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A new catalytic transesterification for the synthesis of ethyl methyl carbonate

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A new transesterification for preparing ethyl methyl carbonate from dimethyl carbonate and diethyl carbonate was carried out in the presence of solid basic catalysts both in the liquid and the vapor phase. Among the catalysts examined, MgO is the most active catalyst. Basic properties of the solid catalysts were measured by temperature-programmed desorption of CO_2. The results revealed that the moderately basic sites on the catalysts play a crucial role in catalytic performance.

KEY WORDS: transesterification; ethyl methyl carbonate; magnesium oxide; solid basic catalyst.

1. Introduction

Nonaqueous electrolytes utilized in electrochemical cells possess a variety of desirable qualities [1]. Ethyl methyl carbonate (EMC) as a cosolvent in a nonaqueous electrolyte is able to improve discharge characteristics of the cells such as the energy density, discharge capacity, etc. [2–4]. But its widespread application is limited by the availability and fairly high price of ethyl methyl carbonate.

Various synthesis methods for ethyl methyl carbonate have been developed, such as the esterification of methyl chloroformate with ethanol under base catalysis, and the transesterification of dimethyl carbonate (DMC) with ethanol [5,6]. However, the esterification route is not an environmentally benign process since the highly toxic methyl chloroformate is used. In the second route, the reaction systems contain three binary azeotropes methanol-DMC, ethanol-DMC, and ethanol-EMC among the five components, implying a challenge in the separation [7]. In addition, the yield of the target product, EMC, was fairly low. Therefore, a new approach of transesterification of dimethyl carbonate and diethyl carbonate becomes more attractive to us. Some homogeneous catalysts such as $Ti(OBu)_4$ and Bu_2SnO were found to be efficient catalysts in this type of transesterification reaction from previous study [8], however, there is an obvious disadvantage due to the difficulty of catalyst-product separation. Hong Gan *et al.* [9] have reported the use of two types of heterogeneous catalysts in this reaction, namely, a nucleophilic reagent such as lithium diethylamide and an electron donating reductant such as lithiated carbon. These catalysts were quite expensive, which limited their application.

In general, transesterification reactions are catalyzed by both acids and bases [10]. The purpose of this study is to develop an effective and inexpensive catalyst for the transesterification of dimethyl carbonate and diethyl carbonate to give ethyl methyl carbonate, and to improve the product/catalyst separation. This paper is the first to report the good catalytic performance of a MgO catalyst in this type of transesterification reaction, with either liquid or vapor-phase reactants.

2. Experimental

2.1. Materials

The solid catalysts used for this study were MgO, La_2O_3, ZnO and CeO_2. MgO was prepared by an improved precipitation method from $Mg(NO_3)_2$ and NH_4OH [11]. A solution of NH_4OH (30%, 100 mL) was added dropwise to a solution of $Mg(NO_3)_2 \cdot 6H_2O$ (50 g) in 80 mL of distilled water under stirring at 40 °C. Magnesium hydroxide was precipitated and digested in the mother liquor at 60 °C for 4 h. The precipitate was washed with distilled water, and then calcinated in the oven from room temperature to 500 °C with a heating rate of 4 °C/min and held at 500 °C for 10 h in air.

ZnO was made from zinc carbonate by calcination in air at 400 °C for 5 h. CeO_2 was prepared by decomposition of cerium carbonate at 500 °C for 5 h in air. La_2O_3 was the commercially available reagent. Dimethyl carbonate and diethyl carbonate were purchased from Shanghai Chemical Reagent Company. They were used without further purification. BET surface areas, determined by nitrogen adsorption over OMNISORP(TM) 100CX 1G, of the metal oxides used in this study were

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98, 5, 31 and 40 m^2/g for MgO, La_2O_3, ZnO and CeO_2, respectively.

2.2. Catalytic performance

The surfaces of the metal oxides are covered with carbon dioxide, water and oxygen as they are handled in air. To have basic sites exposed on the surface, pretreatment at high temperature in nitrogen is required [12]. MgO, La_2O_3, ZnO and CeO_2 are calcinated at 600 °C for 2 h in nitrogen before they are used as the catalysts in the transesterification reactions.

A typical procedure for the liquid-phase reaction was as follows: 9.0 g (0.1 mol) of dimethyl carbonate, 11.8 g (0.1 mol) of diethyl carbonate and 0.5 g of the powdered catalyst (40–60 mesh) were charged to a 50-mL three-neck flask. Then the mixture was heated up to 103 °C with stirring under a nitrogen atmosphere. The reaction products were analyzed by a gas chromatography (HP-1102) equipped with an OV-101 capillary column and FID, then identified by GC-MS (HP6890/5973).

The reaction in the vapor phase was carried out in a continuous flow fixed-bed tubular reactor with an inner diameter of 17 mm and a length of 500 mm. The reactor, loaded with 25 g of granular catalyst with a diameter of 3–4 mm, was heated to the required temperature. The mixture of dimethyl carbonate and diethyl carbonate was pumped into the preheating zone and then the reactant vapors flowed into the reactor. The products were collected and analyzed by GC (HP 1102).

2.3. Measurements of catalyst basicity

Basic properties of the metal oxide catalysts were measured by CO_2 temperature-programmed desorption (TPD) [13]. The measurement in the temperature range from room temperature to 800 °C were performed in a conventional flow apparatus with a helium carrier gas at a flow rate of 25 mL/min. After the pretreatment at 600 °C for 2 h, the samples were cooled down to room temperature and saturated with CO_2. Then, the temperature was ramped at a heating rate of 12.9 °C/min. The desorption process was monitored by a temperature-programmed controller (A1-708) and a thermal conductivity detector was used for recording TPD patterns.

3. Results and discussion

3.1. Liquid-phase reaction

The reaction performance of ethyl methyl carbonate synthesis catalyzed by four different solid catalysts is compared in table 1. The results showed that even at 103 °C, no reaction occurred in the absence of catalyst, while in the presence of a metal oxide the conversion of diethyl carbonate and the yield of ethyl methyl carbonate obviously increased. MgO demonstrated superior catalytic activity compared to the other catalysts. Indeed, the catalytic activity of MgO was even better than that of the homogeneous catalyst, $Ti(OBu)_4$. The catalytic activity decreased in the order: MgO > ZnO > La_2O_3 > CeO_2, and it seemed that there was a relationship between the transesterification activity and the surface properties of the catalysts. As proposed in the literature [9] a methoxy anion must exist as an intermediate in the transesterification reaction, reacting with the diethyl carbonate to generate ethyl methyl carbonate. The presence of basic sites on the surface of the catalyst helped to generate methoxy anions. As a result, the yields of ethyl methyl carbonate increased dramatically for a catalyst with relatively high basicity. This will be confirmed by the following experimental results for CO_2 temperature-programmed desorption.

Figure 1 depicts the TPD profiles of CO_2 adsorbed on MgO, La_2O_3, ZnO and CeO_2. It can be seen that the four catalysts demonstrated differing CO_2 desorption behaviors, with the exception of CO_2 desorption peaks at around 100 °C over all four catalysts; this common peak indicates that weakly basic sites existed on all of the solids. A CO_2 desorption peak at 605 °C on La_2O_3 indicates that La_2O_3 possesses strongly basic sites. However, there were no such strongly basic sites over MgO, ZnO and CeO_2. A desorption peak, accompanied by a shoulder peak, was observed at 350 °C for MgO. For ZnO, a desorption peak was seen at 300 °C. These results reveal that moderately basic sites exist on both MgO and ZnO. For CeO_2, however, the only desorption peak was around 100 °C, suggesting weak basic sites only.

As given in table 1, MgO with moderately basic sites is the most active solid catalyst for the transesterification of dimethyl carbonate and diethyl carbonate to give ethyl methyl carbonate, while La_2O_3 with strong basic sites and CeO_2 with weak basic sites both performed

Table 1
Catalytic performance of EMC synthesis using different catalysts in a liquid-phase reaction

Catalyst	None	MgO	La_2O_3	CeO_2	ZnO	$Ti(OBu)_4$
Conversion (%) of DEC	–	44.2	12.6	7.3	26.5	43.1
Yield (%) of EMC	–	44.2	12.6	7.3	26.5	42.8

Note: Reaction conditions: 103 °C, 4 h, DMC : DEC (molar ratio) = 1 : 1.

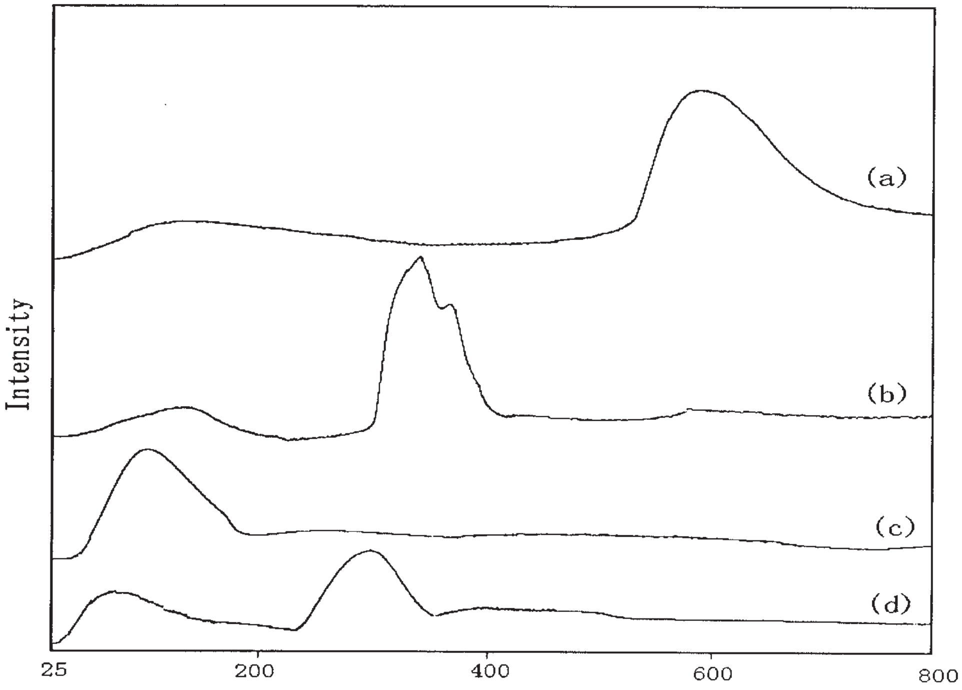


Figure 1. CO_2 TPD spectra for (a) La_2O_3, (b) MgO, (c) CeO_2 and (d) ZnO.

relatively poorly. As described above, ZnO also has moderately basic sites and its activity is higher than that of La_2O_3 and CeO_2. These results imply that the strength of the basic sites of the catalysts is an important property for this transesterification reaction. The lower activity of ZnO than that of MgO would be ascribed to low surface area of ZnO ($31\,m^2/g$) compared to MgO ($98\,m^2/g$). The comparison of the catalytic performances between CeO_2 and ZnO show that even if CeO_2 possesses higher surface area ($40\,m^2/g$), the ZnO having moderately basic sites is more active than CeO_2. Thus, it can be concluded that the moderately basic sites are mainly responsible for the transesterification of dimethyl carbonate and diethyl carbonate to give ethyl methyl carbonate. Meanwhile, the surface areas of the solid basic catalysts show some effects on their activity in this transesterification reaction.

The effects of reaction temperature on the performance of ethyl methyl carbonate synthesis over MgO, La_2O_3, ZnO and CeO_2 were also examined, as shown in figure 2. The yields of ethyl methyl carbonate increased dramatically with increased reaction temperatures from

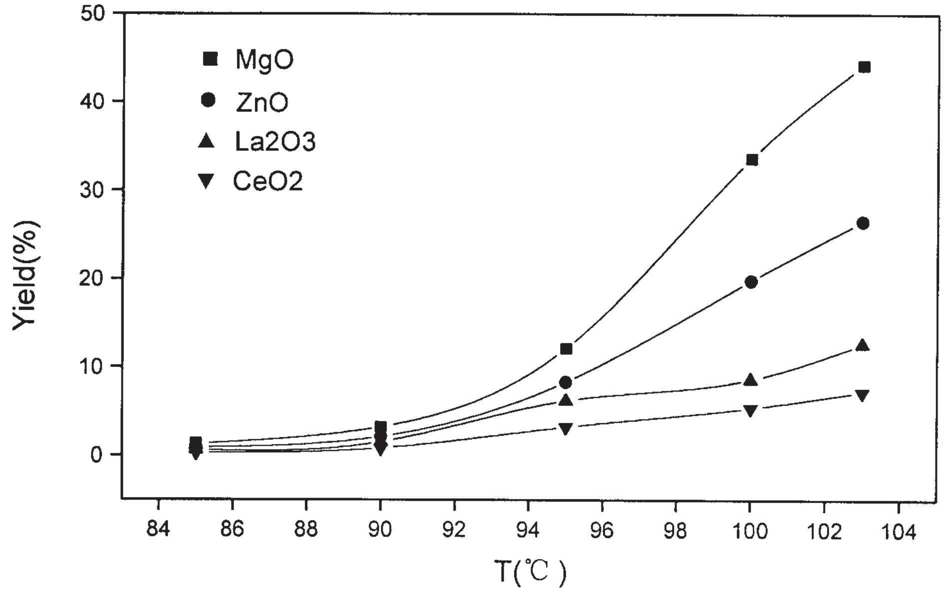


Figure 2. The effect of reaction temperature on EMC synthesis with different catalysts in a liquid-phase process. Reaction conditions: 4 h; DMC : DEC (molar ratio) = 1 : 1.

Table 2
Catalytic performance of EMC synthesis using different catalysts in a vapor-phase reaction

Catalyst	None	MgO	La_2O_3	CeO_2	ZnO
Conversion (%) of DEC	–	44.2	13.4	6.5	30.4
Yield (%) of EMC	–	43.9	12.8	6.3	29.5

Note: Reaction conditions: 160 °C; LHSV: 0.71 h^{-1}; DMC : DEC (molar ratio) = 1 : 1.

85 °C to 103 °C, which is the highest temperature that the reaction system could reach. The highest yield (44.2%) of ethyl methyl carbonate was achieved at 103 °C over a MgO solid catalyst.

Although nearly 100% selectivity of ethyl methyl carbonate was obtained over these solid catalysts, trace amounts of methanol and ethanol were also detected sometimes. It is suggested that the alcohols were produced via reaction of alkoxy anion with traces of water, which is present in dimethyl carbonate or diethyl carbonate as impurity. In addition, it is worthwhile to mention that the solid catalysts were reusable after separating them from the reaction mixture by simple filtration. Their catalytic activities remained almost the same. For instance, a MgO catalyst has been reused four times, with the following yields: 43.9, 43.6, 43.5 and 43.3%.

3.2. Vapor-phase reaction

The catalytic performances of four solid catalysts for the synthesis of ethyl methyl carbonate in the vapor phase are compared in table 2. The results reveal that the catalytic activities of the four catalysts ranked in the same order observed in liquid-phase reaction: MgO > ZnO > La_2O_3 > CeO_2. Therefore, it can be concluded that the moderately basic sites on these catalysts do play a crucial role in the catalytic performance both in the liquid and vapor-phase reactions.

The effects of reaction temperature and LHSV on catalytic performance of MgO for ethyl methyl carbonate formation are presented in figures 3 and 4 respectively. Under optimum conditions (reaction temperature: 160 °C; LHSV: 0.71 h^{-1}), a 44.0% yield of ethyl methyl carbonate is obtained. From figure 3, one can see that the yield of ethyl methyl carbonate at reaction temperature ~100 °C was lower than that at reaction temperature 120 °C. It may be attributed to partial condensation of diethyl carbonate in the tubular reactor. With the reaction temperature increased from 120 °C to 160 °C, the yield of ethyl methyl carbonate increased from 37.6 to 43.9%. The yield of ethyl methyl carbonate decreased when the reaction temperature was raised above 160 °C or the LHSV was less than 0.71 h^{-1}, which was due to the decomposition of dimethyl carbonate and diethyl carbonate over MgO.

The results obtained in this study are fairly significant compared with other reports [5,6,9] for the synthesis of ethyl methyl carbonate. The two new approaches possess obvious advantages: the liquid-phase reaction does not yield side products, and the vapor-phase reaction can operate continuously. We have found that MgO can catalyze this type of transesterification reaction to obtain asymmetric ethyl methyl carbonate.

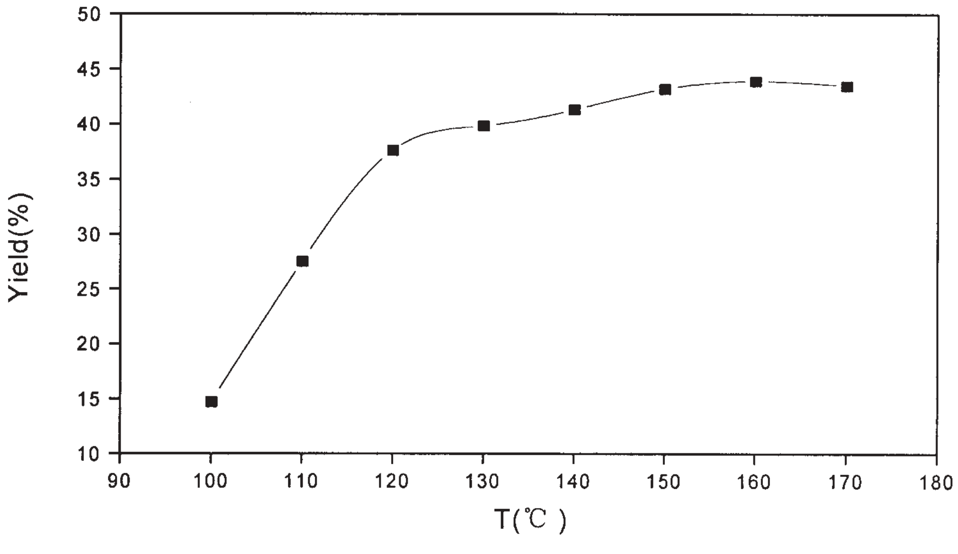


Figure 3. The effect of reaction temperature in EMC synthesis using MgO in a vapor-phase process. Reaction conditions: DMC : DEC (molar ratio) = 1 : 1, LHSV: 0.71 h^{-1}.

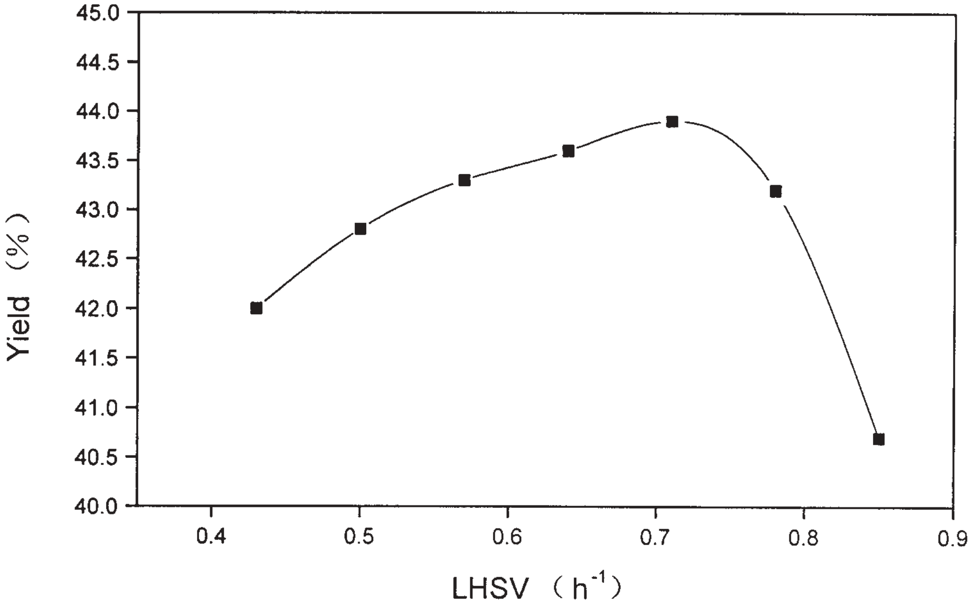
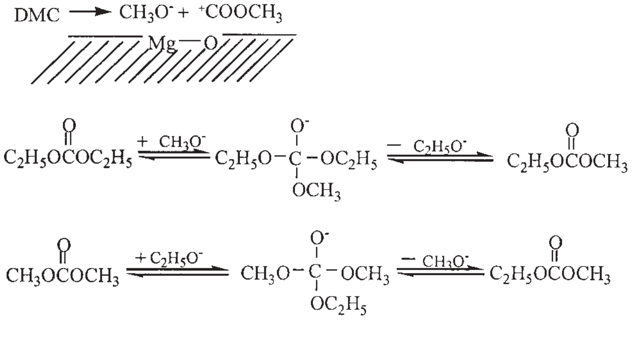


Figure 4. The effect of reaction LHSV in EMC synthesis using MgO in a vapor-phase process. Reaction conditions: 160 °C; DMC : DEC (molar ratio) = 1 : 1.

A possible mechanism for the transesterification reaction between dimethyl carbonate and diethyl carbonate is depicted in scheme 1.



Scheme 1. Possible mechanism of transesterification.

4. Conclusion

Basic metal oxide catalysts can catalyze the transesterification of dimethyl carbonate and diethyl carbonate to give ethyl methyl carbonate efficiently either in a liquid phase or a vapor-phase reaction. Among the catalysts examined, MgO is the most active low cost catalyst. The CO_2 TPD spectra revealed that the moderately basic sites on the catalysts play a crucial role in the catalytic performance. The heterogeneous catalysts could be simply separated from the products of the liquid-phase reaction for reuse.

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