ELSEVIER

Catalysis Today 82 (2003) 83–90

CATALYSIS TODAY

www.elsevier.com/locate/cattod

Study on application of membrane reactor in direct synthesis DMC from CO_2 and CH_3OH over Cu–KF/MgSiO catalyst

Chuan-Feng Li, Shun-He Zhong*

State Key Laboratory of C1 Chemistry and Technology, College of Chemical Engineering and Technology,
Tianjin University, Tianjin 300072, PR China

Abstract

Membrane catalytic reactor (MCR) combing catalytic reaction with membrane separating process has exhibited a promising pathway to improve reaction conversion and selectivity for its selective permeating products online or controlling the addition of key reactants. In this work, three types of supported membranes (i.e. silica inorganic membrane, polyimide-silica and polyimide-titania hybrid membranes) and copper catalyst supported on MgO–SiO_2 composite substrate modified by KF were prepared, were used as MCRs materials and catalyst, respectively, for the direct synthesis of dimethyl carbonate (DMC) from carbon dioxide and methanol. The influences of operating conditions on the conversion of methanol and the selectivity to DMC were discussed. The results show that hybrid membranes have excellent thermal and hydrophilic properties and that water vapor diffusing through them obeyed surface flow mechanism. The reaction behaviors of MCR are higher than those of CCR with the conversion of methanol improved remarkably and the selectivity to DMC increase a few under proper reaction conditions. The catalytic reaction performances are controlled mainly by the characters of catalyst, and the incorporation of MCRs has not changed the reaction mechanism, which played the primary roles as the concentration distributors in the catalytic reaction system.

Keywords: Membrane catalytic reactor; Supported membrane; Cu–KF/MgSiO catalyst; Direct synthesis of DMC

1. Introduction

Recently, membrane catalytic reactor (MCR) is becoming a hot area in new catalytic reaction technology for its potential applications to improve the reaction performance and has attracted a considerable research interest [1–5]. It can promote reaction conversion, restrain or avoid side-reactions and increase reaction selectivity by removal of products on time, or controlling the addition of key reactants, or separating intermediate products (object products).

The synthesis and application of dimethyl carbonate (DMC) have been paid more and more attention since late 1970s due to its toxicity and versatile reactivity. As can be used as environment-friendly intermediate and starting material for organic synthesis via carbonylation and methylation replacing poisonous phosgene and dimethyl sulfate [6]. It is also considered an option for meeting the oxygenate specifications on gasoline. Several reaction routes have been known for DMC production so far, for example, phosgene–methanol process, ester exchange process, carbon monoxide–methyl nitrite process and one-step gas-phase oxidative carbonylation of methanol [7].

At present, DMC has been synthesized mainly via oxidative carbonylation of methanol (non-phosgene

---

* Corresponding author. Tel.: +86-22-87893574.
E-mail address: shzhong@public.tpt.tj.cn (S.-H. Zhong).

0920-5861/$ – see front matter © 2003 Elsevier B.V. All rights reserved.
doi:10.1016/S0920-5861(03)00205-0

route) [8]. However, direct synthesis of DMC from CO_2 and methanol is most attractive due to the low-cost of CO_2. Today, more routes and novel catalysts were used to improve the conversion of CO_2 and methanol to DMC, such as supercritical condition [9–11]. The past research or investigations have been shown that the synthesis was not easy, especially for low conversion of methanol. The difficulty was the activation of carbon dioxide for the catalyst [12]. So in the present work, three types of supported membranes and copper catalyst, which modified by KF and supported on $MgO–SiO_2$ composite carrier (Cu–KF/MgSiO) were prepared, respectively, and employed first to promote that reaction performance. The properties of supported membranes and catalyst were characterized by several measurements. In the configurations of CCR and MCR, The effects of reaction condition such as operating temperature, pressure, reactant component, space velocity and N_2 sweep gas velocity on reaction were investigated. Maybe it can provide an effective route for those catalytic reactions with product water.

2. Experimental

2.1. Preparation and characterization of Cu–KF/MgSiO catalyst

The catalyst was synthesized according to the following procedure. $Mg(ClO_4)_2$ was obtained by adding 20 g $Mg_4(OH)_2CO_3$ to watery $HClO_4$ solution, and followed by filtration, then dried in vacuum. Natrium (5 g) was added to 200 ml alcohol and reacted at room temperature, then turned it to silica gel which had been dried at 200 °C for 6 h previously. The products circumfluenced under 75 °C and stirrer magnetically for 24 h, then the solid material was filtered, and followed by washing with alcohol several times. The silica modified by Natrium was obtained after dried under vacuum. Ions exchange method and equation volume impregnating technology were used to prepare $MgO–SiO_2$ composite carrier (i.e. MgSiO) modified by KF. $Cu(NO_3)_2·3H_2O$ solution was poured into a certain quantity of carrier and dried for some time, and the dried sample was followed by calcining at 400 °C for 6 h. It should be deoxidized when used for catalytic reaction.

The catalyst obtained was characterized by BET, XRD, IR and TPR to make clear its area, crystalline structure, absorption and reduction properties. The experiment results were described in more detail elsewhere [13].

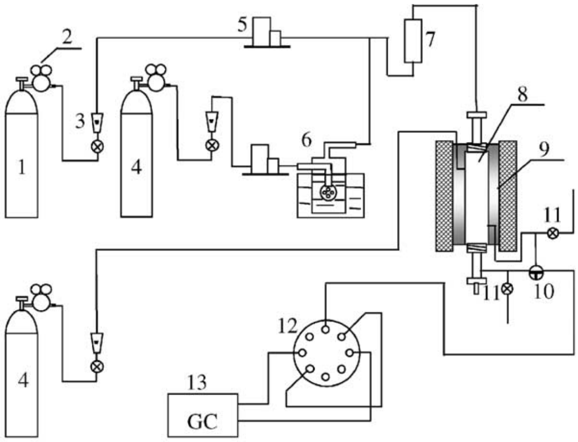
2.2. Preparation and characterization of membrane reactor materials

For studying the effects of different membrane reactors on the direct synthesis by catalyst, three types of membrane reactor materials were prepared and characterized.

Mesoporous silica membrane (marked as S membrane) [14] supported on the TiO_2/K-M ceramic tubes [15] was prepared by the method of combining sol–gel process with template technology. DTAC was used as the template agent and TEOS was used as organic silicon source.

Polyimide-silica hybrid membrane supported on the TiO_2/K-M ceramic tubes (marked as PS membrane) [16] was prepared from PAA and TEOS by combining sol–gel technique with polymerization.

Polyimide-titania hybrid membranes supported on the TiO_2/K-M ceramic tubes (marked as PT membrane) [17] was prepared by prepared from PAA and



1.CO_2 cylinder; 2. Pressure reducer value; 3. Rotor flowmeter; 4. N_2 cylinder; 5. Mass flow controller; 6. Methanol carrier; 7. Buffer; 8. Membrane reactor; 9. Heater; 10. Three-way valve; 11.Cut-off valve; 12. Electric eight-way valve; 13. Gas chromatography

Fig. 1. Schematic diagram of membrane catalytic reaction.

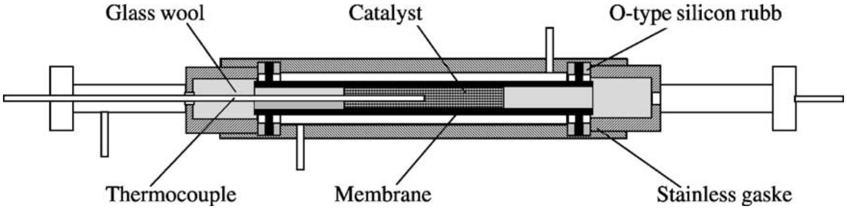


Fig. 2. Principle of the MCR module.

Ti(*iso*-opr)$_4$ by combining sol–gel technique with polymerization.

The three supported membranes were characterized by XRD, TGA-DTA, IR, nitrogen adsorption and gas permeability measurement. The experiment results were described in more detail, respectively, in Refs. [14,16,17].

2.3. CCR and MCR experiments

The reaction performance of conversional catalytic reaction (CCR) was tested on MRS-901 micro-reactor and the products obtained were analyzed by online gas chromatography (GC) with a thermal conductivity detector. Carbon dioxide and nitrogen gases were each passed through their dividual mass flow meter and controller. TDX-01 packed column was used for N_2, CO and CO_2 analysis and PEG-20000 column for organic compounds analysis. Nitrogen gas was used as GC flow gas.

The performance of membrane catalytic reactor (MCR) was measured on the flow chart showed in Fig. 1 with a shell-and-tube reactor configuration in the proportions of 1:10 shown in Fig. 2. Nitrogen gas had to pass through a methanol bubbler in order to bring a certain flow of methanol into the reactor. The gaps between membrane tube and stainless shell were air-proofed by O-type silicon rubber. The glass wool were used to tamp catalysts to prevent their loss.

3. Results and discussions

3.1. The performance of catalyst

The characteristic results of catalyst showed that the BET area (334 m^2/g) of supported catalyst was lower a little than that of silica carrier (350 m^2/g). The bridge-oxide of Mg–O–Si was replaced by F of KF promoter and therefore modified its sorption. XRD pattern showed the copper dispersed well in silica for there were no phenomena of conglomeration. The IR spectra indicated that there were three activation centers, i.e. metallic site, Lewis acidic site and Lewis basic site. The reduction temperature of CuO/MgSiO was 300 °C, and the incorporation of KF promoter could reduce that effectively, it is 285 °C with 5 wt.% KF, 274 °C with 10 wt.% KF and 266 °C with 15 wt.% KF. There had been formed novel adsorption states of linear, shearing and horizontal types of carbon dioxide (shown in Fig. 3), as well as molecular and dissociative types of methanol (shown in Fig. 4) when they adsorbed on the surface of catalyst.

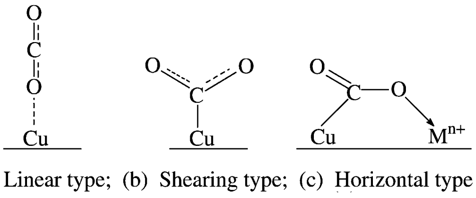


Fig. 3. CO_2 adsorption state on the surface of catalyst.

According to the former investigations [17] this study of CCR was emphasized on the effect parameters of temperature in the range of 80–140 °C pressure of atmosphere to 1.2 MPa, space

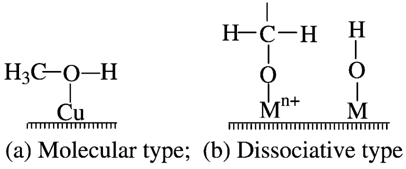


Fig. 4. CH_3OH adsorption states on the surface of catalyst.

Table 1
Effect of operating conditions on CCR

Conditions	X_{CH_3OH} (%)	S_{DMC} (%)	S_{HCHO} (%)	S_{CO} (%)
Different T (°C); P: 0.1 MPa; SV: 1040 h^{-1}; $n_{CH_3OH}/n_{CO_2} = 1.5/1$				
80	2.84	88.94	5.53	5.53
100	3.45	88.39	5.81	5.81
120	4.07	87.60	6.20	6.20
140	4.83	86.28	6.86	6.86
Different P (MPa); SV: 1040 h^{-1}; T: 130 (°C); $n_{CH_3OH}/n_{CO_2} = 1.5/1$				
0.1	4.46	87.17	6.42	6.42
0.2	4.76	87.82	6.09	6.09
0.6	5.08	88.35	5.83	5.83
1.0	5.31	88.86	5.57	5.57
1.2	5.40	89.02	5.49	5.49
Different SV (h^{-1}); P: 1.0 MPa; T: 130 °C; $n_{CH_3OH}/n_{CO_2} = 1.5/1$				
520	5.17	86.82	6.59	6.59
1040	5.31	88.86	5.57	5.57
1480	5.38	89.27	5.37	5.37
2040	5.23	89.81	5.10	5.10
Different n_{CH_3OH}/n_{CO_2}; P: 1.0 MPa; T: 130 °C; SV: 1040 h^{-1}				
1.5/1	5.31	88.40	5.80	5.80
2.0/1	5.38	89.27	5.37	5.37
2.5/1	5.11	89.42	5.29	5.29
3.0/1	4.59	89.53	5.24	5.24

velocity of 500–2040 h^{-1}, and feed gas components (CH_3OH/CO_2, molar ratios) of 0.5–3.0. The results are shown in Table 1.

In CCR, the main reaction products of CO_2 reacting with methanol over this catalyst employed in the present work are DMC and H_2O, and there are a few by-products of CO and HCHO. The two reactions are listed as follows:

$$\text{Primary reaction}: \quad CO_2 + 2CH_3OH \rightarrow DMC + H_2O \tag{1}$$

$$\text{Side-reaction}: \quad CO_2 + CH_3OH \rightarrow HCHO + CO + H_2O \tag{2}$$

From the thermodynamics data, the active energy of side-reaction is higher than that of primary one, therefore with the increasing of reaction temperature, the conversion of methanol (X_{CH_3OH}) increased obviously, whereas the selectivity to DMC (S_{DMC}) decreased at the same time. High reaction pressure benefited to the reaction for its molecular-decreasing reaction. Space velocity influenced reaction performance by controlling residence time, which promoted the S_{DMC} obviously with X_{CH_3OH} increased first and decreased later. The feed gas components affected reactions primarily by the active sites on catalyst. The past researches all considered the activation of carbon dioxide as the key step for the direct synthesized. There existed complete absorption of CO_2 with methanol on the surface of catalyst. The experiment result showed it could get optimal reaction performance with the stoichiometry.

3.2. The performance of membrane reactor materials

The characteristic results of three membranes obtained by experiments indicated that their surface morphologies are well. The S membrane has both crystalline phase and amorphous phase with average pore size of 4.2 nm. The inorganic particles in PS and PT hybrid membranes are finely dispersed in polymers and the phase separation phenomena can be observed. In PS membrane, there are bond-linking between minerals and polymer phases, its glass transition temperature (T_g) was 417 °C. In PT membrane, novel type structures of organic phase contained inorganic phase are formed, which the bond-conjuncts are in the manner of oxygen in O–Ti–O bond of titania linked with azote in imide and oxygen in carboxyl of polyimide. Its discompose temperature is 492 °C and the thermal stability are better than polyimide materials under the temperature of 450 °C.

The gas permeability results are shown in Tables 2 and 3, It can been seen that gas permeance in S membrane are by Knudsen diffusion, which means that the inorganic membrane has certain ability for separating mixture gas, whereas that on PS and PT hybrid membrane are complicated in some degree: non-condense

Table 2
The permeabilities of three membranes

	P ($\times 10^{-7}$ mol m^{-2} s^{-1} Pa^{-1})				
	N_2	CO_2	CO	H_2O	CH_4
S	73.9	67.4	74.4	104	92.2
PS	0.556	12.90	0.582	15.62	0.926
PT	4.48	83.64	5.73	45.25	17.34

Table 3
The permeselectivity of three membranes

	Separation factors			
	H_2O/N_2	H_2O/CH_4	H_2O/CO_2	H_2O/CO
S	1.41	1.13	1.54	1.4
PS	28.09	16.87	1.21	26.84
PT	10.1	2.61	0.54	7.98

gases, such as N_2, CO and CH_4, across through those membranes obeyed Knudsen diffusion, and that condensable ones, for example, water vapor and carbon dioxide, through those membranes followed surface flow. Both hybrid membranes can potentially be applied in the processes of removal of water or humidity and membrane catalytic reaction with reactant or product of water.

3.3. Performances of the MCRs

Based on the results and performances of CCR above investigated, here five groups were selected of experiments to get their optimal operating conditions.

The first group (in Fig. 5(a)) of experiments was designed to investigate the influence of temperature on reactor performance at constant pressure of 0.4 MPa, space velocity of 1480 h^{-1}, feed gas component (CH_3OH/CO_2, molar ratios) of 2 and N_2 sweep space velocity of 90 cm^3 (STP)/min.

The second group (in Fig. 5(b)) of experiments showed the influence of operating pressure with temperature 130 °C, reactants space velocity 1480 h^{-1}, feed gas component 2 and N_2 sweep space velocity 90 cm^3 (STP)/min.

The third group (in Fig. 5(c)) of experiments showed the influence of space velocity with the constant conditions of temperature 130 °C, pressure 0.4 MPa, feed gas component 2 and N_2 sweep space velocity 90 cm^3 (STP)/min.

The fourth set (in Fig. 5(d)) of data showed the effect of feed gas components on reaction result at constant of temperature of 130 °C, pressure of 0.4 MPa, space velocity of 1480 h^{-1}, feed gas component of 2 and N_2 sweep space velocity of 90 cm^3 (STP)/min.

And the last series (in Fig. 5(e)) of work exhibited the influence of N_2 sweep space velocity on reaction performance with the constant conditions of temperature 130 °C, pressure 0.4 MPa, space velocity of 1480 h^{-1} and feed gas component 2.

The reaction results indicated clearly that the incorporation of three types of MCRs have not changed the catalytic reaction process and they worked only as adjusters to control the concentrations of the species in the reaction system. The reaction performances are controlled primarily by the catalytic performance of catalyst. X_{CH_3OH} and S_{DMC} are improved by removing the product of water out of reactor online by the means of hydrophile membranes. So all the factors affected the permeance and permeselectivity of membranes could modify directly the reaction results with different degrees. The operating temperature might improve the adsorption capacity of hybrid membrane materials and influenced little on mesoporous silica membrane. Higher pressure and sweep space velocity could increase the permeate pressure differences between the inner and outside of membrane reactors. But there are many problems that restricted its benefits. First the increasing of operating pressure was limited by air-proof conditions. In this work, silicon rubber was used as air-proof for its excellent heat-resistant, but it could only endure near 0.5 MPa. Secondly, with elevated sweep gas velocity, X_{CH_3OH} and S_{DMC} were inclined to constants, and it would increase the system burden or operating cost when elevated continuously.

The results also showed that the reasonable feed gas components are all higher than 2, which can be explained by the adjust roles for reactants of separate membranes. There are some difference in permeance of methanol and carbon dioxide on membranes and methanol is higher than that of carbon dioxide since methanol can be dissolved in water condensed by membranes.

The different properties of three membranes affected the results differently, especially for their permeating product water. The reaction results of PS and PT MCRs are all higher than those of S one for there were a great deal of organic groups such as carbonyl, amidocyanogen and a little carboxyl in hybrid membrane materials, which were favored to absorb and permeate water. However, those groups were also the ones to permeate methanol and carbon dioxide. Carbon dioxide is a polar molecule to be adsorbed by the dipole–dipole interaction with those groups of the polyimide. So it can be imaged that some feed gas will

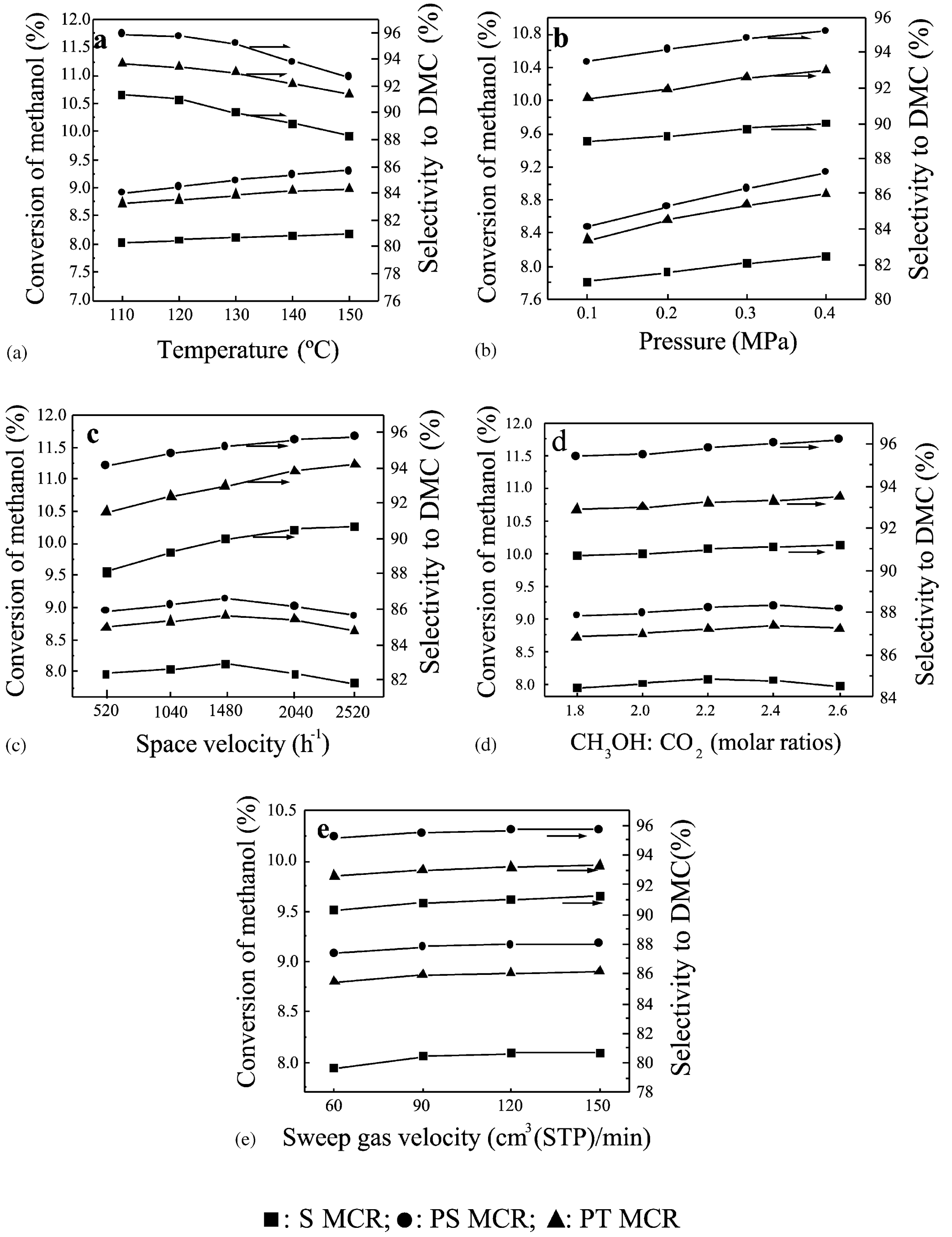


Fig. 5. The effect of reaction conditions on conversion of methanol over MCR.

Table 4
Comparison of reaction results with MCR and CCR[a]

Configurations	Optimal reaction conditions			Results	
	Temperature (°C)	Pressure (MPa)	$CH_3OH:CO_2$ (molar ratios)	X_{CH_3OH} (%)	S_{DMC} (%)
CCR	130	1.0	2.0	6.55	90
S MCR	120	0.4	2.2	8.1	91.4
PS MCR	130	0.4	2.4	9.2	96.0
PT MCR	130	0.4	2.4	8.9	93.3

[a] Space velocity is $1480\,h^{-1}$ and N_2 sweep space velocity is $90\,cm^3$ (STP)/min.

be diffused out of catalytic reaction regions, which led directly to a little loss of reactants. From this point, the practice results should be higher than those obtained and calculated by dividing between products and reactants. If the react conditions selected properly, it can be considered to use circular of carbon dioxide with certain methanol as sweep gas with dry tube or cold trap in the outer of membrane reactor penetrate side, which can prevent the reactants permeating and increase their utilization.

3.4. Comparison of MCR and CCR

With the three type MCRs, the conversions of methanol for S, PS, PT membrane catalytic reactors had increased 1.54, 2.65 and 2.25% with selectivity to DMC of 1.4, 6 and 3.3%, respectively (Table 4). So it can be considered that the introductions of MCRs are able to improve catalytic reaction performances, even the results were not ideal.

4. Conclusions

In this work, three types of supported membranes and copper catalyst supported on $MgO–SiO_2$ composite carrier modified by KF were prepared successfully, and their applications for the direct synthesis of DMC from carbon dioxide and methanol were studied first by membrane catalytic reactor. The influences of operating conditions, such as temperature, pressure, space velocity, feed gas components and N_2 sweep space velocity on the conversion of methanol and the selectivity to DMC were discussed. Those can provide an effective pathway or basic data for further research of direct synthesis of DMC.

Water vapor permeance in hybrid membrane catalytic reactors is loyal to surface flow, and in mesoporous silica one obeyed Knudsen diffusion. They are the excellent MCR materials to the removal of product water in the catalytic reaction procedure. The adsorptions of reactants, i.e. methanol and carbon dioxide on catalyst surface are the competitive ones.

Under proper reaction conditions, the reaction results of MCR are all higher on three type membrane reactors than those of CCR with the conversion of methanol improved remarkably and the selectivity to DMC increased a little. As a result, it cannot be satisfied because of membrane reactors permeating reactants as well. Maybe it is effective to enhance more by using circular of carbon dioxide with certain methanol as sweep gas with dry tube or cold trap in the outer of membrane reactor penetrate side in a proper steady operating conditions.

Acknowledgements

The authors would like to thank for the financial supports by the National Science Foundation of China under the number 20076035.

References

[1] J. Zaman, A. Chakma, J. Membrane Sci. 92 (1994) 1.
[2] H.P. Hsieh, Catal. Rev.-Sci. Eng. 33 (1–2) (1991) 1.
[3] A. Julbe, C. Guizard, et al., Membrane Sci. 77 (1993) 137.
[4] G. Saracco, V. Speccia, Catal. Rev.-Sci. Eng. 36 (1994) 305.
[5] J.N. Armor, J. Membr. Sci. 147 (1998) 217.
[6] Y. Ono, Appl. Catal. 155 (1997) 133.

[7] Process Economics Program, PEP Review 91-1-2, Dimethyl carbonate by vapor-phase oxidative carbonylation, SRI Int., 1992.
[8] Z. Li, K. Xie, C.T. Robert Slade, Appl. Catal. A 205 (2001) 85.
[9] S.N. Fang, K. Fujimoto, Appl. Catal. A 142 (1996) L1.
[10] S.T. King, J. Catal. 161 (1996) 530.
[11] T. Zhao, Y. Han, Y. Sun, Fuel Process. Technol. 62 (2000) 187.
[12] S.H. Zhong, J.W. Wang, X.F. Xiao, Stud. Surf. Sci. Catal. 130 (2000) 1565.
[13] S.H. Zhong, L.L. Kong, Z. Lei, X.F. Xiao, J. Mol. Catal. (China) 16 (6) (2002) 454.
[14] C.F. Li, S.H. Zhong, Q. Li, J. Chin. Ceram. Soc. 30 (3) (2002) 354.
[15] C.F. Li, S.H. Zhong, Bull. Chin. Ceramsoc. 31 (2) (2002) 23–26.
[16] S.H. Zhong, C.F. Li, X.F. Xiao, J. Membrane Sci. 199 (1–2) (2002) 53.
[17] C.F. Li, S.H. Zhong, Acta Polym. Sin. (3) (2002) 317.