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The rate enhancement of methanol steam reforming reaction in a membrane catalytic reactor

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Abstract

Steam reforming reaction of methanol was carried out with commercial G66B catalyst (CuOZnO) and with two modified catalysts, 1% Pd/G66B and 1% La_2O_3/G66B at a temperature of 270, 310 and 350 °C under a pressure of 0.1, 0.4 and 0.9 MPa absolute pressure. The space velocity ranges from 427 to 460 h^{-1} to allow the conversion level small between 3 and 17 mol%. Similar reactions rate studies were carried out with the catalytic reactor inserted with a palladium membrane tube at 310 °C and 0.9 MPa absolute pressure. It was found that the reaction rates in the catalytic membrane rector (CMR) were 50–100% faster than the corresponding reaction without the Pd-membrane in the reactor. Likewise, rate enhancement was also observed in the steam reforming reactions of *n*-hexane at 500 °C under an absolute reaction pressure of 0.9 MPa.

The rate enhancement by the use of Pd-membrane is attributed to the reverse hydrogen spillover from the catalyst sites to the palladium surface of membrane; this hydrogen spillover enables the hydrogen occupancy on the catalyst sites to be shortened and become more efficient for catalytic turning over. Since the observed rate enhancement takes place in the forward reaction, it is proposed that the general phenomena of higher reaction conversion by the use of catalytic membrane reactor is a result of speed up forward reaction rate not the reduced backward reaction rate as generally proposed in the literature.

Keywords: Catalytic membrane reactor; Spillover; Rate enhancement; Steam reforming; Methanol; *n*-hexane; Hydrogen

1. Introduction

With the deployment of hydrogen energy stepping up, the steam reforming of methanol is receiving greater attention for its simplicity in operation, compact in plant layout and lower capital investment [2]. An onsite production of hydrogen is particularly attractive to overcome the high cost of shipping and storage. A membrane assisted catalytic membrane rector (CMR) for the steam reforming of methanol is of greater potential in the near future because this further simplifies the operation and reduces the plant space. Compared with a regular catalytic reactor (RCR) for the stream reforming reaction (SRR), it produces high purity hydrogen directly from the CMR without any external purification facilities and boosts up the reaction conversion level at a lower reaction temperature.

In an endothermic reaction like SRR, incorporation of a palladium membrane is known to lead higher conversion than that allowed by the thermodynamic equilibrium [3]. We found that the conversion level of methanol remains quantitative even with 10-fold shortening of space velocity in our previous study [4]. The higher conversion level is often attributed to the intrinsic removal of product hydrogen reducing the rate of reverse reaction by the decrease of product partial pressure. The conversion level in most of methanol SRR assisted with palladium membrane was generally very high approaching its equilibrium state [2]. Therefore, any reduction of reverse reaction rate will have a significant contribution to the actual level of conversion. Normally, shortening of the space velocity brings about a decrease of the conversion level by a decrease of product

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formation as we actually observed in the SRR of methanol without membrane. Shortening of space velocity without changing the quantitative conversion level of the reaction in the presence of Pd-membrane is indicative of its higher rate of product formation by the membrane. Therefore, the above shortening of the space time may also be attributed to an increase of the forward reaction rate.

To minimize the interference of the reverse reaction on the rate measurement, a rate measurement under a low conversion level would yield mainly a forward reaction rate, and would provide a clue to understand the origin of higher conversion by Pd-membrane. We present here our study of rate measurement of SRR and methanol from a series of reactions conducted under a conversion level of 3–15% at 270, 310 and 350 °C under a reaction pressure of 0.1–0.9 MPa. We also prepared 1% Pd-doped copper catalyst to promote hydrogen spillover on the copper catalyst to compare its effect on the SRR with and without a membrane. In a parallel study with steam reforming reaction of *n*-hexane at 500 °C, the reaction rates were measured under an absolute pressure of 0.9 MPa with and without a palladium membrane tube inserted into the catalyst bed. In both these two series of SRR, we observed rate enhancement of 50–260% not only by the Pd-doped catalysts but also by the use of palladium membrane in the catalytic reactor. The observed rate enhancement by the Pd-membrane is attributed to the spillover of the chemisorbed hydrogen atom from the catalyst site to the Pd-membrane surface permeating out of the system.

2. Experimental

2.1. Palladium membrane tube

Thin Pd-membrane supported on a 9.525 mm o.d. × 30 mm length porous stainless steel tube [0.2 μm, purchased from Mott Filter Co.] was provided by Green Hydrotec Co. of Taipei, Taiwan [reimh@ethome.net.tw] The Pd-membrane tube had a membrane surface of 12 cm^2 (9.575 mm o.d. × 30 mm length) and a thickness of 21 μm. The Pd-membrane was leak tested with nitrogen and carbon dioxide and showed no leakage under a pressure of up to 0.9 MPa absolute, and had a hydrogen flux of 8–15 $m^3/m^2\,h\,atm^{1/2}$.

2.2. Preparation of 1% Pd/CuOZnO catalysts

An industrial CuOZnO catalyst (G66B of Süd-Chemie Catalysts, Japan, Inc., with a composition of 30/60/10% of $CuO/ZnO/Al_2O_3$) was used as the reference catalyst for the rate study and for preparation of the above two catalysts by the incipient wet technique. Palladium chloride (76.4 mg $PdCl_2{\cdot}H_2O$ of Strem Chemicals Co., US) was dissolved in 0.9 cc of DI water and was added onto the 8–10 mesh sized copper catalyst drop wise. After drying under IR lump at 100 °C for 3 h and calcined from room temperature to 350 °C at a heating rate of 2 °C/min and held at 350 °C under a gas mixture of $N_2/H_2 = 9$ for 5 h to expel residual chlorine. The variation of the surface properties of these catalysts (BET area by ASAP2000 of Micromeritics Co.) are presented in Table 1. The surface copper area was measured by the selective oxidation of N_2O [5] followed by hydrogen reduction of the surface copper [6], and their variation caused by the SRR are shown in Table 2.

2.3. Rate measurement

The rate was measured with a tubular reactor of 27 mm i.d. × 460 mm length stainless steel tube in an electric furnace of 1500 W. Methanol was pumped with a metering pump (model: AA-100-S of Eldex Lab., Inc., US.) and preheated in a pre-heater to a reaction temperature by heating tape. The reactor was thermo stated at the desired reaction temperature and the reaction pressure was set by a back pressure controller. Catalyst was placed at the center portion of three heating zones and was fixed with glass sphere and glass wool layers. In the case of membrane assisted reaction, the membrane tube (9.525 mm o.d. × 30 mm length with a membrane area of 0.0009 m^2) was inserted from the top of the reactor to the center of catalyst section; in the conventional reactor without the palladium membrane, a similar stainless steel tube was used to simulate the thermal effect of the membrane tube. The membrane tube used in the kinetic study of methanol SRR had a permeance of 8 $m^3/m^2\,h\,atm^{1/2}$.

Table 1
Surface property of CuOZnO catalysts

Catalysts	Treatment	BET area (m^2)	Average pore diameter (Å)	Pore volume (cc/gm)
G66B CuOZnO	A	52(36)	90 (176)	0.195 (0.159)
	B	29	220	0.162
	C	38	183	0.178
1%Pd on G66B	A	38	175	0.160
	B	34	169	0.142
	C	37	185	0.172

A, the original catalyst was reduced with hydrogen at 350 °C for 3 h. (The original oxide catalyst without hydrogen reduction.); B, the catalyst was subjected to 6 h of methanol steam reforming reaction at 310 °C under pressure ranging from 1 to 9 bars; C, the catalyst was subjected to the same treatment of B except that a Pd-membrane was inserted in the reactor.

Table 2
Variation of surface copper area during reforming reaction of methanol

Catalysts	Modes of treatment[a]	Surface area of copper[b] (m^2/gm)	Exposed (%)	Average surface size of Cu grain[c] (Nm)
G66B CuOZnO	A	47	7	15
	B	26	4	26
	C	34	5	20
1% Pd on G66B	A	35	5	20
	B	29	4	24
	C	33	5	21

[a] The treatments of these catalysts are described in Table 1.

[b] The surface copper area was measured by the quantity hydrogen reduction after N_2O oxidation; this gave the site numbers and the copper surface area by assuming H/Cu = 1.0 and 0.07 m^2/Cu atom from 1.47×10^{19} Cu atoms/m^2.

[c] The average grain size of copper on the catalyst surface was calculated by 6(grain volume/grain surface area) with an equation of $[d_{Av} = 6V/(SA) = 6(\pi d_{Av}{}^3/6\pi d_{Av}{}^2) = 6ANM\rho/(2B\rho(1/1.47 \times 10^{19})) = 0.5A/B]$, A and B are the quantities of hydrogen titration before and after N_2O oxidation, respectively; whereas N, M and ρ are Avogadro's number, atomic weight and density of copper, respectively.

Prior to the reaction, the catalyst (0.51 gm) was activated under a gas stream of $N_2/H_2 = 9$ for 5 h at 350 °C. In a typical run, the sampling of reaction products was initiated at about 30 min after the desired temperature became steady. Water and methanol in a molar ratio of $H_2O/MeOH = 1.25$ was pumped into the preheating coil and then the reactor; the weight of the feed was adjusted to the desired space velocity, WHSV = 426.5 to 460 h^{-1}. The sample was analyzed by a GC (Shimadzu GC-14B equipped with TCD and FID). A control reaction was checked with an empty reactor incorporating the palladium membrane; there was no visible sign of conversion under the given reaction conditions.

3. Results and discussion

As shown in Table 1, doping of 1% Pd resulted in a decrease of copper surface area and pore volume, percent exposed and grain size as shown in Table 2. This was attributed to the growth of copper grain and plugging of that micropore by palladium. When the catalyst was doped with 1 wt.% of Pd, the copper surface area became 35 m^2/gm from the original copper surface area of 47 m^2/gm on G66B as measured by N_2O titration. However, the incorporation of Pd-dopant on copper catalyst and of a Pd-membrane in the reactor appeared to stabilize the surface character of the copper catalyst after the catalyst was exposed to the thermal treatment of reaction condition about 20 h under 270–350 °C. The active copper surface area of the parent G66B catalyst decreased from 47 to 26 m^2/gm while that of 1% Pd/G66B decreased only from 35 to 29 m^2/gm during this thermal treatment. In the presence of Pd-membrane the decrease of Cu-surface area or growth of its grain size appeared to slow down further than without the presence. The cause of this stabilization by the incorporation of Pd-dopant is not clear; one of possibility would be the higher melting palladium crystal playing a role of texture promoter preventing the coalescent of copper crystallites.

SRR of methanol was conducted in a RCR with a commercial copper-zinc catalyst and two other modified G66B catalysts, 1%Pd-doped G66B and 1%La_2O_3/G66B at 270 °C, 310 °C and 350 °C and $H_2O/CH_3OH = 1.25$. The space velocity was set at WHSV = 426.5, 443 and 460 h^{-1} to control the level of conversion between 4 and 18 mol% under a reaction pressure of 0.1, 0.4, 0.9 MPa. Under such low conversion levels, their reaction rates and turnover frequency (TOF) were measured together with the corresponding activation energy. The dissociative chemisoption of methanol was reported to the rate determining step of methanol SRR; the methoxyl moiety undergoes rapid cleavage of C–H bond to form a formyl group as an intermediate. The intermediate combines with water or methanol to form formic acid or methyl formate, respectively, and dissociates into carbon dioxide and hydrogen [7,8]. The kinetic study was reported by Trimm [9] and Peppley [10] to be first order with respect to methanol and zero order to water. The results of rate measurements are shown in Table 3. Here the rate of palladium and La_2O_3-doped catalyst showed a lower reaction rate than the parent catalyst. In the case of rate with 1% Pd/G66B catalyst, it could be attributed to its decrease of BET surface area and the active copper surface area; therefore, the TOF of these rate constants were calculated and the results are tabulated in Table 4.

In the RCR under a reaction pressure of 0.9 MPa absolute without membrane, the reaction rate constants of $k = 49 \times 10^{-3}$, 151×10^{-3} and 245×10^{-3} s^{-1} or TOF of 13.88E-23, 42.86E-23 and 69.53E-23 s^{-1} were obtained at 270, 310 and 350 °C, respectively. And an activation energy of 57 kJ/mol were obtained with the parent G66B catalyst. The corresponding rate constants and TOF of 1% Pd/G66B were 85×10^{-3}, 136×10^{-3} and 162×10^{-3} s^{-1} and 32.38E-23, 51.84E-23, and 61.77E-23 at 270, 310 and 350 °C, respectively. Interestingly the 1% Pd/G66B catalyst had smaller activation energy of 22.9 kJ/mol. By comparing the TOF of G66B and TOF of 1% Pd/G66B, there is a significant increase in TOF by the doping of palladium on the parent catalyst. The cause of this Pd-doping on the rate of SRR is believed to be the result of reverse hydrogen spillover of the newly formed hydrogen atoms from the copper sites to the palladium sites; this hydrogen spillover phenomenon will be discussed later together with the effect of Pd-membrane on the rate.

Table 3
Rate constants of methanol steam reforming reactions without Pd-membrane

Catalyst temperature (°C)	Pressure (MPa)	G66B k (10^{-3} s^{-1})	1% Pd G66B k (10^{-3} s^{-1})	1% La_2O_3 G66B k (10^{-3} s^{-1})
270	0.1	61	127	53
	0.4	40	102	35
	0.9	49	85	23
310	0.1	158	188	146
	0.4	157	163	140
	0.9	151	136	134
350	0.1	262	199	256
	0.4	282	179	244
	0.9	245	162	243
K_O[a]	0.9	1.62×10^4	14.0	3.02×10^6
ΔE_a (kJ/mol)[a]	0.9	57.0	22.9	83.7

[a] $k = K_O e^{(-E_a/RT)}$

Table 4
Turnover frequency (TOF) of the steam reforming reaction of methanol[a]

Catalyst temperature (°C)	Pressure (MPa)	G66B[b] TOF (10^{-23} s^{-1})	1% Pd G66B[c] TOF (10^{-23} s^{-1})
270	0.1	17.28	48.44
	0.4	11.36	38.84
	0.9	13.88	32.38
310	0.1	44.83	71.63
	0.4	44.56	62.11
	0.9	42.86	51.84
350	0.1	74.36	75.85
	0.4	80.00	68.23
	0.9	69.53	61.77

[a] TOF was calculated by k/Cu sites and 1.47×10^{19} Cu atoms/m^2 was used [z].

[b] Total active copper surface area of G66B catalyst was calculated by 0.51 (gm) × 47 (m^2/gm Cu) = 23.95 m^2.

[c] The active Cu-surface area of 1% PdG66B was calculated by 0.51 × 35 = 17.85 m^2.

In order to evaluate the effect of having a Pd-membrane tube on the SRR of methanol, the reaction temperature of 310 °C and pressure of 0.9 MPa were chosen for comparison with G66B and 1% Pd/G66B catalysts. The membrane tube was inserted in the copper–zinc catalyst zone for the reaction as reported before [3]. For this comparison, an empty stainless steel of the same size was also inserted in conventional reactor as a substituent of the membrane tube to simulate the heat transfer effect. With the Pd-membrane in the catalytic reactor, the corresponding rate constants increased to $k = 221 \times 10^{-3}$ and 278×10^{-3} for G66B and 1% Pd/G66B catalysts clearly, there are rate enhancements of 221/151 = 1.46 and 278/136 = 2.04 time for G66B and 1% Pd/G66B catalysts, respectively. Table 5 summarizes the results.

In another series of similar experiments with SRR of n-hexane with a nickel/alumina catalyst (G56H-1 of Süd-Chemie Catalysts Japan, Inc., 0.4% K_2O, 17% Ni/α–Al_2O_3) and a home made catalyst of 1% K_2O, 15%Ni/γ–Al_2O_3 at 500 °C under an absolute pressure of 0.9 MPa with VHSV ranging from 20,000 to 80,000 h^{-1}, the rate constant of $k = 3.26 \times 10^{-3}$ mol/g s was obtained. When the reaction was carried out with a palladium membrane inserted into the catalyst bed, the corresponding rate constant was increased to 5.49×10^{-3} mol/g s. Again there is a 5.49/3.26 = 1.68 time rate enhancement by the incorporation of palladium membrane in the catalytic reaction when the palladium membrane is surrounded with the catalyst for the reaction. As mentioned above, the rate measurement was carried out at very low conversion level; it would practically have very little interference from the reverse reaction. Therefore, the observed rate constants were mainly a measure of the forward reaction rate.

Hydrogen spillover from a metal sites to its surrounding oxide sites has been known to play an important role in the catalysis [11,12]. The hydrogen spillover thus increases hydrogen chemisorption capacity higher than H/M relationship. Miller et al. [13] reported TPD study of hydrogen chemisorption on Pt/H-LTL zeolite with H/Pt = 4.3. The yellow WO_3 was reduced with hydrogen at room temperature when it was mixed with Pt/Al_2O_3 catalyst which

Table 5
The effect of Pd-membrane on the steam reforming reaction rates of methanol and n-hexane under 0.9 MPa reaction pressure

Reactants	Catalysts	Without Pd-membrane		With Pd-membrane	
		k (10^{-3} s^{-1})	Relative rate	k (10^{-3} s^{-1})	Relative rate
Methanol 310 (°C)	G66B	151	1.00	228, 213	1.46 (average)
	1% Pd/G66B	136	1.00	278	2.04
n-hexane 500 (°C)	1% K_2O, 15% Ni/γ–Al_2O_3	3.26	1.00	5.49	1.68

facilitated the migration of hydrogen adatoms from platinum sites to tungsten oxide for reduction. [14]. Metal on a metal oxide supported catalyst often desorbs its hydrogen adsorbate from the oxide site to lower its desorption energy through reverse hydrogen spillover. Eguchi et al. [15] reported a higher temperature TPD peak on Ru/Al_2O_3 catalyst. In dehydrogenation of cyclohexane to benzene with active carbon, addition of transition metal accelerates the reaction rate considerably; this is caused by the reverse spillover of the intrinsic hydrogen product from the carbon site to the metal site [16]. Zinc oxide is particularly effective in promoting hydrogen spillover between transition metal and zeolite or other metal oxides [17] and in methanol synthesis using copper/zinc catalyst [18,19]. Finally Eguchi et al. [15] also reported an enhanced hydrogen flux through Pd, Pt or Ru modified porous alumina membrane.

With the literature background above, one would readily expect that Pd-doped copper–zinc catalyst would speed up the removal of hydrogen atom from its copper site, which is a poor site for hydrogen desorption, to a more facile Pd-site for desorption to molecular hydrogen via reverse hydrogen spillover. This is indeed the case shown in this study that all the Pd-modified CuOZnO catalysts showed higher TOF than the parent copper catalyst does. We were surprised to find that catalyst deteriorated slower with the palladium doping or the use of Pd-membrane as indicated by the change of surface area and the size of copper grain presented in Tables 1 and 2. We had no sound explanation to account for this observation. An interesting observation is the lowering of activation energy by the doping of palladium on copper catalyst; the rapid removal of hydrogen adatoms and refreshing of copper sites by reverse hydrogen spillover may have improved the efficiency of copper sites to make its activation energy lower since the activation energy of hydrogen spillover in Pt/SiO_2 was reported to be only in the order of 1 kcal/mol [8].

In the presence of Pd-membrane, the above hydrogen spillover is further stretched to the membrane surface and permeates out of the system. During this surface migration, the adatoms remains in atomic structure without changing into molecular stage as it is required in the parent catalyst (RCR). In a CMR, the hydrogen adatoms permeate directly from high pressure side of the membrane to the low pressure side of membrane and departs as H_2 out of the system; this departure of hydrogen atom from an active catalyst site to the other side of membrane is irreversible and driven by the pressure difference on the two sides of the membrane. The hydrogen adsorbate on the copper site may find it is ‘‘cheaper’’ to pay the 1 kcal/mol cost to spillover from a poor copper site to a more efficient palladium site or palladium membrane; otherwise, the product hydrogen atom would have to pay a higher energy cost of 10–25 kcal/mol for desorption from the copper site [20]. In the case having a Pd-membrane, there is an additional driving force of pressure differential and irreversibility of the migration steps to revitalize the catalyst site for new chemisorption. Because of the facile surface migration of adatoms and the requirement of low activation energy, hydrogen spillover or reverse spillover builds a kinetic bridge linking a poor catalyst site to a more efficient catalyst or to a Pd-membrane surface, brings about a rate enhancement. A similar observation of hydrogen spillover from a catalyst to a membrane was reported by Küssner and Bunsenges [21]. Küssner found that when palladium black catalyst was used to contact a bright surface palladium membrane, hydrogen permeation was able to reach its gas–solid equilibrium at a temperature well below 0 °C; without the palladium black, however, he was unable to reach the equilibrium even at 120 °C. He attributed this result to the action of ‘‘hydrogen transfer catalyst’’ speeding up the chemisorption of hydrogen on the palladium membrane.

Such rate enhancement in the forward reaction of the above SRR is believed to be the major contributor to the observed increase of the reaction conversion when membrane is incorporated into a catalytic reactor. The traditional rationalization that the decreased partial pressure of product hydrogen fraction reducing the backward reaction rate accounts for the increased reaction conversion over thermodynamic equilibrium control is incompatible with our study. Moreover, we had invariably found that the partial pressure of hydrogen in the product mixture is either increase or unchanged by the incorporation of the palladium membrane.

4. Conclusion

Our kinetic study of the SRR of methanol and *n*-hexane with very low conversion level revealed a rate enhancement. Under such low conversion level, the measured rate enhancement is from the increase of the forward reaction rate. We believe that this is the first report in literature that a palladium membrane can bring about not only a higher reaction conversion but also a rate increase in the forward reaction rate. The hydrogen spillover plays a kinetic bridge linking the catalyst site to the Pd-membrane surface and makes the active sites more efficient for reuse by the second reactant molecule to speed up the forward reaction rate. Because of the much smaller backward rate, this enhanced forward reaction rate also increases the hydrogen partial pressure in the mixture. Therefore, the traditional rationalization that the increased reaction conversion is brought about by the slower backward reaction rate arising from the decreased partial pressure or concentration product is incompatible with our observation.

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