

Synthesis of dimethyl carbonate from methanol, propylene oxide and carbon dioxide over KOH/4A molecular sieve catalyst

Yuan Li^{a,*}, Xin-qiang Zhao^b, Yan-ji Wang^b

^a*School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, PR China*

^b*School of Chemical Engineering and Technology, Hebei University of Technology, Tianjin 300130, PR China*

Received 14 April 2004; received in revised form 10 October 2004; accepted 21 October 2004

Available online 8 December 2004

Abstract

The synthesis of dimethyl carbonate (DMC) from methanol, propylene oxide (PO) and carbon dioxide (CO₂) over supported catalysts was studied for the first time. A series of supported solid base catalysts were prepared by impregnation and their catalytic activities were evaluated. It was found that KOH/4A molecular sieve was the most effective catalyst. The effects of various conditions, such as reaction time, reaction temperature, molar ratio of the reactants and KOH loading, on the yield of DMC was investigated. It was proposed that DMC was formed from the transesterification of propylene carbonate (PC) with methanol, where PC was synthesized from PO and carbon dioxide. Methanol was favorable to such cycloaddition of PO with CO₂. Under the optimized conditions, PO was converted completely and the yield of DMC was up to 16.8%.

© 2004 Elsevier B.V. All rights reserved.

Keywords: Dimethyl carbonate; Propylene oxide; Methanol; Carbon dioxide; Supported catalyst

1. Introduction

In recent years, much attention has been paid to utilization of CO₂. DMC synthesis using CO₂ is one of the promising reactions in the development of environmentally benign processes based on the utilization of naturally abundant carbon resources such as CO₂. DMC is an important raw material in organic synthesis via carbonylation and methylation, as a substitute for highly toxic phosgene and dimethyl sulfate in many chemical processes. DMC can also be used as a solvent in chemical reactions or as a booster in gasoline.

There are three processes commercialized for the large-scale production of DMC: the phosgene–methanol process, the ester exchange process and the oxidative carbonylation of methanol process [1–4].

PC is widely used as the electrolyte component for lithium batteries, polar solvents and chemical intermediates.

Nowadays, the demand of PC is increasing greatly because it can be used to synthesize DMC by the ester exchange reaction with methanol.

As DMC and PC have a wide range of uses in chemical industry, it is very significant to study their synthesis. The cost of DMC will be reduced if a process in which DMC can be formed directly from PO, methanol and CO₂ can be developed successfully. However, there are few reports about this [5,6].

In this research, the synthesis of DMC from PO, methanol and CO₂ was studied. A suitable solid catalyst was developed and its activity was evaluated. The reaction conditions were optimized.

2. Experimental

2.1. Chemical reagents

Methanol, KOH, NaOH, K₂CO₃, KNO₃ were supplied by Tianjin Guangfu Fine Chemical Research Institute. All the

* Corresponding author. Tel.: +86 22 27401674; fax: +86 22 27406590.
E-mail address: wwwlycj@163.com (Y. Li).

chemicals were of analytical grade and were used without further purification. CO₂ (>99.95%) was purchased from Beijing Analytical Instrument Factory. 4A molecular sieve, active Al₂O₃, X zeolite and H β zeolite were purchased from Nankai Gongyun Corporation (Tianjin, China).

2.2. Catalyst preparation

A typical catalyst was prepared by impregnating a support with an aqueous solution of base; this was then dried at 333 K. The calcination of the catalyst was performed at 973 K for 12 h.

2.3. Reaction apparatus and operations

The activity tests of the catalysts were carried out in a stainless autoclave reactor with an inner volume of 250 cm³. A typical procedure was as follows: a certain amount of PO, methanol and catalyst was put into the autoclave, and then CO₂ was introduced into the autoclave with an initial pressure of 3.0 MPa at room temperature. The autoclave was heated up to 453 K with stirring for 6 h reaction. The products were detected by a gas chromatography (GC). The GC column was packed with GDX203. A thermal conduction detector was used and hydrogen was used as the carrier gas.

3. Results and discussion

DMC was formed from the transesterification of methanol with PC, which was synthesized from PO and CO₂. At the same time, PO has a very high activity in chemical reactions and it can react with CO₂ to form PC in the presence of acid or base as a catalyst. Some bases could be used to catalyze the esterification reaction. Therefore, base catalysts should be selected for synthesis of DMC from PO, methanol and CO₂.

3.1. Screening of the catalyst

3.1.1. Activities of several bases supported on 4A molecular sieve

Using four different kinds of base as active species, we prepared the four catalyst samples supported on the 4A molecular sieve and we compared their activities under the same condition (reaction temperature 453 K, catalyst 5 g, base loading of the catalyst 17.5%, volume of PO 58.1 mL, volume of methanol 50 mL, reaction time 6 h and the initial pressure of CO₂ 3 MPa). As PO was converted completely over those catalysts under the conditions mentioned above, the selectivity of PO to DMC was equal to the yield of DMC. The result is illustrated in Fig. 1. Each of the solid bases that we investigated when supported on the 4A molecular sieve had high activity. But KOH/4A molecular sieve catalyst was the most active and selective and the yield of PC and DMC

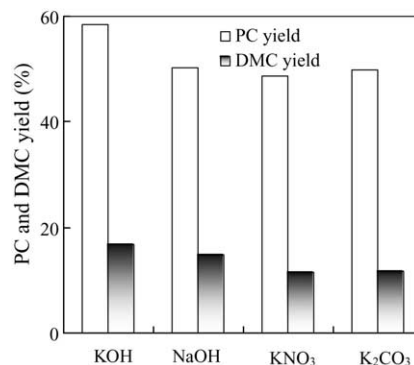


Fig. 1. Activity of different bases supported on 4A molecular sieve. Reaction conditions: temperature 453 K, mass of catalyst 5 g, active content of the catalyst 17.5%, volume of PO 58.1 mL, volume of methanol 50 mL, reaction time 6 h and the initial pressure of CO₂ 3 MPa.

was up to 58.7 and 16.8%, respectively (calculated based on PO). The main by-product of this process was 1,2-propanediol.

3.1.2. Effect of support

The activities of KOH on different supports are illustrated in Fig. 2. The reaction conditions are identical with those for Fig. 1. PO was also converted completely. From this figure, it could be seen that KOH supported on 4A molecular sieve, active Al₂O₃, H β zeolite and X zeolite had high catalytic activity and that KOH/4A molecular sieve catalyst was the most active and selective. The reason that the catalytic activity of KOH supported on 4A molecular sieve was higher than that of KOH on other supports was not very clear.

The following study was based on KOH/4A molecular sieve catalysts.

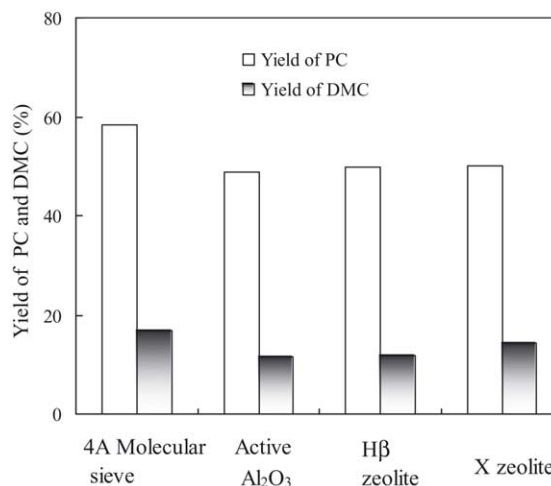


Fig. 2. Activity of KOH on different supports. Reaction conditions: temperature 453 K, mass of catalyst 5 g, active content of the catalyst 17.5%, volume of PO 58.1 mL, volume of methanol 50 mL, reaction time 6 h and the initial pressure of CO₂ 3 MPa.

Table 1
PC and DMC yields in different reaction paths

Raw material	Y_{PC} (%)	Y_{DMC} (%)	S_{DMC}
Methanol, PO, CO	58.7	16.8	16.8
Methanol, CO ₂	–	–	–
PO, methanol	–	–	–
PC (0.8 mol), methanol	–	59.1	90.1

Reaction conditions: catalyst 5 g, volume of PO 58.1 mL, volume of methanol 50 mL, reaction temperature 453 K, reaction time 6 h, initial pressure of CO₂ 3 MPa, Y_{PC} is PC yield, Y_{DMC} is DMC yield, and S_{DMC} is selectivity of PO to DMC.

3.2. Catalytic activities of KOH/4A molecular sieve catalyst on the possible reaction paths in this system

Table 1 shows the activities of KOH/4A molecular sieve catalyst on the possible reaction paths in the system composed of PO, methanol and CO₂. From this table, it can be concluded that DMC was not formed from reaction between methanol and CO₂ or reaction between PO and methanol, but formed from the transesterification of methanol with PC that was synthesized from PO and CO₂.

3.3. Functions of methanol

Table 2 reflects the effect of methanol on the yield of PC from PO and CO₂. The yield of PC from PO and CO₂ increased to 58.7% from 1.63% when a certain amount of methanol was introduced. So we propose that methanol was not only a raw material for synthesis of DMC but also a promoter for synthesis of PC from PO and CO₂ [6].

3.4. Effect of molar ratio of methanol to PO

Fig. 3 presents plots of the selectivity of PC and DMC versus the molar ratio of methanol to PO. The reaction was carried out using 5 g of KOH/4A molecular sieve catalyst at 453 K. The reaction time was 6 h and the initial pressure of CO₂ was 3 MPa. The selectivity of PO to DMC increased with the molar ratio rise of methanol to PO, while the selectivity of PO to PC decreased. The appropriate feed molar ratio of methanol to PO was about 2.5:1.

3.5. Effect of reaction time

Fig. 4 reflects the effect of reaction time on the yield of PC and DMC. From this figure, we can see that the yield of

Table 2
Effect of methanol on yield of PC from PO and CO₂

Raw material	X_{PO} (%)	Y_{PC} (%)	S_{PC} (%)	S_{DMC} (%)
Methanol, PO, CO ₂	100	58.7	58.7	16.8
PO, CO ₂	4.93	1.63	33	–

Reaction conditions: catalyst 5 g, volume of PO 58.1 mL, volume of methanol 50 mL, reaction temperature 453 K, reaction time 6 h, initial pressure of CO₂ 3 MPa, X_{PO} is PO conversion, Y_{PC} is PC yield, S_{PC} is selectivity of PO to PC, and S_{DMC} is selectivity of PO to DMC.

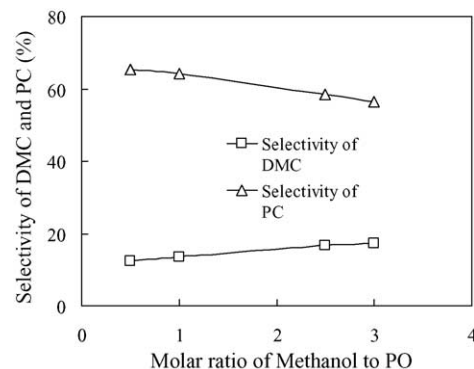


Fig. 3. Effect of the molar ratio of methanol to PO on the selectivity to PC and DMC. Reaction conditions: temperature 453 K, mass of catalyst 5 g, active content of the catalyst 17.5%, reaction time 6 h and the initial pressure of CO₂ 3 MPa.

PC reached the maximum value when the reaction time was about 4 h. The yield of DMC increased with the reaction time, but the change was not significant after about 6 h. The change trend of selectivity of PO to DMC was the same as that of DMC yield.

3.6. Effect of KOH content

The dependence of the catalytic activity on the KOH loading was investigated. Several catalyst samples with different KOH content had been prepared and their activities had been tested under the same conditions as those in Fig. 1. The experimental results are illustrated in Fig. 5, which indicates that the catalytic activity of the KOH/4A molecular sieve catalyst was improved with the increasing of KOH content when the KOH loading was below 17.5%, but when the KOH loading was above 17.5%, the catalytic activity dropped.

3.7. Effect of reaction temperature

To investigate the catalytic activity at different temperatures, we carried out the experiments in the range of 413–

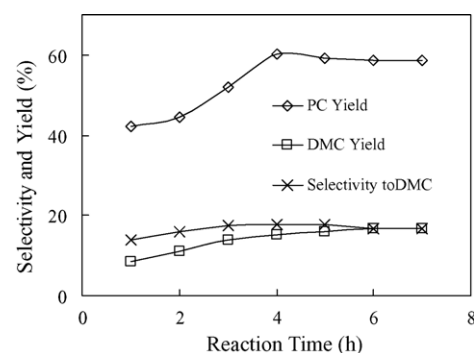


Fig. 4. Effect of reaction time on the reaction results. Reaction conditions: temperature 453 K, mass of catalyst 5 g, active content of the catalyst 17.5%, volume of PO 58.1 mL, volume of methanol 50 mL, and the initial pressure of CO₂ 3 MPa.

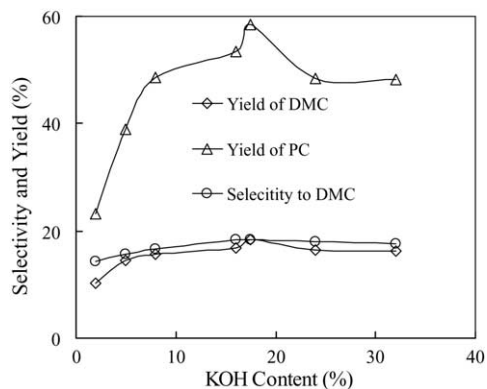


Fig. 5. Effect of KOH loading on the reaction results. Reaction conditions: temperature 453 K, mass of catalyst 5 g, volume of PO 58.1 mL, volume of methanol 50 mL, reaction time 6 h and the initial pressure of CO₂ 3 MPa.

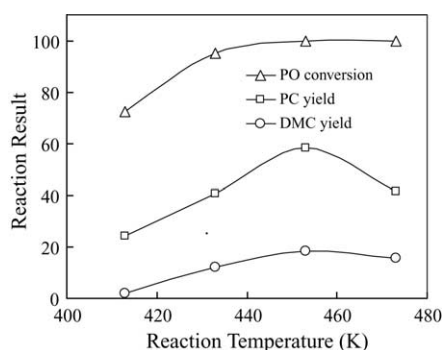


Fig. 6. Influence of temperature on the reaction results. Reaction conditions: mass of catalyst 5 g, volume of PO 58.1 mL, volume of methanol 50 mL, reaction time 6 h and the initial pressure of CO₂ 3 MPa.

453 K. The others conditions besides temperature were the same as those for Fig. 1. The result is shown in Fig. 6. At 413 K, the yields of PC and DMC were very low. With the rise of temperature from 413 to 453 K, the yields of PC and DMC increased gradually and came up to the maxima of 58.7 and 16.8%, respectively, when the temperature was 453 K. When the reaction temperature was higher than 453 K, the yields of PC and DMC dropped because the number of side reactions increased.

3.8. Stability of KOH/4A molecular sieve catalyst

The results of recycling experiments using KOH/4A molecular sieve catalyst are in Fig. 7. The conversion of PO and the selectivity to DMC were still very high after the catalyst had been used several times. PO still could be

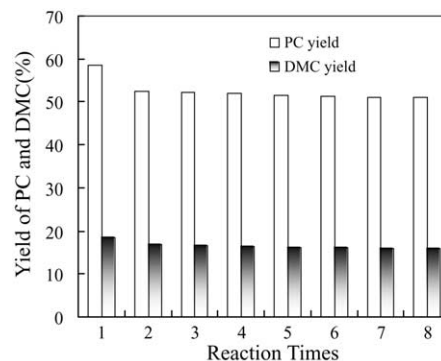


Fig. 7. Stability of the catalyst. Reaction conditions: temperature 453 K, mass of catalyst 5 g, active content of the catalyst 17.5%, volume of PO 58.1 mL, volume of methanol 50 mL, reaction time 6 h and the initial pressure of CO₂ 3 MPa.

converted completely and the changes of PC and DMC yield were not less than 10% after the catalyst had been recycled eight times.

4. Conclusions

KOH/4A molecular sieve was found to be the most effective catalyst for the direct synthesis of DMC from methanol, PO and CO₂. Under the optimized conditions, PO could be converted completely and the yield of DMC could reach 16.8%. It was found that methanol was not only a raw material for synthesis of DMC but also a promoter for synthesis of PC from PO and CO₂. As the catalyst was heterogeneous, it can be recycled easily and efficiently.

Acknowledgments

The authors wish to thank the Natural Science Foundation of Hebei province, People's Republic of China for providing financial support (Grant No. 20020677).

References

- [1] R.X. Jiang, X.Q. Zhao, Y.J. Wang, Appl. Catal. A 238 (2003) 131.
- [2] Y.J. Wang, X.Q. Zhao, B.G. Yuan, Appl. Catal. A 171 (1998) 255.
- [3] K. Nishihara, T. Mitsuzaki, S. Tanaka, Shokubai 37 (1995) 135.
- [4] G. Curnutt, US Patent 4,625,044 (1986), to Dow Chemical Company.
- [5] B.M. Bhanage, S. Fujita, Y. Ikushima, M. Arai, Appl. Catal. A 219 (2001) 259.
- [6] M.J. Green, WO 38,403,701 (1984), to BP Chemical Limited.