Pd−Ag−Au−Ni Membrane Reactor for Methoxymethane Steam Reforming[†]

Dongmei Feng, Yuanyuan Wang, Dezheng Wang, and Jinfu Wang*

Beijing Key Laboratory of Green Chemical Reaction Engineering and Technology, Department of Chemical Engineering, Tsinghua University, Beijing 100084, China

The permeability of hydrogen through a Pd−Ag−Au−Ni membrane was determined at temperatures between (473 and 573) K at a hydrogen pressure of between (1.0 and 4.0) 10^5 Pa. Methoxymethane steam reforming ($C_2H_6O + 3H_2O(g) = 6H_2 + 2CO_2$) with a Pd−Ag−Au−Ni membrane reactor is used to produce hydrogen in proton exchange membrane fuel cells (PEMFCs). This process uses a bifunctional catalyst of ($CuO-ZnO-Al_2O_3-ZrO_2$ + ZSM-5) in mass fraction ratio of each component of 50 %. The determined methoxymethane conversion, hydrogen yield, and hydrogen recovery flow in a reactor were compared to those in a fixed bed reactor. The operating parameters were pressures of $(1.0 \text{ to } 4.0)\cdot 10^5$ Pa, temperatures of (473 to 573) K, and input mass fraction ratios of H_2O-to-C_2H_6O of (3 to 7) at velocities of between (1180 and 9000) $cm^3\cdot g^{-1}\cdot h^{-1}$. The conversion of C_2H_6O was higher in the membrane reactor due to the countercurrent removal of hydrogen. In the membrane reactor, the thermal energy needed for the endothermic steam reforming can be provided by the combustion of the exit stream from the membrane reactor. The enthalpy for the reactions indicated coupling, and both reforming and oxidation reactions gave a energy recovery of about 85 %.

Introduction

One of the most promising technologies for lightweight portable power generation is the proton exchange membrane fuel cell (PEMFC), which has several attractive features including the following: compact size, higher power density, rapid start-up, and high energy conversion efficiency.[1,2] The PEMFC uses hydrogen as fuel for its electrochemical reaction, and the process is considered clean because it does not form harmful byproducts, such as oxides of either sulfur or nitrogen, and also exhibits relatively high energy efficiency particularly when compared with the internal combustion engine. From the fuel cell's viewpoint, pure hydrogen is a superior fuel. Nevertheless, on the commercial level, this poses a number of problems: the lack of infrastructure for hydrogen production and distribution, mechanical problems involved with refueling the vehicle at the stations, low-energy density (implying a shorter driving range) of hydrogen storage technology current at the time of writing this, mass and size of the storage cylinder, and safety concerns of carrying a high-pressure gaseous hydrogen. Thus, there are challenges and opportunities for the improvement of existing processes, as well as for finding new types of clean fuels for H_2 production. These concerns have led to the search for alternate hydrogen storage systems or alternative fuels from which hydrogen can be generated in situ.

Natural gas, methanol, gasoline, and methoxymethane (commonly known as dimethyl ether and given the acronym DME) can be used to produce hydrogen. Among these, methoxymethane has the advantages of relatively high energy density, nontoxicity, easy availability, safe handling and storage, and that the infrastructure in place for liquefied petroleum gas distribution can be readily adapted for methoxymethane. The use of methoxymethane as an on-board hydrogen source represents an attractive solution for fuel cell engines in transportation applications. The feasibility of producing hydrogen from a methoxymethane steam reforming process has already been discussed.[3−10]

Hydrogen production from methoxymethane steam reforming is a two-step process. The first step is the acid catalyst catalyzed hydrolysis of methoxymethane to methanol according to

$$CH_3OCH_3 + H_2O = 2CH_3OH \tag{1}$$

for which the enthalpy of reaction is $\Delta H_r^0 = +36.6\ kJ\cdot mol^{-1}$ followed by methanol steam reforming over Cu or Cu/ZnO-based catalysts to give

$$CH_3OH + H_2O = CO_2 + 3H_2 \tag{2}$$

where $\Delta H_r^0 = +49.1\ kJ\cdot mol^{-1}$. In both eqs 1 and 2, ΔH_r^0 is the standard enthalpy of reaction at $T = 298$ K. Methoxymethane steam reforming is given by the reaction

$$CH_3OCH_3 + 3H_2O = 2CO_2 + 6H_2 \tag{3}$$

for which $\Delta H_r^0 = +135.0\ kJ\cdot mol^{-1}$. The integrated system for methoxymethane steam reforming includes the reaction known as the water−gas shift (WGS)

$$CO + H_2O = CO_2 + H_2 \tag{4}$$

for which $\Delta H_r^0 = -41.17\ kJ\cdot mol^{-1}$. Methoxymethane hydrolysis is an equilibrium-limited reaction, and it is considered the rate-limiting step for the overall methoxymethane steam reforming. The hydrolysis reaction is known to take place over an acidic catalyst. Thermodynamic analysis[11,12] has indicated that

---

* Corresponding author. E-mail: wangjfu@mail.tsinghua.edu.cn. Tel.: +86-10-62797490. Fax: +86-10-62772051.

[†] Part of the "William A. Wakeham Festschrift".

10.1021/je8009072 CCC: $40.75

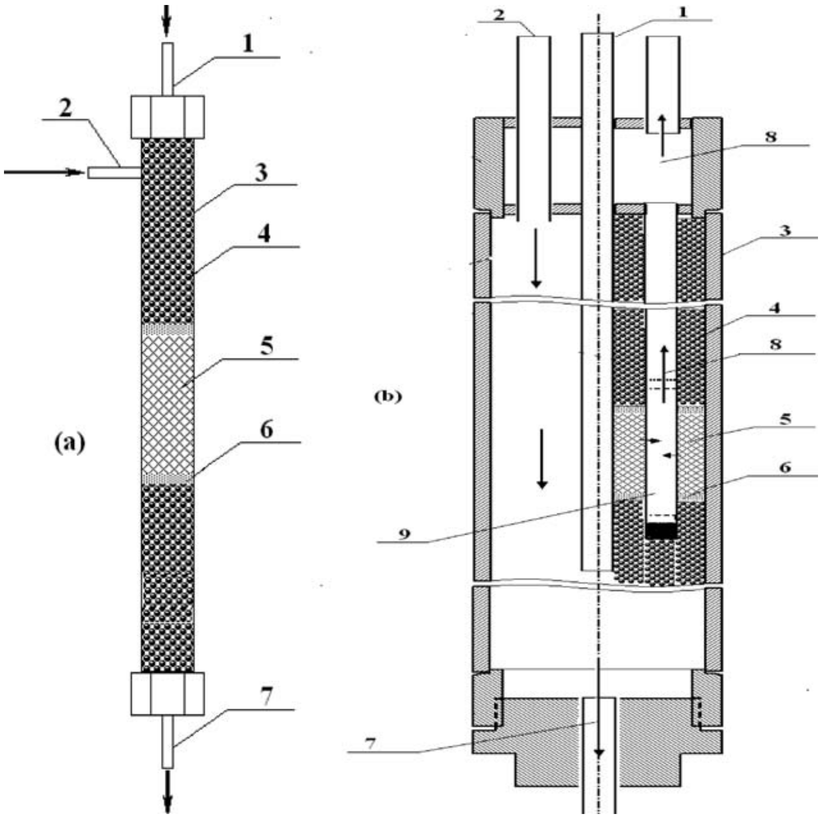

Figure 1. Schematic of the reactors: (a) fixed bed reactor and (b) membrane reactor. 1, thermocouple; 2, feed; 3, stainless steel tube; 4, glass spheres; 5, catalyst pellets; 6, quartz; 7, products; 8, hydrogen; 9, palladium tube.

a high methoxymethane conversion cannot be attained by only the hydrolysis of methoxymethane, but the equilibrium of eq 1 can be shifted in the forward direction, leading to high methoxymethane conversion if there is a simultaneous consecutive methanol conversion by steam reforming reaction eq 2. It is well-known that Cu−ZnO and $CuO-ZnO-Al_2O_3$ showed high activity for the synthesis and steam reforming of methanol. Thus, the preferred catalyst should be bifunctional, for example, comprising ZSM-5 as the methoxymethane hydrolysis component and CuO−ZnO as the methanol steam reforming component. Most major differences in the methoxymethane steam reforming process arise from the method used for catalyst preparation. Some attention has also been paid to methoxymethane hydrolysis with the use of zeolite or alumina as the catalyst.[13−17] Research has also been undertaken[18−20] to formulate the kinetics of methanol steam reforming.

The aim is to produce hydrogen for fuel cell applications from steam reforming of methoxymethane conducted in a fixed bed reactor. The hydrogen-rich stream requires purification before it can be fed to a PEMFC. It is crucial to remove CO because it poisons the anodic catalyst of the fuel cell. A membrane reactor is an attractive alternative because the reaction and separation steps can be combined in one unit. Moreover, the continuous withdrawal of hydrogen from the system shifts the equilibrium of the reforming reaction to the products and thus enhances the yield. A membrane reactor steam reformer has good potential in the near future because it further simplifies the operation and reduces the volume occupied by device. A methoxymethane steam reformation was performed in a membrane reactor using the stainless steel-supported Knudsen membrane with remarkably high permeability.[21,22] The typical membranes for hydrogen permeation reported in the literature are dense palladium membranes or silver−palladium membranes. Here, a commercial Pd−Ag−Au−Ni alloy tube of thickness 0.1 mm was used for hydrogen purification and separation. The DME SR membrane reactors comprised filling the annular region surrounding these Pd−Ag−Au−Ni membrane tubes with a catalyst bed.

The objective of this research work is to study the behavior of a dense Pd−Ag−Au−Ni membrane reactor and compare it with a fixed bed reactor operated at the same experimental conditions. The influences of the following were determined on the membrane reactor: pressure, the feedstock as determined by the ratio of the amount of substance of water to that of methoxymethane, temperature, and space velocity. These studies used a bifunctional catalyst of ($CuO-ZnO-Al_2O_3-ZrO_2$ + ZSM-5) with equal proportions of both by mass concentration of the components. The results are presented in terms of methoxymethane conversion, hydrogen production, and hydrogen recovery.

Experimental Section

Catalyst Preparation. The catalyst comprised a physical mixture of a solid zeolite ZSM-5 catalyst with an amount of substance ratio of Si to Al of 25 that was obtained from the Catalyst Plant of Nankai University for methoxymethane hydrolysis. The $CuO-ZnO-Al_2O_3-ZrO_2$ catalyst was synthesized by a coprecipitation procedure[23,24] and used for methanol steam reforming. The mass ratio of the two components in the bifunctional catalyst was about 1. The copper catalyst was prepared using the corresponding nitrates as the metal sources and sodium carbonate as the precipitant. The corresponding nitrates and sodium carbonate solutions had a molarity of 1 $mol \cdot cm^{-3}$. The precipitate was prepared in pH = 7, washed, and dried overnight at $T = 373$ K, and calcified at $T = 623$ K

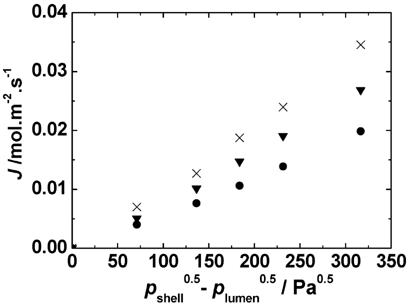

Figure 2. Relationship between the hydrogen permeation rate J as a function of the difference $p_{\text{shell}}^{0.5} - p_{\text{shell}}^{0.5}$ of the square root of hydrogen pressures on the shell and tube sides at temperatures T: ●, $T = 475$ K; ▼, $T = 514$ K; ×, $T = 577$ K.

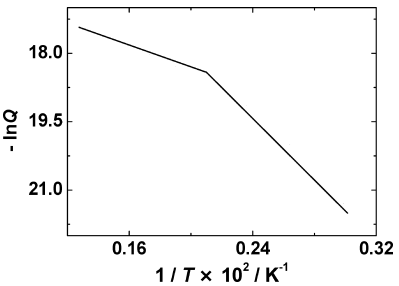

Figure 3. Hydrogen permeation Q as a function of the inverse of temperature T^{-1}.

for a time of 4 h to yield the catalyst with a molar composition of 0.6CuO, 0.3ZnO, $0.05Al_2O_3$, and $0.05ZrO_2$. A constant pH (± 0.03) was maintained. During the experiments, the actual fluctuation of the temperature was within ± 0.03 K. A mass of 1 g of this bifunctional catalyst was mixed with 2 g of inert quartz chips of about 80 mesh to form the catalyst bed of total length equal to that of the membrane zone. Catalysts for the measurements had an uncertainly of ± 0.0001 g.

Fixed and Membrane Reactor Description. Figure 1a shows a schematic of the fixed bed reactor. It consisted of a stainless steel tube packed with the catalyst. The fixed bed reactor had a length of 40 cm, o.d. of 20 mm, and i.d. of about 10 mm. In the fixed bed and membrane reactors, the catalyst pellets were placed in the constant temperature zone of length of about 15 cm that was between zones packed with quartz, (40 to 60) mesh, and glass spheres of diameter between (1.5 and 2) mm.

Figure 1b shows a schematic of the membrane. It consisted of a stainless steel tube housing a Pd−Ag−Au−Ni membrane tube packed with the catalyst. The membrane reactor had a length of 40 cm, o.d. of 20 mm, and i.d. of 16 mm with four Pd−Ag−Au−Ni membrane tubes each containing 23 % Ag, 3 % Au, and 0.3 % Ni of thickness 0.1 mm, diameter 3 mm, and length 10 mm that were obtained from Western Metal Materials Company Ltd., China. The shell side of the Pd−Ag−Au−Ni membrane tube served as the reaction chamber and the tube side as the permeation chamber. The membrane tube was welded to two stainless steel supports and was closed at one end. Four membrane tubes were uniformly distributed in the stainless steel reactor tube. One provided the inlet for the methoxymethane of 99.99 % and another for steam with two outlet streams, one for the shell stream and the other for lumen outlets. The methoxymethane steam reforming reaction takes place in the shell side of the membrane reactor. The hydrogen produced permeated through the palladium membrane into the membrane tube and was removed by a rotary vacuum pump. A wet gas flowmeter was connected to the vacuum pump exit to measure the hydrogen flow.

Permeation and Purification Tests. The four Pd−Ag−Au−Ni membrane tubes used in this study each contained 23 % Ag, 3 % Au, and 0.3 % Ni and had a thickness of 0.1 mm. The metal membrane was stable and showed a high selectivity toward hydrogen. Figures 2 and 3 show the hydrogen permeation rate of the investigated membrane. The experimental tests on the dense Pd−Ag−Au−Ni membrane showed that H_2 gas selectivity was infinite, and Figures 2 and 3 show that both the half-power pressure law and Arrhenius law were obeyed, respectively. The linear plots were used to calculate the main permeation parameters: pre-exponential factor Q_0 and apparent activation energy E_a. The temperature dependence of hydrogen permeability can then be expressed by an Arrhenius expression: $Q = Q_0 \exp(-E_a/RT)$. The overall hydrogen permeation flux, J_{H_2}, through the Pd−Ag−Au−Ni membrane can be written using the Richardson equation[25] for two different temperature ranges. First, for temperatuires between (334 and 475) K

$$J_{H_2}/(\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}) = \frac{9.47\cdot10^{-6}\exp\{-26.82\cdot10^{3}/(RT)\}(\sqrt{p_{\text{shell}}} - \sqrt{p_{\text{lumen}}})}{l} \tag{5}$$

and

$$J_{H_2}/(\text{mol}\cdot\text{m}^{-2}\cdot\text{s}^{-1}) = \frac{3.2\cdot10^{-8}\exp\{-4.65\cdot10^{3}/(RT)\}(\sqrt{p_{\text{shell}}} - \sqrt{p_{\text{lumen}}})}{l} \tag{6}$$

for temperatures between (475 and 573) K. In eqs 5 and 6, p_{shell} and p_{lumen} are the partial pressures of hydrogen on the feed and permeate sides, respectively. These results are in agreement with the literature data.[26]

Steam Reforming Testing. The schematic of the membrane reactor system is shown in Figure 4. The reactant methoxymethane and reduction gases N_2 and H_2 were controlled by mass flow controllers. The methoxymethane steam reforming was carried out using both the isothermal fixed bed reactor[27] and membrane reactor with space velocities of between (1180 and 9000) $\text{cm}^3\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, where g refers to the catalyst mass, and the amount of substance ratio of H_2O to methoxymethane varied between (3 and 7). Both the fixed bed reactor and the membrane reactor were packed with 1 g of the bifunctional catalyst ($CuO-ZnO-Al_2O_3-ZrO_2$ + ZSM-5). Before conducting the reaction, the catalyst was reduced with ($0.04H_2 + 0.96N_2$) at atmospheric pressure by raising the temperature of the reactor temperature over a time of 10 h to $T = 503$ K where it was held for a time of 2 h. A preheater was used to evaporate water for the experiments so that steam was added to the feed. The water was metered to the preheater with a metering pump, and methoxymethane gas was also introduced by a mass flow controller into the reactor. In the membrane reactor, both effluent streams were analyzed for their flow rates and compositions with online gas chromatography. The first sample of the effluent was taken at a time of 2 h after steady reaction conditions were established. Then samples were taken every 0.67 h for online analysis of the effluent composition by a gas chromatograph. The average of five data points is shown in Figure 4.

Kinetic Parameter Formulation. The reactant methoxymethane conversion denoted by $x(C_2H_6O)$, the hydrogen yield denoted

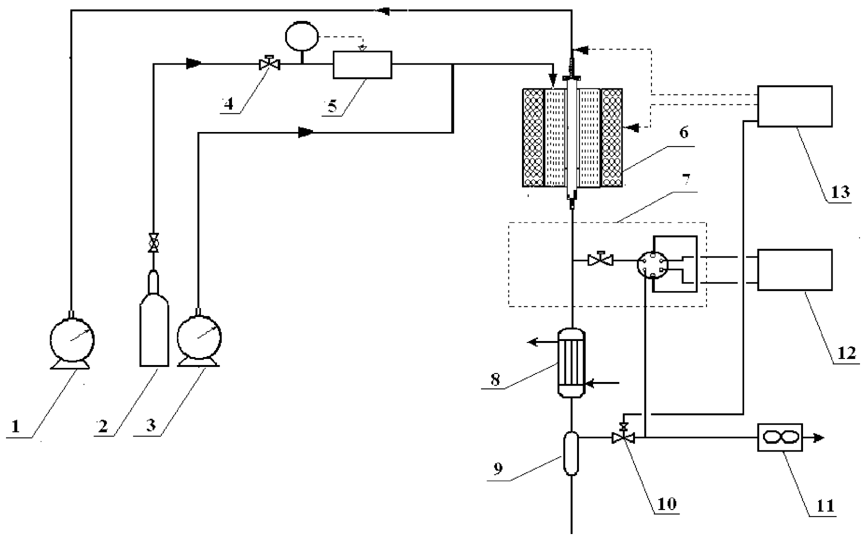

Figure 4. Schematic of the membrane reactor system. 1, vacuum pump; 2, methoxymethane or reduction gas cylinder; 3, pump; 4, pressure reducing valve; 5, mass flowmeter; 6, reactor; 7, incubators; 8, cold hydrazine; 9, sets of a tank; 10, back pressure valve; 11, wet flowmeter; 12, GC; 13, control system.

by $Y(H_2)$, and the hydrogen recovery flow $R(H_2)$ (for the membrane reactor) were calculated from

$$x(C_2H_6O) = \left[\frac{F(C_2H_6O)_{in} - F(C_2H_6O)_{out}}{F(C_2H_6O)_{in}}\right] \cdot 10^2 \qquad (7)$$

$$Y(H_2) = \left[\frac{F(H_2)_{out}}{6F(C_2H_6O)_{in}}\right] \cdot 10^2 \qquad (8)$$

and

$$R(H_2) = \left[\frac{F(H_2, \text{lumen})}{F(H_2, \text{shell}) + F(H_2, \text{lumen})}\right] \cdot 10^2 \qquad (9)$$

In eqs 7 through 9 $F(i$, in or out) represents the molar flow rate of the i species measured at the inlet or at the outlet of the reactor while $F(H_2$, shell) and $F(H_2$, lumen) are the effluent molar flow rate of H_2 in the shell side and lumen side of the membrane reactor. For eq 9 the hydrogen recovery was defined as the ratio of the hydrogen flow in the permeate to the theoretical hydrogen flow in the reactor assuming 100 % conversion to H_2 and CO_2.

Results and Discussion

Methoxymethane steam reforming was tested in the fixed bed and membrane reactors and with the intent of verifying the performance of the palladium membrane reactor. An enhancement of the membrane separation efficiency by continually pumping the permeation side (tube side) with a vacuum pump was used. The pumping kept the permeation side essentially hydrogen free, which resulted in a higher driving force for hydrogen permeation through the Pd membrane. The results showed that the membrane had the capability to remove the hydrogen produced and to shift the equilibrium. Figures 5 to 9 show the effect of the molar ratio of H_2O to methoxymethane, temperature, space velocity, and pressure on methoxymethane conversion, hydrogen yield, and hydrogen recovery.

Effect of Molar Ratio of H_2O/Methoxymethane. Figure 5 shows in part (a) the results of methoxymethane conversion and in part (b) the hydrogen yield for both fixed bed and membrane reactors as a function of the molar ratio of the feed under the following experimental conditions: 1 g of catalyst, $T = 513$ K, space velocity $v = 4922\ \text{cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$, and $p_{shell} = 2 \cdot 10^5$ Pa, $p_{lumen} = 1 \cdot 10^5$ Pa. From eq 3, an increase in the H_2O/DME feed ratio produces an increase in the methoxymethane conver-

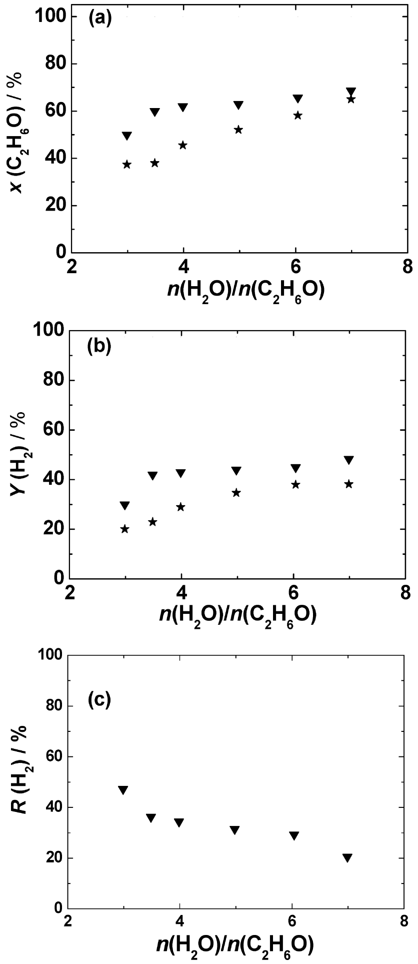

Figure 5. Effect of the ratio of the amount of substance n of H_2O to that of methoxymethane (commonly known as dimethyl ether by the acronym DME). (a) DME conversion, (b) H_2 yield, (c) H_2 recovery. Catalyst, 1 g; $p_{shell} = 2 \cdot 10^5$ Pa, $p_{lumen} = 1 \cdot 10^5$ Pa; space velocity $v = 4922\ \text{cm}^3 \cdot \text{g}^{-1} \cdot \text{h}^{-1}$; $T = 513$ K; ▼, in membrane reactor; ★, in fixed-bed reactor.

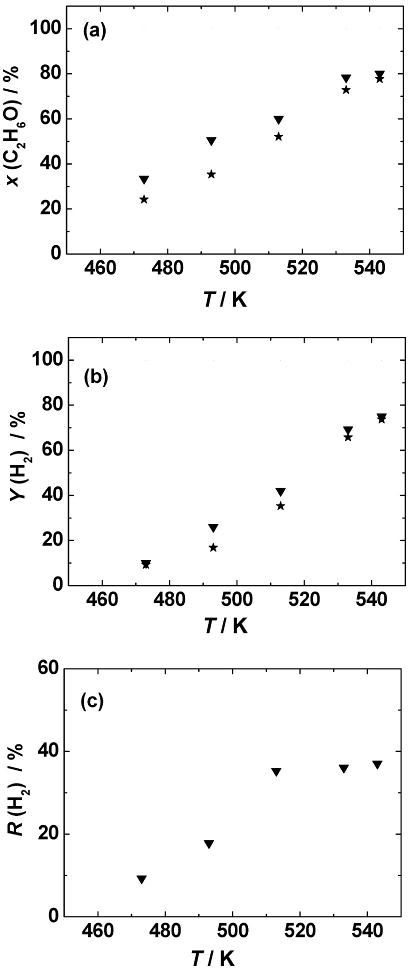

Figure 6. Effect of reaction temperature on (C_2H_6O + H_2O). (a) DME conversion, (b) H_2 yield, (c) H_2 recovery. Catalyst, 1 g; $n(C_2H_6O)/n(H_2O)$ = 1/3.5; $p_{\text{shell}} = 2\cdot10^5$ Pa, $p_{\text{lumen}} = 1\cdot10^5$ Pa; space velocity v = 4922 $cm^3\cdot g^{-1}\cdot h^{-1}$; T = 513 K; ▼, in membrane reactor; ★, in fixed-bed reactor.

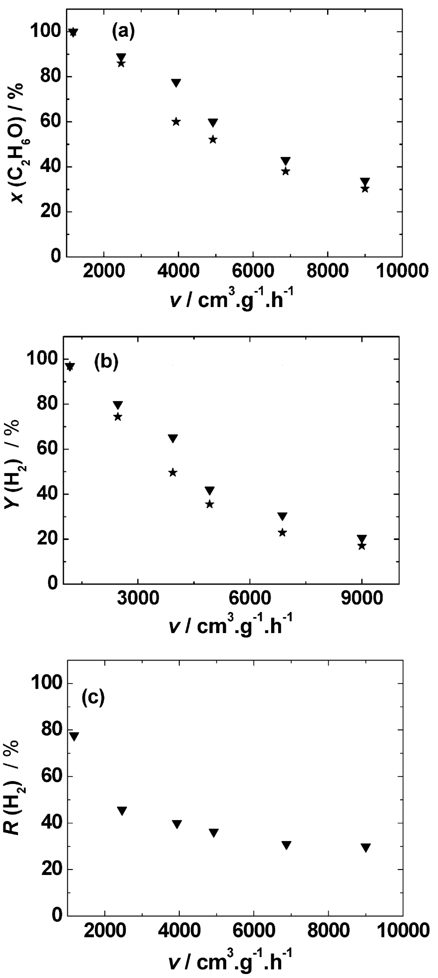

Figure 7. Effect of space velocity v on (C_2H_6O + H_2O). (a) Methoxymethane conversion, (b) H_2 yield, (c) H_2 recovery. Catalyst, 1 g; $n(C_2H_6O)/n(H_2O)$ = 1/3.5; $p_{\text{shell}} = 2\cdot10^5$ Pa, $p_{\text{lumen}} = 1\cdot10^5$ Pa; T = 513 K; ▼, in membrane reactor; ★, in fixed-bed reactor.

sion and hydrogen yield. In the fixed bed reactor, increasing the feed ratio from (3 to 7) always increased the methoxymethane conversion and hydrogen yield. For example, at T = 513 K and $n(H_2O)/n(C_2H_6O)$ = 3.5, the methoxymethane conversion was 38 % and hydrogen yield was 23 %. For $n(H_2O)/n(C_2H_6O)$ = 7 at the same temperature, the methoxymethane conversion was 65 % and hydrogen yield was 38 %. In contrast, for the membrane reactor, the methoxymethane conversion showed a minimum at $n(H_2O)/n(C_2H_6O)$ = 3, and the methoxymethane conversion was 50 % at $n(H_2O)/n(C_2H_6O)$ = 3 and 68.7 % at $n(H_2O)/n(C_2H_6O)$ = 7.

Figure 5 also shows a comparison between the performances of the fixed bed and membrane reactors as a function of various feed ratios. It is evident that the membrane reactor gave greater methoxymethane conversions and hydrogen yields than the fixed bed. This was due to the hydrogen permeation through the membrane which shifted the equilibrium which was responsible for the low conversion in the fixed bed.

Figure 5c shows the hydrogen recovery in the membrane reactor which represents the part of the hydrogen recovered as a CO-free stream. The hydrogen recovery decreased on increasing the feed molar ratio because the excess of water diluted the hydrogen produced in the reaction zone, which resulted in a lower hydrogen partial pressure difference across the membrane and in a lower hydrogen recovery. Methoxymethane steam reforming is usually performed in the presence of an excess of steam to prevent carbon deposition on the catalyst surface and to enhance the steam reforming. On taking into account the thermal load and energy supply, the optimum $n(H_2O)/n(C_2H_6O)$ = 3.5 can be recommended.

Effect of Reaction Temperature. Figure 6 shows increasing the temperature will increase the methoxymethane conversion and hydrogen yield and have a significant effect on hydrogen recovery. Figure 6 shows a direct comparison of methoxymethane conversion, H_2 yield, and H_2 recovery as a function of temperature at the same space velocity of 4922 $cm^3\cdot g^{-1}\cdot h^{-1}$ in both fixed bed and membrane reactors. For the range of temperatures investigated, methoxymethane conversion and hydrogen yield in the membrane reactor are higher than in the fixed bed. Methoxymethane conversion and hydrogen yield increased with increasing temperature in the membrane reactor because of both increased catalytic activity and increased hydrogen permeation flux. The difference between the two reactors was mainly owing to the hydrogen removal through the Pd−Ag−Au−Ni membrane which shifted the equilibrium toward the products.

Effect of Space Velocity. The effect of space velocity, which is a parameter that reflects the efficiency of a reactor, is shown in Figure 7. Space velocities of between (1180 and 9000) $cm^3\cdot g^{-1}\cdot h^{-1}$ were used with a $n(H_2O)/n(C_2H_6O)$ = 3.5 at atmospheric pressure and T = 513 K. As Figure 7 shows, decreasing space velocity increased the methoxymethane conversion in pane and hydrogen yield for both the reactors.

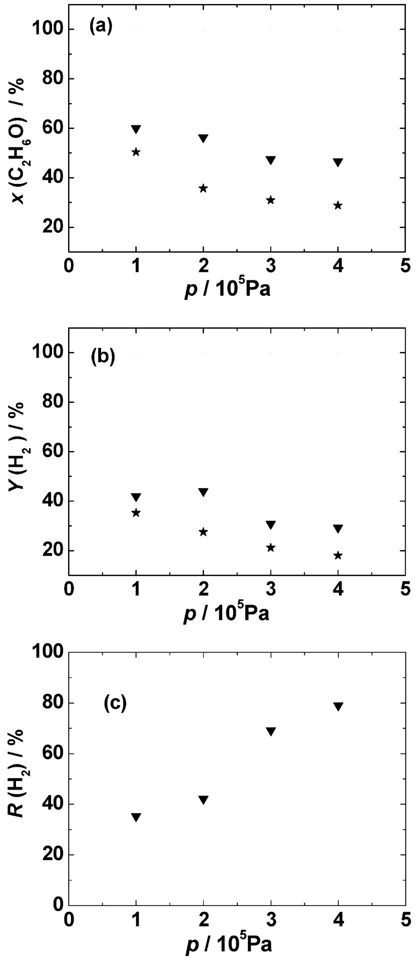

Figure 8. Effect of pressure p on (C_2H_6O + H_2O). (a) Methoxymthane conversion, (b) H_2 yield. Catalyst, 1 g; $n(C_2H_6O)/n(H_2O)$ = 1/3.5; space velocity v = 4922 $cm^3 \cdot g^{-1} \cdot h^{-1}$; ▼, in membrane reactor; ★, in fixed-bed reactor.

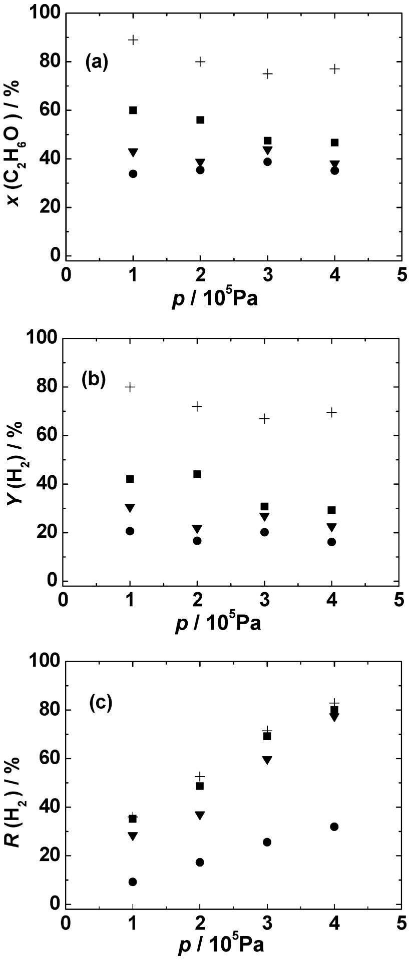

Figure 9. Effect of pressure p and space velocity v on (C_2H_6O + H_2O) at T = 513 K in a membrane reactor. (a) Methoxymethane conversion, (b) H_2 yield, (c) H_2 recovery flow. Catalyst, 1 g; $n(C_2H_6O)/n(H_2O)$ = 1/3.5; for the following v: ●, 9000 $cm^3 \cdot g^{-1} \cdot h^{-1}$; ▼, 6872 $cm^3 \cdot g^{-1} \cdot h^{-1}$; ■, 4922 $cm^3 \cdot g^{-1} \cdot h^{-1}$; +, 2461 $cm^3 \cdot g^{-1} \cdot h^{-1}$.

For the range of space velocity considered, the methoxymethane conversion was greater in the membrane than in the fixed bed reactor. For example, at v = 4922 $cm^3 \cdot g^{-1} \cdot h^{-1}$ and T = 513 K, the methoxymethane conversion was 52 % in the fixed bed reactor but 60 % in the membrane reactor. In the latter, a decreased space velocity resulted in an increase of the hydrogen flux through the membrane and in a higher conversion. This comparison shows that the dense Pd−Ag−Au−Ni membrane reactor gave higher conversion and higher total hydrogen production than the fixed bed reactor, and hydrogen recovery decreased with increasing space velocity because the hydrogen yield decrease resulted in a lower hydrogen partial pressure. In terms of the methoxymethane conversion and hydrogen yield, the membrane reactor performance was better that that of the fixed bed reactor owing to the presence of the membrane, which removed the hydrogen produced during the reaction.

Effect of Pressure. An important parameter that influenced the performance of the reactor was the reaction pressure. According to the stoichiometry of the global methoxymethane steam reforming reaction given by eq 1, the ratio $n(H_2O)/n(C_2H_6O)$ was fixed at 3.5 to have an excess of water and yet be appropriate for a tank of reasonable capacity and mass. The effect of pressure on the methoxymethane steam reforming in the fixed bed and membrane reactors at T = 513 K is shown in Figure 8. For the pressure range investigated, the methoxymethane conversion and hydrogen yield in the membrane reactor was greater than the fixed bed, although it was lower than the equilibrium value (100 %). The effect of pressure on the hydrogen yield in the membrane reactor and the fixed bed reactor is shown in Figure 8b. The methoxymethane conversions in the fixed bed and membrane reactor show a similar decrease with increasing pressure. The enhancement of separation through the membrane for the methoxymethane was observed giving higher conversions at all pressures studied. The pressure was found to have opposing effects in methoxymethane steam reforming: it decreased the equilibrium conversion but increased the permeate rate. The better performance of the membrane reactor compared to the fixed bed reactor for methoxymethane conversion and hydrogen yield was due to the function of the membrane, which removed the hydrogen produced during the reaction.

The influence of space velocity at T = 513 K on the methoxymethane conversion and on the hydrogen yield is illustrated in Figure 9. Space velocities of (2461 to 9000) $cm^3 \cdot g^{-1} \cdot h^{-1}$ were used to test the catalytic behavior with $n(H_2O)/n(C_2H_6O)$ = 3.5 at atmospheric pressure of 0.1 MPa. Figure 9a shows that decreasing space velocity increased the methoxymethane conversion, while Figure 9b shows the hydrogen yield increased for both the membranes and fixed-bed reactors. At the lowest space velocity studied, the hydrogen recovery flow in the Pd−Ag membrane was the least. At the highest space velocity studied, drawing off hydrogen in the membrane reactor permitted a high hydrogen recovery flow.

Table 1. Effect of Recovery Yield of Hydrogen on the External Heat Supply in the $C_2H_6 + 3H_2O = 6H_2 + 2CO_2$ Membrane Reactor[a]

T / K	ΔH_r^0(eq 1) / $kJ \cdot mol^{-1}$	ΔH_r^0(eq 10) / $kJ \cdot mol^{-1}$	$\Delta H_f^0(C_2H_6O)$ / $kJ \cdot mol^{-1}$	$\Delta H_f^0(H_2O)$ / $kJ \cdot mol^{-1}$	ΔH_f^0(air) / $kJ \cdot mol^{-1}$	$R(H_2)$/%	
						a	*b*
473	178.07	−244.21	8.81	49.45	6.03	87.8	84.8
493	176.66	−244.03	9.91	50.14	6.61	87.9	84.8
513	173.61	−243.64	12.26	51.48	7.78	88	84.9
533	173.61	−243.64	12.27	51.48	7.78	88.1	84.9

[a] Note: *a*, Vaporization and heating of the feedstock not supplied by the heat released from reaction 10; *b*, vaporization and heating of the feedstock supplied by the heat released from reaction 10.

The hydrogen recovery flow (permeate hydrogen flow) also increased with increasing pressure.

Analysis of Energy Balance. Equation 1 shows the methoxymethane steam reforming is endothermic. In the overall process, unrecovered hydrogen in the membrane can be combusted, and the enthalpy is used to preheat the reformer feed. The membrane reactor can provide a solution for this by the coupling of the endothermic methoxymethane steam reforming and the exothermic oxidation of the remaining exit gases from the reactor. To simplify the calculation, we have assumed the methoxymethane is completely converted to H_2 and CO_2 according to eq 1. The H_2 that did not permeate through the Pd−Ag−Au−Ni membrane tube goes through the oxidation catalyst bed to undergo complete oxidation as follows

$$H_2 + 0.5O_2 = H_2O \quad \Delta H_r^0 = -242.00\ kJ \cdot mol^{-1} \tag{10}$$

for which $\Delta H_r^0 = -242.00\ kJ \cdot mol^{-1}$. The reactions given in eqs 1 and 10 can be written in the general form

$$\upsilon_A A + \upsilon_B B = \upsilon_L L + \upsilon_M M \tag{11}$$

where A and B are reactions and L and M are products; υ_A, υ_B, υ_L, and υ_M, are the stoichiometric numbers of reagents or products, respectively.

The constant pressure gas heat capacity C_p can be estimated from an empirical expression

$$C_p = a + bT + cT^2 + dT^3 \tag{12}$$

where the parameters a, b, c, and d were obtained from the literature.[28]

The ideal gas standard enthalpy of reaction can be estimated from C_p with

$$\Delta H_{r,T}^0 = \Delta H_r^0 + \int_{298}^{T} \Delta C_p^0 dT \tag{13}$$

where the standard enthalpy at $T = 298.15$ K, ΔH_r^0, defined as the heat difference between the reagents and products, $\Delta_f H_{i,\ 298}^0$ is given by

$$. \qquad \Delta H_r^0 = \sum \upsilon_i \Delta_f H_i^0 \tag{14}$$

The enthalpy of eq 1 $\Delta H_r^0(T, C_2H_6O + H_2O)$ should, if adiabatic, be equal to the enthalpy released by eq 10 of $\Delta H_r^0(T, H_2)$[29,30] to give

$$\Delta H_r^0(T, C_2H_6O + H_2O) = \Delta H_r^0(T, H_2)6\{1 - R(H_2)\} \tag{15}$$

The recovery yield of hydrogen that satisfied the energy balance was determined to be $R(H_2) = 0.88$; that is, the energy efficiency for producing hydrogen from DME was about 88 %.

If the vaporization and feedstock were heated to the reaction temperature by the energy released from eq 10, the enthalpy required for reactants of eq 1 and 10 would decrease. For reactants at a temperature of 298 K heated to the reaction temperature, the required enthalpy was determined from the literature data,[28] where $\Delta H^0(\Delta T, C_2H_6O)$ is the enthalpy to increase the methoxymethane at temperature ΔT; $\Delta H^0(\Delta T, H_2O)$ for water; and $\Delta H^0(\Delta T$, air) for air. Thus, the enthalpy of eqs 1 and 10 should conform to

$$\Delta H_r^0(T, C_2H_6O + H_2O) + \Delta H^0(\Delta T, C_2H_6O) + \Delta H^0(\Delta T, H_2O) + \Delta H^0(\Delta T, \text{air})300/21\{1 - R(H_2)\} = \Delta H_r^0(T, H_2)6\{1 - R(H_2)\} \tag{16}$$

At temperatures between (473 and 533) K, the enthalpies of eq 1 and eq 10 were estimated and listed in Table 1. The energy required for vaporization of the feed was not a major portion of the energy required for methoxymethane steam reforming.

Conclusions

Methoxymethane may be used as an on-board hydrogen storage medium for fuel cell-powered vehicles. In the temperature range of (473 to 573) K, hydrogen permeation through a Pd−Ag−Au−Ni membrane obeyed Fick's first law and the Arrhenius law in two different temperature ranges. A Pd−Ag−Au−Ni membrane reactor packed with ($CuO-ZnO-Al_2O_3-ZrO_2$ + ZSM-5) bifunctional catalysts has been investigated for producing pure hydrogen by steam reforming of methoxymethane at temperatures between (473 and 543) K. The influence of the molar ratio of the feed, temperature, space velocity, and pressure was determined. The membrane reactor gave methoxymethane conversion, hydrogen production, and low carbon dioxide selectivity compared to a fixed-bed reactor. The hydrogen produced was recovered as a CO-free hydrogen stream.

On the basis of the primary analysis of the energy balance, an energy efficiency for producing pure hydrogen from methoxymethane steam reforming was estimated to be about 84.9 %.

Literature Cited

(1) Isono, T.; Suzuki, S.; Kaneko, M.; Akiyama, Y.; Miyake, Y.; Yonezu, I. Development of A High-Performance PEFC Module Operated by Reformed Gas. *J. Power Sources* **2000**, *86*, 269–273.

(2) Ahmed, S.; Krumpelt, M. Hydrogen from Hydrocarbon Fuels for Fuel Cells. *Int. J. Hydrogen Energy* **2001**, *26*, 291–301.

(3) Tanaka, Y.; Kikuchi, R.; Takeguchi, T.; Eguchi, K. Steam Reforming of Methoxymethaneover Composite Catalysts of γ-Al2O3 and Cu-based *Spinel. Appl. Catal. B: Environ.* **2005**, *57*, 211–222.

(4) Faungnawakij, K.; Tanaka, Y.; Shimoda, N.; Fukunaga, T.; Kawashima, S.; Kikuchi, R.; Eguchi, K. Influence of Solid-acid Catalysts

on Steam Reforming and Hydrolysis of Methoxymethanefor Hydrogen Production. *Appl. Catal. A: Gen.* **2006**, *304*, 40–48.

(5) Semelsberger, T. A.; Ott, K. C.; Borup, R. L.; Greene, H. L. Generating Hydrogen-rich Fuel-cell Feeds from Methoxymethane (DME) using Cu/Zn Supported on Various Solid-acid Substrates. *Appl. Catal. A: Gen.* **2006**, *309*, 210–223.

(6) Kawabata, T.; Matsuoka, H.; Shishido, T.; Li, D.; Tian, Y.; Sano, T.; Takehira, K. Steam Reforming of Methoxymethaneover ZSM-5 Coupled with Cu/ZnO/Al_2O_3 Catalyst Prepared by Homogeneous Precipitation. *Appl. Catal. A: Gen.* **2006**, *308*, 82–90.

(7) Semelsberger, T. A.; Ott, K. C.; Borup, R. L.; Greene, H. L. Generating Hydrogen-rich Fuel-cell Feeds from Methoxymethane(DME) Using Physical Mixtures of a Commercial Cu/Zn/Al_2O_3 Catalyst and Several Solid-acid Catalysts. *Appl. Catal. A: Gen.* **2006**, *65*, 291–300.

(8) Faungnawakij, K.; Tanaka, Y.; Shimoda, N.; Fukunaga, T.; Kawashima, S.; Kikuchi, R.; Eguchi, K. Hydrogen Production from MethoxymethaneSteam Reforming over Composite Catalysts of Copper Ferrite Spinel and Alumina. *Appl. Catal. B: Env.* **2007**, *74*, 144–151.

(9) Galvita, V. V.; Semin, G. L.; Belyaev, V. D.; Semilolenov, V. A.; Tsiakaras, P.; Sobyanin, V. A. Production of Hydrogen from Dimethyl Ether. *Appl. Catal. A: Gen.* **2001**, *216*, 85–90.

(10) Yamada, Y.; Mathew, T.; Ueda, A.; Hiroshi, S.; Tetsuhiko, K. A Novel DME Steam-reforming Catalyst Designed with Fact Database On-demand. *Appl. Surf. Sci.* **2006**, *252*, 2593–2597.

(11) Semelsberger, T. A.; Borup, R. L. Thermodynamic Equilibrium Calculations of MethoxymethaneSteam Reforming and Methoxymethane-Hydrolysis. *J. Power Sources* **2005**, *152*, 87–96.

(12) Faungnawakij, K.; Kikuchi, R.; Eguchi, K. Thermodynamic Analysis of Carbon Formation Boundary and Reforming Performance for Steam Reforming of Dimethyl Ether. *J. Power Sources* **2007**, *164*, 73–79.

(13) Kawabata, T.; H.; Matsuoka, T.; Shishido, D Li.; Tian, Y.; Sano, T.; Takehira, K. Steam Reforming of Methoxymethaneover ZSM-5 Coupled with Cu/ZnO/Al_2O_3 Catalyst Prepared by Homogeneous Precipitation. *Appl. Catal. A: Gen.* **2006**, *308*, 82–90.

(14) Tanaka, Y.; Kikuchi, R.; Takeguchi, T. Steam Reforming of Methoxymethaneover Composite Catalysts of γ-Al_2O_3 and Cu-based *Spinel. Appl. Catal. B: Environ.* **2005**, *57*, 211–222.

(15) Semelsberger, T. A.; Ott, K. C.; Borup, R. L.; Greene, H. L. Generating Hydrogen-rich Fuel-cell Feeds from Methoxymethane (DME) using Physical Mixtures of a Commercial Cu/Zn/Al_2O_3 Catalyst and Several Solid-acid Catalysts. *Appl. Catal. B: Environ.* **2005**, *286*, 11–22.

(16) Faungnawakij, K.; Kikuchi, R.; Matsui, T.; Fukunaga, T.; Eguchi, K. A Comparative Study of Solid Acids in Hydrolysis and Steam Reforming of Dimethyl Ether. *Appl. Catal. A: Gen.* **2007**, *333*, 114–121.

(17) Faungnawakij, K.; Tanaka, Y.; Shimoda, N.; Funkunaga, T.; Kawashima, S.; Kikuchi, R.; Eguchi, K. Influence of Solid-Acid Catalysts on Steam Reforming and Hydrolysis of Methoxymethanefor Hydrogen Production. *Appl. Catal. A: Gen.* **2006**, *304*, 40–48.

(18) Agell, J.; Birgersson, H.; Boutonnet, M. Steam Reforming of Methanol over a Cu/ZnO/Al_2O_3 Catalyst: a Kinetic Analysis and Strategies for Suppression of CO Formation. *J. Power Sources* **2002**, *106*, 249–257.

(19) Harold, M. P.; Nair, B.; Kolios, G. Hydrogen Generation in a Pd Membrane Fuel Processor: Assessment of Methanol-Based Reaction Systems. *Chem. Eng. Sci.* **2003**, *58*, 2551–2571.

(20) Jiang, C. J.; Trimm, D. L.; Wainwright, M. S. Kinetic Study of Steam Reforming of Methanol over Copper-Based Catalysts. *Appl. Catal. A: Gen.* **1993**, *93*, 245–255.

(21) Sanq-Jun, P.; Dong-Wook, L.; Chang-Yeol, Y.; Kwan-Young, L.; Kew-Ho, L. Hydrogen Production from a DME Reforming-Membrane Reactor Using Stainless Steel-Supported Knudsen Membranes with High Permeability. *J. Membr. Sci.* **2008**, *318*, 123–128.

(22) Sanq-Jun, P.; Dong-Wook, L.; Chang-Yeol, Y.; Kwan-Young, L.; Kew-Ho, L. MethoxymethaneReforming in a Mesoporous γ-alumina Membrane Reactor Combined with a Water Gas Shift Reaction. *Ind. Eng. Chem. Res.* **2008**, *47*, 1416–1420.

(23) An, Xin.; Ren, F.; Li, J. L.; Wang, J. F. A Highly Active Cu/ZnO/Al_2O_3 Nanofiber Catalyst for Methanol Synthesis Through CO_2 and CO Hydrogenation. *Chin. J. Catal.* **2005**, *26*, 729–736.

(24) An, Xin.; Ren, F.; Li, J. L.; Zuo, Y. Z.; Wang, D. Zh.; Wang, J. F. A. CuO-ZnO-Al_2O_3-ZrO_2 Fibrous Catalyst that is an Improved CO_2 Hydrogenation to Methanol. *Catal. Lett* **2007**, *118*, 264–269.

(25) Kikuchi, E. Membrane Reactor Application to Hydrogen Production. *Catal. Today* **2000**, *56*, 97–101.

(26) Tosti, S.; Basile, A.; Chiappetta, G.; Rizzello, C.; Violante, V. Pd-Ag Membrane Reactors for Water Gas Shift Reaction. *J. Chem. Eng. Data* **2003**, *93*, 23–30.

(27) Feng, D. M.; Wang, Y. Y.; Wang, D. Zh.; Wang, J. F. Steam reforming of methoxymethaneover CuO-ZnO-Al_2O_3-ZrO_2 + ZSM-5: a kinetic study. *Chem. Eng. J.* **2009**, *146*, 477–485.

(28) Daubert, T. E.; Danner, R. P. *Physical and Thermodynamic Properties of Pure Chemicals: Data Compilation*; Hemisphere Publishing Corporation: New York, 1989.

(29) Reid, R. C.; Prausnitz, J. M.; Poling, B. F. *The properties of gases and liquids*; McGraw-Hill Book Company: New York, 1987.

(30) Yu-Ming, L.; Min-Hon, R. Process Development for Generating High Purity Hydrogen by Using Supported Palladium Membrane Reactor as Steam Reformer. *Int. J. Hydrogen Energy* **2000**, *25*, 211–219.

Received for review November 26, 2008. Accepted March 6, 2009. The authors gratefully acknowledge the financial support by the Chinese Ministry of Science and Technology (no. 2005CB221405).

JE8009072