Vapor phase dehydrogenation of methanol to methyl formate in the catalytic membrane reactor with Cu/SiO$_2$/ ceramic composite membrane

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The Cu/SiO$_2$/ceramic composite membrane was prepared on the SiO$_2$/ceramic mesoporous membrane by an ion exchange method, and vapor phase dehydrogenation of methanol to methyl formate in the catalytic membrane reactor was investigated. It showed much better performance in the catalytic membrane reactor than that in the fixed-bed reactor under the same reaction conditions. At 240 °C, 57.3% conversion of methanol and 50.0% yield of methyl formate were achieved in the catalytic membrane reactor and only 43.1% conversion of methanol and 36.9% yield of methyl formate were achieved in the fixed-bed reactor.

KEY WORDS: catalytic membrane reactor; Cu/SiO$_2$/ceramic composite membrane; methanol, methyl formate; vapor phase dehydrogenation.

1. Introduction

Methyl formate has been considered as one of the building block molecules in C$_1$ chemistry [1], which is an important and versatile chemical intermediate to be used for the production of a wide range of chemicals including formic acid and higher carboxylic acids such as acetic acid, propionic acid and their esters, cyanhydric acid, formamide, dimethyl formamide, and so on. Maybe methyl formate can be used as a gasoline octane enhancer instead of methyl t-butyl ether (MTBE), which means to have a large potential market of methyl formate.

Methyl formate can be prepared by many processes [1]: dehydrogenation of methanol, carbonylation of methanol, oxidative dehydrogenation of methanol, dimerization of formaldehyde, direct synthesis from CO and H$_2$, and hydrocondensation of carbon dioxide with methanol. Among these aforementioned processes, vapor phase dehydrogenation of methanol is a commercially attractive process, and has many advantages such as simpler process, easier operation, less investment, feedstock of methanol to be readily available, byproduct hydrogen be a very useful raw material and clean fuel, and so on.

The copper-based catalysts, such as Cu–Si [2–6], Cu–Ti and Cu–Zr [3,7], Cu–La, Cu–Y and Cu–Ce [7], Cu–Cr [6,8], Cu–Al [9], Cu–Cement [10], Cu–Zn–Si [6], Cu–Zn–Cr [11], Cu–Zn–Al [12], Cu–Zr–Zn and Cu–Zr–Zn–Al [13], Cu–Cr–Na [14], Cu–La–Mn and Cu–La–Ti [15], Cu–Zn–Al–Na [16], Cu–Si–Mg–Ba–Cr–Zn [17], behave very high activity and selectivity for the dehydrogenation of methanol to methyl formate. The uniqueness of copper may be associated with its ability for sequential hydrogen removal from methanol and other oxygen-containing fragments stopping just before carbon monoxide formation [15]. However, due to thermodynamic equilibrium limitation, the conversion of methanol in the dehydrogenation of methanol to methyl formate attains usually several tens percent only.

In the catalytic membrane reactor [18,19], the pores of a catylic memebrane show two ways corresponding to the two sides of the membrane wall, however a conventional catalyst presents only one way to enter and get out of the catalyst pores. Therefore, the high surface area of the membrane top layers supporting the active components is available to maximize the interfacial contact between the reactant gas and solid catalyst active sites, which may have better performance than the conventional catalyst or catalytic process. If the dehydrogenation reaction is operated in the membrane reactor, the continuous and selective removal of product hydrogen from the reaction zone by a permselective membrane will shift the equilibrium towards the product side, and overcome a thermodynamic limitation in the conventional fixed-bed reactor [20]. The catalytic membrane reactor is expected to attain higher conversion at lower temperatures, and then conceivably avoid the deactivation of catalyst and undesirable side reations.

In this paper, the Cu/SiO$_2$/ceramic composite membrane was prepared by ion exchange method, and vapor phase dehydrogenation of methanol to methyl formate in the catalytic membrane reactor was investigated, which have not yet been reported.

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2. Experimental

2.1. Membrane preparation

A porous ceramic membrane tube (Φ12 mm × 250 mm × 1.5 mm, the average pore size is ca. 1 μm, Shandong Research Institute of Industrial Ceramic) was used as a support tube. SiO_2 mesoporous membrane was coated on the outer surface of the support tube by sol–gel method [21], in which SiO_2 existed in an amorphous phase and the average pore size of the top SiO_2 layer was ca. 4 nm.

The Cu/SiO_2/ceramic composite membrane was prepared by ion exchange method. The SiO_2/ceramic mesoporous membrane was dipped in an excess amount of the $Cu(NH_3)_4(NO_3)_2$ aqueous solution at 25°C for 24 h, and its pH value was adjusted to 12 by aqueous NH_3. After cleaned in the distilled water by ultrasonic treatment, this membrane was dried at 110 °C overnight, and then heated programmedly to 500 °C at 1.5 °C/min in air and kept for 2 h. The composite membrane prepared should be activated in hydrogen flow at 300 °C for 2 h before use.

2.2. Catalytic membrane reactor [20]

The catalytic membrane reactor (CMR) was a double-tubular type consisting of a stainless-steel tube(l6 mm ID) and a catalytic membrane tube as the outer and inner tube, respectively. In order to attain an isothermal memebrane zone, only 4 cm length Cu/SiO_2/ceramic composite membrane was prepared in the middle part of the support tube, and its other part was sealed with a commercial ceramic glaze. The membrane tube was installed concentrically in the reactor with graphite O-rings and compression fittings at both ends.

2.3. Methanol dehydrogenation

Vapor phase dehydrogenation of methanol was carried out in the catalytic membrane reactor at atmospheric pressure. The mixture gas of methanol and nitrogen by bubbling nitrogen stream (60 cm^3 min^{-1}) through the methanol saturation apparatus at 30 °C, flowed in the shell side of the membrane reactor, and the purge gas of argon flowed cocurrently in the tube side. The flow rates of effluents from the shell side and tube side were measured by a soap-film flow meter, and their compositions were analyzed by an on-line gas chromatograph (PE Autosystem XL).

Permeability experiment was similar to the above, β(permeation ratio) was defined as the ratio of the amount of one gas permeating through the membrane to the total amount of this gas in feed gas, such as H_2/N_2 or CH_3OH/N_2 mixtures.

The comparative experiment in the conventional fixed-bed reactor (FBR) was carried out using a nonporous stainless-steel (l2 mm OD) tube instead of Cu/SiO_2/ceramic composite membrane, in which the the grains (0.45–0.90 mm) of the crushed composite membrane as a catalyst were packed in the shell side.

Table 1
Permeability of Cu/SiO_2/ceramic composite membrane

Membrane	β_{H_2} (%)	β_{CH_3OH}(%)	β_{N_2} (%)
SiO_2/ceramic	24.7	18.7	0
Cu/SiO_2/ceramic	24.3	18.6	0

(Flow rate feed gas 100 cm^3 min^{-1}, flow rate of purge gas 30 cm^3 min^{-1}, 200 °C, at atmospheric pressure).

3. Results and discussion

3.1. Permeability of Cu/SiO_2/ceramic membrane

Table 1 shows the permeability of the Cu/SiO_2/ceramic composite membrane for hydrogen, methanol and nitrogen.

There is little difference on the permeabilities between the Cu/SiO_2/ceramic composite membrane and the SiO_2/ceramic mesoporous membrane. Hydrogen and methanol could permeate through the membranes, but nitrogen was not detected in the tube side of the membrane reactor.

3.2. Effects of preparation parameters on performance of Cu/SiO_2/ceramic membrane

In order to investigate conveniently vapor phase dehydrogenation of methanol to methyl formate (MeF) in the catalytic membrane reactor, no purge gas was used and the selectivity to methyl formate (or conversion of methanol) was calculated only by the data in the reaction side and not including the amount of methyl formate (or methanol) through the composite membrane. X_{CH_3OH}, S_{MeF} and Y_{MeF} denote the conversion of methanol, selectivity to methyl formate and yield of methyl formate, respectively. They are calculated as follows:

$$X_{CH_3OH} = \frac{F^0_{CH_3OH} - F^t_{CH_3OH} - F^s_{CH_3OH}}{F^0_{CH_3OH}} \times 100\%$$

$$= \frac{F^0_{CH_3OH}(1 - \beta_{CH_3OH}) - F^s_{CH_3OH}}{F^0_{CH_3OH}} \times 100\%$$

$$S_{MeF} = \frac{2(F^s_{MeF} + F^t_{MeF})}{F^0_{CH_3OH} - F^t_{CH_3OH} - F^s_{CH_3OH}} \times 100\%$$

$$= \frac{2F^s_{MeF}}{F^0_{CH_3OH} X_{CH_3OH}(1 - \beta_{MeF})} \times 100\%$$

F is the molar flow rate (mol s^{-1}), β is the permeation ratio; F^0 is the initial flow rate, F^t or F^s is the flow rate in the tube side or in the shell side.

3.2.1. Effect of concentration of $Cu(NH_3)_4(NO_3)_2$ solution

As seen from figure 1, when the membrane was prepared with 0.3–0.5 mol L^{-1} $Cu(NH_3)_4(NO_3)_2$

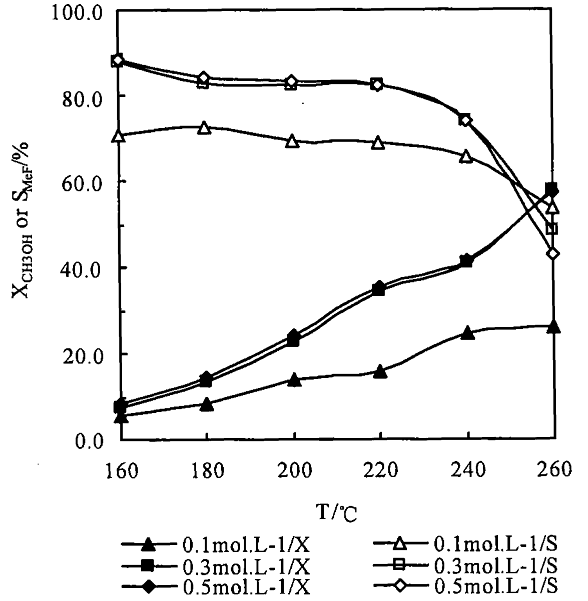

Figure 1. Dehydrogenation of methanol in CMR versus the concentration of $Cu(NH_3)_4(NO_3)_2$ solution (Flow rate of feed gas 60 cm^3 min^{-1}, no purge gas, at atmospheric pressure).

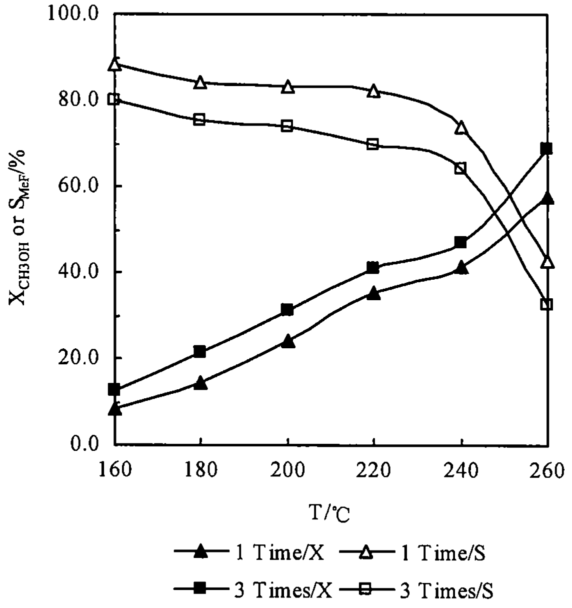

Figure 2. Dehydrogenation of methanol in CMR versus the ion-exchange times of 0.5 mol L^{-1} $Cu(NH_3)_4(NO_3)_2$ solution (Flow rate of feed gas 60 cm^3 min^{-1}, no purge gas, at atmospheric pressure).

solution, higher conversion of methanol and higher selectivity to methyl formate were achieved in the catalytic membrane reaction; when 0.1 mol L^{-1} $Cu(NH_3)_4(NO_3)_2$ solution was used to prepare the membrane, the conversion of methanol and selectivity to methyl formate were much lower.

3.2.2. *Effect of ion-exchange times of $Cu(NH_3)_4(NO_3)_2$ solution*

Figure 2 shows the effect of ion-exchange times of 0.5 mol L^{-1} $Cu(NH_3)_4(NO_3)_2$ solution on the performance of the catalytic membrane reactor. Using the catalytic membrane reactor of the SiO_2/ceramic mesoporous membrane ion-exchanged by 0.5 mol L^{-1} $Cu(NH_3)_4(NO_3)_2$ solution for one time, slightly lower conversion of methanol and much higher selectivity to methyl formate were achieved than that in the CMR of the membrane ion-exchanged for three times. In the membrane prepared by the ion exchange method, copper was dispersed highly on the SiO_2/ceramic mesoporous membrane by some interactions between the silanol groups on surface and $Cu(NH_3)_4^{2+}$ cations. When the amount of $Cu(NH_3)_4^{2+}$cations was far beyond that of surface silanol groups, the $Cu(NH_3)_4^{2+}$cations would absorb on the surface of the mesoporous membrane and thus reduced the dispersion degree of copper, which slightly increased the conversion of methanol and significantly decreased the selectivity to methyl formate.

3.2.3. *Effect of calcination atmosphere*

As seen from figure 3, when the Cu/SiO_2/ceramic composite membrane was calcined in air, the similar conversion of methanol and much higher selectivity to methyl formate were achieved than that using the CMR of the membrane calcined in nitrogen. It shows that air is more available atmosphere of calcining the Cu/SiO_2/ceramic composite membrane than nitrogen, but the reason should be studied further.

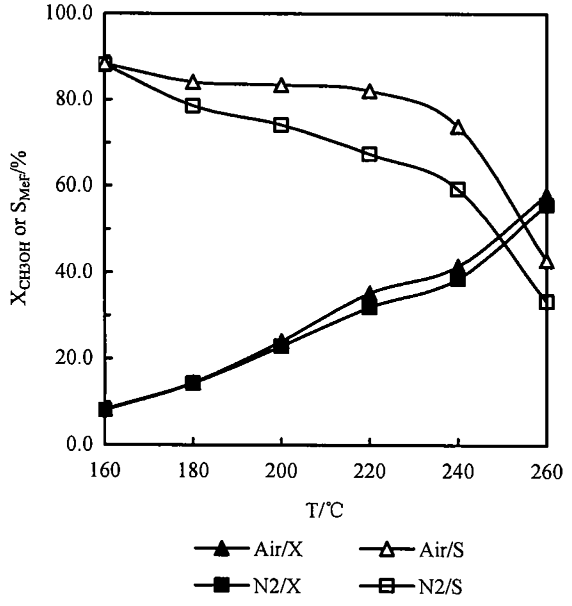

Figure 3. Dehydrogenation of methanol in CMR versus the calcination atmosphere of the Cu/SiO_2/ceramic membrane (Flow rate of feed gas 60 cm^3 min^{-1}, no purge gas, at atmospheric pressure).

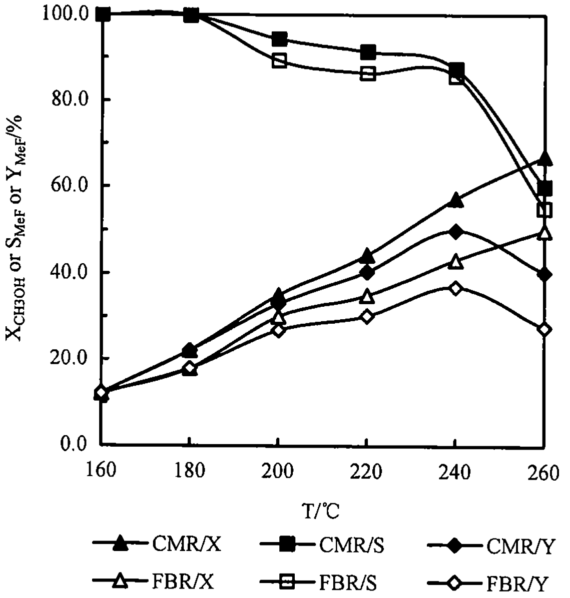

Figure 4. Dehydrogenation of methanol in CMR and FBR (Flow rate of feed gas 60 cm^3 min^{-1}, flow rate of purge gas 30 cm^{3}min^{-1}, at atmospheric pressure).

3.3. *Comparison of performance between catalytic membrane reactor and fixed-bed reactor*

Figure 4 shows the effect of reaction temperature on the dehydrogenation of methanol in the catalytic membrane reactor and the conventional fixed-bed reactor. Using the CMR or FBR, the conversion of methonal and the selectivity to methyl formate have changed in a similar curvilinear trend with an increase of reaction temperature, but much higher conversion of methanol and yield of methyl formate were achieved in the CMR. For example, at 240 °C 57.3% conversion of methanol and 50.0% yield of methyl formate were achieved in the CMR, and only 43.1% conversion of methanol and 36.9% yield of methyl formate were achieved in the FBR. The reason is that in the CMR hydrogen produced in the dehydrogenation reaction is continuously removed from the reaction zone through the composite membrane, to overcome chemical equilibrium limitation of catalytic dehydrogenation reaction in the conventional FBR and therefore enhance the conversion of methanol greatly.

Figure 4 also shows that at 240 °C maximum yields of methyl formate is obtained in both reactors. Thermodynamically, increasing the reaction temperature is favorable to vapor phase dehydrogenation of methanol to methyl formate. However, high temperature can make the small copper particles dispersed on the SiO$_2$/ceramic mesoporous membrane aggregate into bigger metal ensembles, which accelerates consecutively decomposition of methyl formate to carbon monoxide and hydrogen.

4. Conclusions

In the preparation of the Cu/SiO$_2$/ceramic composite membrane by an ion-exchange method, the preparation parameters in the ion-exchange method affect its properties. For the vapor phase dehydrogenation of methanol to methyl formate in the catalytic membrane reactor, the suitable condition of preparing the Cu/SiO$_2$/ceramic memebrane is as follows:the SiO$_2$/ceramic mesoporous membrane was ion-exchanged by 0.5 mol L^{-1} Cu(NH$_3$)$_4$(NO$_3$)$_2$ solution for 24 h, and calcined in air at 500 °C for 2 h. Using the catalytic membrane reactor, at 240 °C 57.3% conversion of methanol and 50.0% yield of methyl formate were achieved; using the fixed-bed reactor, 43.1% conversion of methanol and 36.9% yield of methyl formate were achieved.

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References

[1] J.S. Lee, J.C. Kim and Y.G. Kim, Appl. Catal. 57 (1990) 1.
[2] T. Sodesawa, React. Kinet. Catal. Lett. 24 (3/4) (1984) 259.
[3] T. Sodesawa, React. Kinet. Catal. Lett. 32 (1) (1986) 63.
[4] T. Sodesawa, M. Nagacho, A. Onodera and F. Nozaki, J. Catal. 102 (1986) 460.
[5] E.D. Guerreiro, O.F. Gorriz, G. Larsen and L.A. Arrua, Appl. Catal. A: Gen. 204 (2000) 33.
[6] T.P. Minyukova, I.I. Simentsova, A.V. Khasin, N.V. Shtertser, N.A. Baronskaya, A.A. Khassin and T.M. Yurieva, Appl. Catal. A: Gen. 237 (2002) 171.
[7] M. Yoneoka, U. S. Patent 4,319,037, (1982).
[8] Y. Wang, R. Gang and S. Han, React. Kinet. Catal. Lett. 67 (2) (1999) 305.
[9] S. Sato, M. Iijima, T. Nakayama, T. Sodesawa and F. Nozaki, J. Catal. 169 (1997) 447.
[10] M. Yoneoka, M. Osugi and T. Ikarashi, U. S. Patent 4,232,171, (1980).
[11] K.D. Jung and O.S. Joo, Catal. Lett. 84 (1–2) (2002) 21.
[12] T. Horlenko and A. Aguilo, U. S. Patent 4,480,122, (1984).
[13] M. Yoneoka and M. Osugi, *U. S. Patent 4,149,009*, (1979).
[14] S.C. Chen, W.J. Cheng, F.S. Lin and F.J. Huang, U. S. Patent 5,144,062, (1992).
[15] I. Rodriguez-Ramos, A. Guerrero-Ruiz, M.L. Rojas and J.L.G. Fierro, Appl. Catal. 68 (1991) 217.
[16] S. Horie, Y. Yamamoto and T. Ikarashi, U. S. Patent 4,436,835, (1984).
[17] K. Joerg, F.J. Mueller, M. Irgang, L. Marosi and G. Borchert, U. S. Patent 5,194,675, (1993).
[18] D. Uzio, J. Peureux, A. Giroir-Fendler, M. Torres, J. Ramsay and J.-A. Dalmon, Appl. Catal. A:Gen. 96 (1993) 83.
[19] D. Uzio, S. Miachon and J.-A. Dalmon, Catal. Today 82 (2003) 67.
[20] Y.L. Guo, G.Z. Lu, Y.S. Wang and R. Wang, Sep. Purif. Technol. 32 (1–3) (2003) 271.
[21] G.Z. Lu, S.C. Shen and R. Wang, Catal. Today 30 (1996) 41.