K/MgO촉매상에서 메탄올과 에틸렌카보네이트의 에스테르 교환반응

한만석, 오광석, 이병권, 안병성, 김훈식, 임종성
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Transesterification between Methanol and Ethylene Carbonate Using K/MgO as Heterogeneous Catalyst

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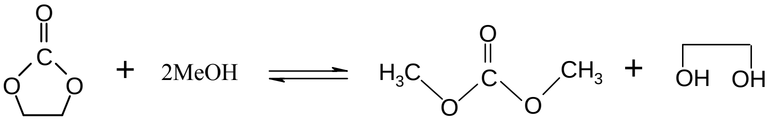
Introduction

Dimethyl carbonate (DMC) is a useful organic compound having versatile chemical reactivities. In many aspects, DMC has various chemical applications such as a solvent for organic synthesis via carbonylation and methylation and a gasoline octane enhancer. Because of the negligible toxicity of DMC, it is promising as a substitute for phosgene, dimethyl sulfate and methyl iodide [1].

DMC has been synthesized by reaction of methanol with phosgene [2]. Recently, a lot of research has been pursued to establish environmentally compatible non-phosgene routes for the production of DMC. So far, a number of DMC synthetic processes have been suggested and some processes have already been industrialized.

For example, the oxidative carbonylation of methanol and the carbonylation of methylnitrite processes have been commercialized in EniChem and Ube, respectively. Besides, vapor phase oxidative carbonylation of methanol, transesterification, urea alcoholysis, esterification of methanol and electrochemical method are being approached for DMC synthetic process development [3,4]. The process for the cosynthesis of DMC and ethylene glycol through the transesterification of ethylene carbonate (EC) with methanol has been developed by Texaco Chemical and carried out as follows [5].



(1)

Reaction (1) is a classic ester exchange reaction, which is subject to the general rules of acid and base catalyst [6]. Knifton *et al.* asserted that a base catalyst is generally more effective in the ester exchange reaction because of their comparable *pK* values. Generally, the soluble base catalysts such as alkali metal alkoxides, carbonates, bicarbonates and phenoxides are effective catalysts. Particularly, sodium and potassium bicarbonate are very effective [7,8].

The methods using those homogeneous catalysts have the advantage that high catalytic activity can be obtained using a small amount of catalyst. However, there is the drawback that separation and recovery of the catalyst from reaction liquid are difficult. Since heterogeneous catalysts can be easily separated from the reaction liquid, the methods using them are free from the above problems involved in the homogeneous catalysts. Thus, Methods using inorganic solid catalysts as heterogeneous catalysts have been proposed [9,10].

Tatsumi *et al.* suggested that TS-1 (titanium silicate molecular sieve) exchanged with an aqueous solution of K_2CO_3 is an excellent solid base catalyst [9]. Also, methods using hydrotalcite-type compounds as heterogeneous catalysts have been proposed [10].

In this work, DMC was synthesized from EC and methanol using a heterogeneous basic catalyst. A series of heterogeneous catalysts were prepared and their activities were evaluated. After intensive studies on the synthesis of DMC by a transesterification between EC and MeOH, we have found that

DMC can be very effectively synthesized by using K/MgO as a solid base catalyst.

Experimental

Four kinds of metal oxides (SiO_2, TiO_2, MgO, γ-Al_2O_3) and activated carbon (AC) which were impregnated with K_2CO_3 aqueous solution were prepared by the conventional incipient wetness method. All the metal oxides solids were dried in an oven at 100°C overnight and calcined in an electric furnace at 550°C for 3 h, whereas AC at 300°C for 3 h.

All the experiments were carried out in a batch-wise liquid phase reaction system (100 ml autoclave). Reaction conditions and procedures are as follows. EC (27.28 g, 0.31 mol), methanol (39.68 g, 1.24 mol) and solid catalyst (1.0 g, 1.5 wt.%) were charged into the reactor. And then, N_2 was introduced into the reactor for refreshing the air remained in the reactor. The mixture was heated up to 80°C and stirred for 2 h. After reaction, the reactor was cooled to room temperature and the reaction products were analyzed using the gas chromatograph (Younglin Model M600D) equipped with a FID detector and a capillary column (HP-1, 30m).

Results and Discussion

MgO has been used as a basic solid catalyst as well as a support in many fields of heterogeneous catalysis reaction. B.M. Bahanage *et al.* reported that MgO as a basic oxide catalyst showed a high activity in a two-step synthesis of DMC from epoxides, carbon dioxide and methanol at 150°C [11]. It is also reported that the basic homogeneous catalysts such as KOH, K_2CO_3, NaOH and LiOH were effective for DMC synthesis from EC and MeOH [6,12]. In terms of the reaction rate, the basicity of catalysts is believed to play an important role for DMC synthesis.

Several other metal oxide catalysts were tested for DMC synthesis from EC and MeOH. Table 1 showed the activities of MgO, SiO_2, TiO_2, silica-alumina and γ-Al_2O_3. Among the catalysts, MgO and γ-Al_2O_3 have shown good activities for reaction (1). Since these catalysts generally have a large number of basic sites, it can be concluded that the basic sites are an active factor for the ester exchange reaction of the EC and MeOH. However, EC conversion and DMC yield were still considerably lower compared with equilibrium values. In order to increase the basicity of solid catalysts, we prepared the solid base catalysts impregnated with K_2CO_3 aqueous solution. Table 2 showed the activities of solid base catalysts for the ester exchange reaction between EC and methanol. K/MgO catalyst showed higher activity than the other solid base catalysts: EC conversion of 52.9% and DMC selectivity of 99.3% were attained after 2 h and very small amount of by-product was formed. A typical basic homogeneous catalyst of K_2CO_3, as compared with K/MgO, has shown EC conversion and DMC selectivity of 55.08% and 98.5%, respectively. The EC conversion of K/MgO was very similar to that of K_2CO_3 and rather showed higher DMC selectivity than that of K_2CO_3.

The amount of potassium in solid base catalysts was determined by Atomic Absorption Spectrophotometer (AAS). As shown in table 2, the presence of potassium in sample catalysts played an important role in the ester exchange reaction. K/MgO displaying the best activity among the sample catalysts includes potassium of 5.12 wt.%. In spite of relatively low content of potassium, the activity of sample catalysts was much more improved than before the K_2CO_3 impregnation. This result indicates that the many ion exchange sites on solid catalysts are occupied by potassium ions, which promotes the activity of solid catalysts. After the reaction, K/MgO was separated by filtration, washed with methanol, dried at 100°C overnight and calcined at 550 °C for 4 h. And then, the reaction was carried out again with the regenerated K/MgO catalysts. As shown in Table 3, K/MgO catalyst treated by both drying and calcining showed higher activity than one treated by only drying. In this case, we obtained EC conversion of 45.7% and DMC yield of 45.1%. K/MgO has not shown a significant difference in activity from fresh K/MgO catalyst, which indicated that K/MgO catalyst can be regenerated. Generally, it is known that the reaction rates of heterogeneous catalysts are much lower than that of homogeneous catalysts due to low surface area. Owing to the drawback of heterogeneous catalysts as mentioned above, it takes much time to reach the equilibrium.

In order to investigate the reaction rates of K/MgO, we observed the activity change of K/MgO catalyst for transesterification reaction with time on stream. As shown in the Fig. 1, EC conversion already reached 51.5% within 1 h and was constantly maintained to the end of reaction and the selectivity of DMC was around 99% through the reaction. This high activity and reaction rate can be explained by the fact that K/MgO dispersed well in the reactant solution and behaved like a homogeneous catalyst such as K_2CO_3 during the reaction.

In the transesterification reaction, the significant improvements in EC conversion and DMC selectivity could be achieved by the solid catalysts impregnated with K_2CO_3 aqueous solution. Among these solid base catalysts, K/MgO was found to be effective for the synthesis of DMC from EC and methanol. EC conversion of 52.9% and DMC yield of 52.5% were obtained at 80°C. These values were very close to those of K_2CO_3 which was well known as efficient homogeneous base catalyst for DMC synthesis. In addition, due to the heterogeneous character of K/MgO, the catalyst could be easily separated from reactants/products and be regenerated efficiently.

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Table 1. Effect of metal oxides support on DMC synthesis

Catalyst	EC conversion (%)	DMC yield (%)
SiO_2	3.54	3.38
TiO_2	4.21	4.10
SiO_2-Al_2O_3	4.86	4.55
MgO	6.25	6.15
γ-Al_2O_3	5.14	4.98

Reaction conditions: EC 27.28 g (0.31 mol), methanol 39.68 g (1.24 mol), 80°C, 2 h, catalyst 1.0 g (1.5 wt.%).

Table 2. Activities of various heterogeneous catalysts for DMC synthesis

Catalyst	K content (wt.%)	EC conversion (%)	DMC selectivity (%)	DMC yield (%)
K/SiO_2	4.25	22.63	99.1	22.43
K/TiO_2	4.21	37.38	99.4	37.16
K/MgO	5.13	52.91	99.3	52.56
K/γ-Al_2O_3	5.14	48.12	99.5	47.89
K/^{a}AC	5.05	35.09	99.4	34.91
$^b K_2CO_3$	-	55.08	98.5	54.26

Reaction conditions: EC 27.28 g (0.31 mol), methanol 39.68 g (1.24 mol), 80°C, 2 h,
catalyst 1.0 g (1.5 wt.%). a. Activated carbon, b. Compared homogeneous catalyst.

Table 3. Synthesis of DMC catalyzed by K/MgO and regenerated K/MgO

Catalyst	EC conversion (%)	DMC selectivity (%)	DMC yield (%)
K/MgO	52.91	99.3	52.56
^{a}Regenerated K/MgO-A	39.55	98.5	38.95
^{b}Regenerated K/MgO-B	45.71	98.7	45.14

Reaction conditions: EC 27.28 g (0.31 mol), methanol 39.68 g (1.24 mol), 80°C, 2 h,
catalyst 1.0 g (1.5 wt.%). a. Treated with only drying, b. Treated with both drying and calcining.

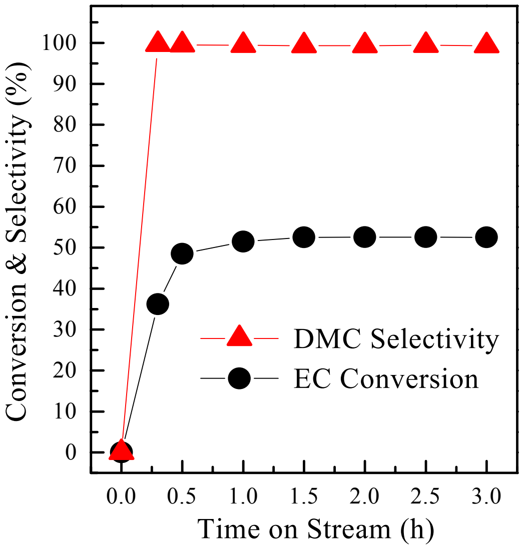

Fig. 1. Activity change of K/MgO catalyst for transesterification reaction.