts are demonstrated in figure 1.

Figure 1 indicates that the supported catalysts still show reasonable activities toward DMC formation through the consecutive use. The reason for decreasing catalytic activity through catalytic runs seems to be some loss of basicity after the reaction (see table 3).

In order to study the surface species absorbed on the surface of catalyst, DRIFT researches of catalyst samples have been carried out before and after reaction (see figure 2). The stretching and flexural vibrations of C–H and O–H around 3400, 2900 and 1800 cm^{-1} exhibit the formations of absorbed organic species during the reaction. However, these vibrations disappeared after the catalyst sample has been washed with acetone. This indicates that these vibrations were caused by physical absorption of methanol, dimethyl carbonate and other

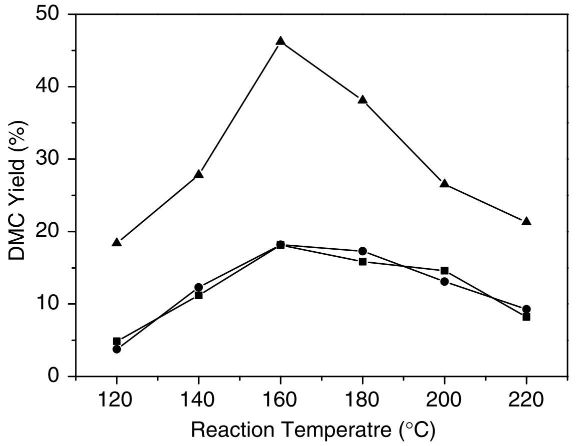

Figure 7. The effects of reaction temperature on the DMC yield ▲ K_2CO_3–KCl/MgO calcined at 600 °C; ● Na_2CO_3–KCl/MgO; ■ KCl–Na_2CO_3.

organic compounds. Vibration in the range of 1550–1700 cm^{-1} can be assigned as the stretching vibrations of C–O of carbonyl groups. It is still observed after the catalyst sample has been washed with acetone and dried in vacuum. It was caused by the surface species containing carbonyl groups. Carbon dioxide was activated over the catalyst, and the reaction intermediate containing carbonyl group was produced and absorbed on the surface of catalyst.

As stated above, the promotion for transesterification reaction is most important in improving DMC yield. Transesterification reaction is assisted by alkali catalyst. Methoxyl anion produced through the reaction of methanol and alkali active center attacks the carbon atom of carbonyl group of cyclic carbonate, and results in transesterification. The alkalinity of alkali active center affects catalytic activity greatly. As showed in table 2, the activity of catalyst loaded on alkaline alumina is higher than that of catalyst loaded on acidic one. In order to enhance catalytic activity, supported double component catalysts were calcined under air atmosphere. And the catalysts with strong base sites were obtained. Their activities and basicities were investigated. The results are listed in table 3.

The researches of solid base have been frequently reported in recent years. The base strength can be quantified by the Hammett–Deyrup *H*-function. It is assumed that if a solid base can change the color of an indicator, the base strength of this sample is greater than or equal to the p*K* of the indicator [18]. In this paper 2,4-dinitroaniline ($pK = 15$) and aniline ($pK = 27$) was chose as the indicators [19].

The experimental results indicate that calcined catalysts loaded on the surface of MgO, Al_2O_3, SiO_2 possess much stronger base site than those not calcined. Their activities are prominently higher than those of catalysts without strong base sites. Results also show that p*K* of the catalyst separated from DMC synthesis reaction system decreases (table 3, catalyst with superscript c). It appears that there is some loss of basicity after the reaction, and the catalytic activity also decreases.

Strong base sites of loaded catalysts are produced during calcining procedure. Alkali metal carbonate loaded on inorganic oxide is decomposed at certain temperature to produce the strong base sites. In order to investigate the formation of strong base site, XRD of catalyst samples before and after calcination have been tested. The results are showed in figure 3.

As showed in figure 3, catalysts after calcination have characteristic diffraction of potassium oxide species. We believe these species are formed in the decomposition of alkali metal carbonate dispersed on the support surface. The slight weight loss at 625 °C in TGA of supported catalyst also supports this opinion (see figure 4). The strong base sites on the catalyst surface may be attributed to the formation of alkali metal oxide species.

The investigations of the relationship between calcining temperature and catalytic activity are listed in figure 5.

Figure 5 shows that DMC yield increases remarkably with the calcination temperature in the range of 200–700 °C , and decreases quickly beyond 700 °C . This can be explained as the sinter of catalyst at high temperature. The SEM of catalyst samples calcined at 600 and 900 °C support this explain (see figure 6).

Figure 7 shows the effect of temperature on the catalyic reaction. As listed in figure 7, DMC yield increases with reaction temperature in the range of 120–160 °C. When the reaction temperature is more than 160 °C, DMC yield decreases significantly. This may be caused by the decomposition of DMC at high temperature. We also found that cyclic carbonate cannot be detected in the reaction system operated at 200 °C . It indicates that high temperature is beneficial for transesterification, but the decomposition of DMC cannot be avoided at such a high temperature. So the reaction temperature should be controlled at about 160 °C.

Results also show that the relationships between calcination temperatures and DMC yields are similar no matter what catalysts are used. This indicates that the reaction mechanism cannot be changed by the loading of catalyst or the introduction of strong base site.

It can be concluded that DMC can be directly synthesized from carbon dioxide, methanol and propylene oxide assisted by double component catalyst consisted of metal halide and inorganic alkali. The participation of propylene oxide in the direct synthesis changes the activation route of carbon dioxide and make the reaction easier be carried out. The catalytic activity can be enhanced significantly by the introduction of strong base site.

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References

[1] Y. Ono, Pure and Appl. Chem. 68 (1996) 367.
[2] Y. Ono, Appl. Catal. 155 (1997) 133.
[3] U. Romano, Chim. Ind. 75 (1993) 303.
[4] D. Delledonne, F. Rivetti and U. Romano, J. Organometal. Chem. 48 (1995) C15.
[5] J.F. Knifton and R.G. Duranleau, J. Mol. Catal. 67 (1990) 380.
[6] R. Srivastava, D. Srinivas and P. Ratnasamy, Catal. Lett. 89 (2003) 81.
[7] S. Inoue and H. Koinuma, Rev. Inorg. Chem. 6 (1984) 291.
[8] P. Braunstein, D. Matt and D. Nobel, Chem. Rev. 27 (1988) 747.
[9] J. Kizlink, Collect. Czech. Chem. Commun. 58 (1993) 1399.
[10] N.S. Isaccs, B. O'Sullivan and C. Verhaelen, Tetrahedron 55 (1999) 11949.
[11] G.H. Chu. J.B. Park and M. Cheong, Inorg. Chim Acta 307 (2000) 131.
[12] T. Sakakura, J.C. Choi, Y. Saito and T. Sako, Polyhedron 19 (2000) 573.
[13] M. Cheong, S.C. Kim and J.B. Park, New J. Chem. 21 (1997) 1143.
[14] S. Fang and K. Fujimoto, Appl. Catal. A 142 (1996) L1.
[15] L.P. Hammett, *Physical Organic Chemistry* (McDraw-Hill, New York, 1940), p. 269.
[16] T.S. Zhao, Y.Z. Han and Y.H. Sun, Natural Gas Chem. Indust. 23 (1998) 52.
[17] E.N. Suciu, B. Kuhlmann, G.A. Knudsen and R.C. Michaelson, J. Organometal. Chem. 556 (1998) 41.
[18] J. Take, N. Kikuchi and Y. Oneda, J. Catal. 21 (1971) 164.
[19] N. Sun and K.J. Klabunde, J. Catal. 185 (1999) 506.