[Regular Paper]

Steam Reforming of Methanol on Ni/Al₂O₃ Catalyst in a Pd-membrane Reactor

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The application of the membrane reactor to steam reforming of methanol was studied as a hydrogen producing reaction. The activities, stabilities and selectivities of Cu/ZnO, Ni/Al₂O₃ and Ru/Al₂O₃ catalysts were tested using a conventional fixed-bed flow reactor. Ni/Al₂O₃ catalyst showed the most stable activity at 723 K but relatively low hydrogen yield because of methanation. However, the hydrogen-permeable membrane reactor suppressed methanation and hydrogen yield was enhanced compared with the conventional reactor. The membrane reactor was more effective at higher temperatures and higher W/F.

Keywords

Membrane reactor, Palladium membrane, Steam reforming, Methanol, Hydrogen production

1. Introduction

Hydrogen is an important material for the chemical industry, particularly in the synthesis of ammonia or methanol, and for hydrodesulfurization in petroleum refineries. Recently, hydrogen has shown great potential as a clean fuel in fuel cell systems. Hydrogen is most economically produced by steam reforming of hydrocarbons, particularly CH₄, using supported nickel catalysts. This reaction is extremely endothermic, so high reaction temperatures, around 1073 K, are required to achieve efficient production of hydrogen and carbon monoxide. Carbon monoxide is then further reformed with steam through the exothermic water gas shift reaction (WGSR) to produce more hydrogen and carbon dioxide.

An alternative route to produce hydrogen is the steam reforming of methanol, which requires much lower temperatures than the steam reforming of hydrocarbons, unless methane is concurrently formed from methanol. Supported Cu-based catalysts are exclusively used for steam reforming of methanol because of the activity at low temperatures around 523 K and absence of methane formation (methanation). The drawback of Cu-based catalysts is the relatively low thermal resistance, which restricts the reaction temperature to 523 K or lower. Consequently the rate of reaction cannot provide the flexible production of hydrogen required in the fuel processor of the fuel cell system. Supported transition metal catalysts are possible candidates for steam reforming of methanol with higher rates of reaction. The problem with transition metal catalysts is the possible formation of CH₄ by hydrogenation of carbon monoxide formed from methanol.

Pd-membrane reactors are effective in steam reforming of methane¹, WGSR², and some other hydrogenforming reactions³, through the shift of the thermodynamic position of the reaction equilibrium (thermodynamic effect). Steam reforming of methanol on a Cubased catalyst is promoted by use of a Pd-membrane reactor⁴). The effect of the membrane is to increase the driving force of the reaction by suppressing the reverse reaction (kinetic effect).

The present study applied the Pd-membrane reactor to steam reforming of methanol on supported Ni and Ru catalysts. Selective removal of hydrogen from the reaction system through the Pd membrane was expected to suppress methanation, and the rate of hydrogen production to be increased by use of these catalysts.

2. Experimental

2.1. Preparation of Hydrogen-permeable Membrane

Palladium composite membranes were prepared using the electroless-plating method, as explained elsewhere⁵⁾. The membrane was completely covered with palladium. Palladium was deposited on a porous alumina tube with an outer diameter of 10 mm and mean pore size of the effective top layer of 200 nm, supplied by NGK Insulators, Ltd. Palladium nuclei were deposit-

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Table 1 Composition of Pd Plating Bath

Material	Concentration
[Pd(NH ₃) ₄]Cl ₂	5.4 g· <i>l</i> ^{−1}
$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	$67.2 \text{ g} \cdot l^{-1}$
NH3(28 wt% aq.)	651.3 m <i>l</i> · <i>l</i> ⁻¹
$H_2NNH_2 \cdot H_2O$	$0.35 \text{ m} l \cdot l^{-1}$

Temperature, 323 K.

Table 2 Composition of Ag Plating Bath

Material	Concentration
AgNO ₃	4.86 g ⋅ <i>l</i> ⁻¹
[Pd(NH ₃) ₄]Cl ₂	$0.54 \text{ g} \cdot l^{-1}$
$C_{10}H_{14}N_2Na_2O_8 \cdot 2H_2O$	33.6 g· <i>l</i> ⁻¹
NH3(28 wt% aq.)	$651.3 \text{ m}l \cdot l^{-1}$
$H_2NNH_2 \cdot H_2O$	$0.35 \text{ m}l \cdot l^{-1}$

Temperature, 323 K.

ed on the outer surface of the tube by sensitization and activation treatments by using alternate aqueous solutions of SnCl₂ and PdCl₂, followed by dipping the tube in an aqueous solution of hydrazine for 1 h. Then palladium was plated on the outer surface of the tube from the electroless-plating bath described in **Table 1**. A palladium thin film of about 20 μ m thickness was prepared after 3 h of electroless-plating. The effective area of Pd plating was 6.28 cm² in the central part of the tube, and the remainder was covered by Ag deposited similarly using the electroless-plating bath described in **Table 2**.

2.2. Catalysts

Cu/ZnO catalyst was supplied by SÜD CHEMIE CATALYSTS CO. Ni/Al₂O₃ catalyst containing 20 wt% Ni was prepared by the coprecipitation method using Ni(NO₃)₂·6H₂O, Al(NO₃)₃·9H₂O and an aqueous solution of ammonia, followed by drying at 373 K for 24 h and calcination at 773 K for 2 h. Ru/Al₂O₃ catalyst containing 3 wt% Ru was prepared by impregnating Al₂O₃ support with an aqueous solution of RuCl₃. The Al₂O₃ support was prepared by precipitating Al(OH)₃ from an aqueous solution of Al(NO₃)₃·9H₂O with an aqueous solution of ammonia, followed by calcination at 773 K for 2 h.

2.3. Catalytic Reaction

Steam reforming of methanol was carried in a double tubular type reactor containing the hydrogen-permeable Pd/alumina composite membrane, as shown in **Fig. 1**. The catalyst was packed between the palladium membrane (length 2 cm) and the outer tube of reactor. The amount of packed catalyst was 0.25 g diluted with SiC. Cu/ZnO and Ru/Al₂O₃ catalysts were reduced in a stream of H₂ at 573 K for 1 h, and Ni/Al₂O₃ catalyst was reduced in a stream of H₂ at 773 K for 3 h. Reaction was carried in the temperature range of 573-



Fig. 1 Membrane Reactor

723 K under atmospheric pressure, with a CH₃OH/H₂O feed of molar ratio 1:1. The permeation side was evacuated by use of a rotary vacuum pump which maintained a permeation side pressure of 10-4 Torr (1 Torr = 133.322 Pa) to lower the partial pressure of permeated hydrogen which was the driving force of hydrogen permeation. The reactor was also operated as a conventional flow reactor without evacuating the permeation side. Reaction products were analyzed by means of a TCD (thermal conductivity detector) gas chromatography using the following separation columns: active carbon for analysis of H₂, CO, CO₂, CH4 and Gaskuropack54 for CH3OH, H2O, both maintained at 373 K.

3. Results and Discussion

3.1. Catalytic Activity and Selectivity

The activity and selectivity of Cu/ZnO, Ni/Al₂O₃ and Ru/Al₂O₃ catalysts were estimated in the conventional flow reactor. The catalytic activity was evaluated by the percentage conversion of methanol.

The catalytic activity and stability of Cu/ZnO are shown in **Fig. 2**. The test was carried out for 4 h at each temperature from 493 K to 623 K in a stepwise temperature rising mode. The catalytic activity was stable for about 4 h below 533 K, slightly deactivated at 573 K and markedly deactivated at 623 K. The deactivation was irreversible, probably due to sintering. These results clearly show that the Cu/ZnO catalyst should be used below 573 K.

Figure 3 shows the variation in the activity of Ru/Al₂O₃ catalyst at 623 K with time on stream. The activity decreased and almost ceased after 30 h. The decrease in methanol conversion on the Ru/Al₂O₃ catalyst resulted in alternative formation of dimethyl ether: 60% of methanol was converted to dimethyl ether after 30 h. The stability of the Ni/Al₂O₃ and Cu/ZnO catalysts at 723 K are compared in **Fig. 4**. Ni/Al₂O₃ catalyst showed more stable activity after about 6 h than Cu/ZnO catalyst. Ni/Al₂O₃ catalyst showed stable



Fig. 2 Stability of Cu/ZnO Catalyst



Temperature, 623 K; W/F, 730 g·min·mol⁻¹.

Fig. 3 Stability of Ru/Al₂O₃ Catalyst

activity above 573 K.

The selectivities of Cu/ZnO and Ni/Al₂O₃ catalysts were evaluated in the conventional reactor. **Figure 5** shows the composition of products produced over the Cu/ZnO and Ni/Al₂O₃ catalysts. Reaction was carried out at the temperature at which each catalyst showed stable activity, 573 K for Cu/ZnO and 723 K for Ni/Al₂O₃. Under these conditions, methanol was almost completely converted, so that the composition of products was determined by the selectivities toward the water-gas shift reaction (1) and the methanation



Temperature, 723 K; W/F, 90 g·min·mol-1.

Fig. 4 Comparison of Stability of Cu/ZnO and Ni/Al₂O₃ Catalysts



W/F, 730 g·min·mol⁻¹; Temperature, 573 K(Cu/ZnO), 723 K (Ni/Al₂O₃).

Fig. 5 Composition of the Product Gas from Cu/ZnO and Ni/ Al₂O₃ Catalysts

reaction (2).

$\rm CO + H_2O \rightleftharpoons \rm CO_2 + H_2$	(1)
$CO + 3H_2 \rightleftharpoons CH_4 + H_2O$	(2)

The product was 70 mol% hydrogen when using Cu/ZnO catalyst, but 29 mol% hydrogen when using Ni/Al₂O₃ catalyst. The difference in H₂ selectivity could be attributed to the production of CH₄, which was not produced on Cu/ZnO, but formed 19 mol% of the product on Ni/Al₂O₃. Therefore, hydrogen was consumed by the methanation reaction on Ni/Al₂O₃ cata

 Table 3
 Effects of Membrane Reactor on Product Yields on Ni/Al₂O₃ Catalyst

 [%]

Reactor	$Y_{\rm H_2}$	$Y_{\rm CO_2}$	$Y_{\rm CH_4}$
Conventional	36.1	14.0	30.1
Membrane	59.4	28.9	11.6

Reaction conditions: temperature, 623 K; W/F, 730 g·min·mol⁻¹.



W/F, 730 g·min·mol⁻¹. \Box , \blacksquare : Cu/ZnO. \bigcirc , \spadesuit : Ni/Al₂O₃. \Box , \bigcirc : in conventional reactor. \blacksquare , \spadesuit : in membrane reactor.

Fig. 6 Effect of Reaction Temperature on H₂ Yield

lyst.

3. 2. Steam Reforming of Methanol

3.2.1. Relationship between Hydrogen Yield and Reaction Temperature

The reaction products formed on the Ni/Al₂O₃ catalyst at 623 K in the conventional and membrane reactors are shown in **Table 3**. The membrane reactor promoted formation of more CO₂ and less CH₄ and consequently promoted production of hydrogen. The promotion of the water-gas shift reaction and suppression of the methanation reaction by selective removal of hydrogen through the membrane are reflected in the product composition.

The promotion of H₂ production by use of the membrane reactor is illustrated in **Fig. 6** as a function of reaction temperature. Reaction on Cu/ZnO catalyst at 573 K gave a higher hydrogen yield in the membrane reactor than in the conventional reactor. Therefore, the membrane reactor is also effective for steam reforming of methanol on Cu/ZnO catalyst, as previously reported⁴). The membrane reactor promoted hydrogen production on Ni/Al₂O₃ catalyst at all temperatures tested as shown in **Fig. 6**. The hydrogen yield in the membrane reactor increased with increasing reaction temperature, but decreased with increasing

Table 4Effects of Reaction Temperature on the Yield of CH4in the Conventional Reactor

Temperature [K]	Y _{CH4} [%]	
623	30.1	
673	48.8	
723	56.1	



Fig. 7 Effect of Temperature on H₂ Flux through Pd Membrane during Steam Reforming of Methanol over Ni/Al₂O₃ Catalyst

reaction temperature in the conventional reactor, in which methanation was accelerated at higher temperatures. **Table 4** shows the yield of CH_4 in the conventional reactor. Methanation is an exothermic reaction, but the reaction did not reach equilibrium under the conditions tested, causing the CH_4 yield to increase at higher reaction temperatures.

Figure 7 shows the hydrogen flux and hydrogen removal ratio in the membrane reactor as a function of reaction temperature. The hydrogen removal ratio was defined as the ratio of permeated hydrogen through the membrane to the total amount of produced hydrogen. The hydrogen flux increased with increasing temperature and the hydrogen removal ratio also increased. These results can be explained by considering the combined effects of increasing permeability of hydrogen and increasing hydrogen production rate with the increase in temperature. If more hydrogen is removed from the reaction system, the kinetic effect more strongly promotes the reaction. The largest hydrogen removal ratio (about 95%) was attained at 723 K, resulting in a 76% yield of hydrogen.

3. 2. 2. Relationships between Hydrogen Yield and *W/F*

Relationships between the hydrogen yield and W/F



Fig. 8 Effect of *W/F* on H₂ Yield during Steam Reforming of Methanol over Ni/Al₂O₃ Catalyst

are shown in **Fig. 8**. The reaction temperature was 723 K, which enables high permeability of hydrogen. W/F was adjusted by changing the feed rate of reactants. The increase in hydrogen yield was not observed in the membrane reactor when the W/F was smaller.

Total amounts of produced hydrogen, permeated hydrogen, and the hydrogen removal ratio in the membrane reactor are shown in **Fig. 9** as a function of *W/F*. Total amounts of produced hydrogen increased with decreasing *W/F*. However, permeated hydrogen little increased, so that the removal ratio decreased. These results indicate that the membrane reactor effectively promotes the reaction when *W/F* is greater than 240 g·min·mol⁻¹ under these conditions.

4. Conclusions

This study found the following results.

(1) Cu/ZnO was deactivated above 573 K, and Ru/ Al_2O_3 was deactivated at 623 K, whereas Ni/ Al_2O_3 showed stable activity at 723 K.



Fig. 9 Effect of *W/F* on the Amount of Hydrogen Produced and Hydrogen Removal Ratio during Steam Reforming of Methanol over Ni/Al₂O₃ Catalyst at 723 K

(2) Although Ni/Al₂O₃ was active for methanation, the water-gas shift reaction was promoted and methanation was suppressed by use of the membrane reactor, so that a high hydrogen yield was attained.

(3) Reaction in the membrane reactor yielded hydrogen more effectively at higher temperatures, although hydrogen permeation was limited at small W/F values, reducing the effect of the membrane reactor.

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要旨

パラジウムメンブレンリアクターにおける Ni/Al2O3 触媒上でのメタノール水蒸気改質

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水素製造を目的としたメタノール水蒸気改質へのメンブレン リアクターの適用を検討した。触媒にCu/ZnO,Ni/Al₂O₃,Ru/ Al₂O₃を用い,固定床流通系反応器にて触媒活性,安定性の検 討を行った。これらの触媒の中でNi/Al₂O₃触媒は723Kにお いても安定した活性を示したが,メタネーション反応が起こる ことにより水素収率は低かった。そこで Ni/Al₂O₃ を用いた反応系に水素透過型メンブレンリアクターを適用すると水素収率 は増加した。また、メンブレンリアクターの効果は高温、高 W/F 条件ほど大きかった。

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