

## Vapor-Phase Dehydrogenation of Methanol to Methyl Formate in Catalytic Membrane Reactor with Pd/SiO<sub>2</sub>/Ceramic Composite Membrane

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Vapor-phase dehydrogenation of methanol to methyl formate was investigated in the catalytic membrane reactor (CMR) with the Pd/SiO<sub>2</sub>/ceramic composite membrane prepared by an impregnation method. The studies show that the CMR has much better performance than the fixed-bed reactor, in which no methyl formate is detected under the similar reaction conditions.

Methyl formate (MeF) is an important and versatile chemical intermediate, and has been considered as one of the building block molecules in C<sub>1</sub> chemistry.<sup>1</sup> Furthermore, methyl formate can be used as a gasoline octane number enhancer instead of methyl *tert*-butyl ether (MTBE), which means to have a large potential market for methyl formate.

Methyl formate can be prepared by many processes, dehydrogenation of methanol, carbonylation of methanol, oxidative dehydrogenation of methanol, dimerization of formaldehyde, direct synthesis from CO and H<sub>2</sub>, and hydrocondensation of carbon dioxide with methanol.<sup>1</sup> Among these processes aforementioned, 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 and by-product hydrogen to be a very useful raw material and clean fuel, and so on.

Vapor-phase dehydrogenation of methanol to methyl formate is usually catalyzed by the copper-substrate catalysts.<sup>2-11</sup> However, over other transition-metal catalysts except for tungsten carbide<sup>12,13</sup> and Pd/ZnO catalyst,<sup>14</sup> no methyl formate is produced.

In the catalytic membrane reactor (CMR), the pores of a catalytic membrane show two ways corresponding to two sides of the membrane wall. For the conventional catalysts used in the fixed-bed reactor (FBR), there is only one way to enter and get out of their pores. Therefore, the high surface area of a membrane with mesoporous top layers supporting an active component is available to maximize the interfacial contacts between the reactant gases and active sites of solid catalyst, which shows better performance than the conventional catalysts or catalytic processes.<sup>15,16</sup> If the dehydrogenation reaction is operated in the membrane reactor, a continuous and selective removal of product hydrogen from the reaction zone through the permselective membrane will shift the chemical equilibrium towards the product side, to break the limit of thermodynamic equilibrium in the FBR.<sup>17</sup> The CMR is expected to attain higher conversion at lower temperature, and then avoid conceivably a deactivation of catalyst and an occurrence of undesirable side reactions.

In this paper, the Pd/SiO<sub>2</sub>/ceramic composite membrane was prepared by an impregnation method. In the catalytic mem-

brane reactor with the Pd/SiO<sub>2</sub>/ceramic composite membrane, vapor-phase dehydrogenation of methanol to methyl formate was investigated, which have not yet been reported.

The SiO<sub>2</sub> mesoporous membrane was coated on the outer surface of a porous ceramic tube ( $\phi 12 \times 250 \times 1.5$  mm, the average pore size is ca. 1  $\mu\text{m}$ , Shandong Research Institute of Industrial Ceramic) by a sol-gel method.<sup>18</sup> The top SiO<sub>2</sub> layer existed as an amorphous phase and its average pore size was ca. 4 nm. The Pd/SiO<sub>2</sub>/ceramic composite membrane was prepared by immersing the SiO<sub>2</sub>/ceramic mesoporous membrane in the PdCl<sub>2</sub> solution at 25 °C. Then it was dried at 110 °C overnight, and heated programmedly to 300 °C at 1.5 °C·min<sup>-1</sup> in air and kept for 10 h. This catalytic membrane was reduced by hydrogen at 250 °C for 2 h before use. In order to ensure the reaction catalyzed by a membrane catalyst to be operated in an isothermal zone, only 4 cm-length Pd/SiO<sub>2</sub>/ceramic composite membrane was prepared in the middle part of supporting ceramic tube, and its other part was sealed with a commercial ceramic glaze.

Vapor-phase dehydrogenation of methanol was carried out at atmospheric pressure in the catalytic membrane reactor that was a double-tubular type reactor consisted of a stainless-steel tube (16-mm i.d.) and a catalytic membrane tube as the outer and inner tube, respectively.<sup>17</sup> The gas mixture of methanol and nitrogen by bubbling nitrogen stream (100 cm<sup>3</sup>·min<sup>-1</sup>) through the methanol saturation apparatus at 30 °C, flowed in the shell side of the membrane reactor, and the purge gas of argon (30 cm<sup>3</sup>·min<sup>-1</sup>) flowed cocurrently in the tube side. The flow rates of gas in the shell side and tube side were measured by a soap-film flow meter. The composition of effluent was analyzed by an on-line gas chromatograph (PE Autosystem XL).

Permeability experiment was similar to the above.  $\beta$  (permeation ratio) was defined as the ratio of the amount of one gas permeating through a membrane to the total amount of this gas in feed gas, such as H<sub>2</sub>/N<sub>2</sub> or CH<sub>3</sub>OH/N<sub>2</sub>.

When the CMR was used as the fixed-bed reactor, a nonporous stainless-steel ( $\phi 12$  mm) tube was used instead of the Pd/SiO<sub>2</sub>/ceramic composite membrane, and the particles of Pd/SiO<sub>2</sub>/ceramic membrane crushed (0.45–0.90 mm) were packed in the shell side as the granular catalyst.

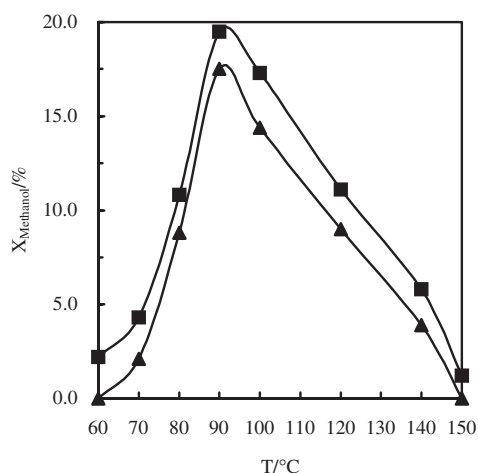
Tables 1 and 2 show the permeability of the Pd/SiO<sub>2</sub>/ceramic composite membrane for H<sub>2</sub>, N<sub>2</sub>, and CH<sub>3</sub>OH. It is found that the permeability of the Pd/SiO<sub>2</sub>/ceramic composite membrane is greatly different from that of the SiO<sub>2</sub>/ceramic mesoporous membrane. For hydrogen, the permeability of the Pd/SiO<sub>2</sub>/ceramic membrane is similar to that of the SiO<sub>2</sub>/ceramic membrane, but methanol and nitrogen permeating the Pd composite membrane are not detected.  $\beta_{\text{H}_2}$  of the Pd/SiO<sub>2</sub>/ceramic membrane increases with an increase of temperature. Maybe it is attributed to an acceleration of surface diffusion and hydrogen

**Table 1.** Permeability of the Pd/SiO<sub>2</sub>/ceramic composite membrane at 200 °C

Membrane	$\beta_{\text{H}_2}$ /%	$\beta_{\text{N}_2}$ /%	$\beta_{\text{CH}_3\text{OH}}$ /%
SiO <sub>2</sub> /ceramic	35.9	2.6	24.3
Pd/SiO <sub>2</sub> /ceramic	35.2	0	0

**Table 2.**  $\beta_{\text{H}_2}$  of the Pd/SiO<sub>2</sub>/ceramic composite membrane at different temperatures

T /°C	50	100	150	200
$\beta_{\text{H}_2}$ /%	18.3	27.2	31.7	35.2

**Figure 1.** The conversion of methanol versus reaction temperature for vapor-phase dehydrogenation of methanol in the CMR with 30 cm<sup>3</sup>·min<sup>-1</sup> purge gas (■) and no purge gas (▲).

spillover through the Pd/SiO<sub>2</sub>/ceramic membrane at higher temperature.

Figure 1 shows the relation between the conversion of methanol and reaction temperature for dehydrogenation of methanol in the CMR. The selectivity to methyl formate is close to 100% at 60–150 °C. At 90 °C, the maximum conversion of methanol (19.5%) is achieved. When the reaction temperature is higher or lower than 90 °C, the conversion of methanol declines obviously, and it is nearly zero at 60 or 150 °C (no purge gas).

In the fixed-bed reactor packed with the granular catalyst of the crushed Pd/SiO<sub>2</sub>/ceramic membrane, the conversion of methanol is nearly zero under the similar reaction conditions as the CMR. Even at 200 °C, the conversion of methanol is only 1.5%, and the products are carbon monoxide and hydrogen exclusively, and no methyl formate is detected in the effluent, which agrees with the results in the Ref. 14.

The results in Figure 1 also show that the presence of purge gas affects greatly the conversion of methanol. Increasing the flow rate of purge gas reduces the partial pressure of hydrogen in the tube side, to result in an increase in the difference of hy-

drogen pressure between the shell side and tube side and an increase of hydrogen flux through the Pd/SiO<sub>2</sub>/ceramic composite membrane from the reaction zone. Therefore, the chemical equilibrium is shifted towards the product side to enhance greatly the conversion of methanol.

In conclusion, in the catalytic membrane reactor, the product of H<sub>2</sub> can be removed from the reaction zone continuously and selectively to break the thermodynamic equilibrium of vapor-phase dehydrogenation of methanol to methyl formate in the fixed-bed reactor, which makes it possible to attain higher conversion at lower temperature.

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