

ULTRA-RAPID SYNTHESIS OF SYNGAS BY THE CATALYTIC REFORMING OF METHANE ENHANCED BY *IN-SITU* HEAT SUPPLY THROUGH COMBUSTION

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Abstract – Development in highly active catalysts for the reforming of methane with CO₂ and partial oxidation of methane was conducted to produce hydrogen and carbon monoxide with high reaction rates. An Ni-based four-components catalyst, Ni-Ce₂O₃-Pt-Rh, supported on an alumina wash-coated ceramic fiber in a plate shape was suitable for the objective reaction. By combining the catalytic combustion of ethane or propane, methane conversion was markedly enhanced, and a high space-time yield of syngas, 25,000 mol/l·h was obtained at a catalyst temperature of 700 °C or furnace temperature of 500 °C. The extraordinary high space-time yield of syngas was also confirmed even under the very rapid flow rate conditions as a contact time of 3 m-sec by using a monolithic shape of catalyst bed without back pressure.

Key words: Ni-based Catalyst, Methane Reforming, Milli-second Reaction, Catalytic Combustion, On-site Heat Supply

INTRODUCTION

Synthesis of high quality liquid fuels from alternative carbon-containing lower valued resources is strongly expected recently. Especially, conversion of light, clean, and easily handled resources such as natural gas, associated gas, gaseous hydrocarbons produced during the course of petroleum refinery, and even carbon dioxide into more valuable compounds are now regarded as the relief technology before the ultimate development of coal conversion technologies. However, indispensable conditions for the effective conversion of chemically stable compounds such as CH₄ and CO₂ must be the rapid conversion rate and the minimal energy consumption, and both of them has not been realized yet.

The major conventional production method of H₂ is the steam reforming of saturated hydrocarbons, in particular natural gas or methane on the stabilized Ni catalyst, in which Ni is ventured to sinter and supported on the ceramic carrier having a very low surface area, and the reaction is operated at a high temperature around 900 °C. Since the coke deposit owing to the decomposition of methane is unavoidable, and in order to moderate the coke deposit, a larger concentration of steam than that needed from the reaction stoichiometry is added in the feed. Consequently, the energy and economic load in the process are heavy and the objective reaction is markedly retarded by the predominant covering of the coke on the most active sites. Furthermore, the activity of the catalyst is so low that CO once formed by steam reforming of CH₄ is successively converted into CO₂ reacting with the excess H₂O

by the water shift reaction. As the conventional catalyst has no ability for CO₂ activation, CO₂ once formed by the shift reaction cannot be converted to other molecules by both the inverse reaction of the shift reaction and the CO₂-reforming of methane. If the catalyst on which no coke formation occurs could be developed, it would be expected that the reaction rate will become so fast even around several hundred °C. The heat to maintain that medium-range temperature could be supplied by the waste heat of large scale facilities of industries.

In our previous study, a highly active methane-reforming catalyst composed of Ni-Ce₂O₃-Pt-Rh has been developed [Inui, 1993]. The catalyst exhibits the high catalytic performance for not only steam reforming but also CO₂ reforming and partial-oxidation reforming with an extremely short contact time around several milli-second without coke formation. These reactions occurred with a contact time of m-sec order correspond to 10⁴ times of the conventional industrial catalyst for steam reforming. Even such a highly active catalyst, the conversion of methane cannot be proceeded beyond the level determined by the reaction equilibrium.

In order to overcome the restriction due to the reaction equilibrium, normally, ceramic membrane is considered to escape the situation [Kikuchi, 1997], however, since the rate of permeability of hydrogen through the membrane is so late that the rapid conversion of methane with the m-sec order contact time cannot be realized.

Another problem to be solved in case of the rapid reforming of methane, is the supply of heat against the large endothermic reaction heat. The reaction rate is easily limited by the resistance of heat transfer to the catalyst bed from the wall of reactor. Too high heating of the reactor accelerates coke deposit on the inner surface of the reactor wall and on

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the catalyst zone near the wall.

In this paper, more practical solution to overcome the restriction in a high reaction rate will be demonstrated by the application of the catalytic combustion on the same catalyst surface to supply heat for compensating the large endothermic reaction heat.

EXPERIMENTAL

1. Catalyst Preparation

For the reforming reaction of methane, Ni-based four-components catalyst, which was coated on ceramic fibers formed into a thin plate shape, was used. The catalyst preparation procedure is as follows; non-woven fabric material Fiberfrax (FF) produced by Toshiba Monofrax was adopted as the support. This support is formed in a plate shape of 1 mm thickness with ceramic fibers of 5-10 mm in diameter, and has a void space of 88 %. Before impregnation of the catalytic components, the Fiberfrax was coated with an alumina layer by 17 wt% to increase the surface area. This was conducted by applying the uniform-gelation method [Inui et al., 1979a]. The FF was immersed in a water-methanol solution of $\text{Al}(\text{NO}_3)_3$, dried and then transformed into gel by treating it with $\text{NH}_3\text{-H}_2\text{O}$ vapor. Nickel-based four component catalyst Ni-Ce₂O₃-Pt-Rh [Inui, 1993] was prepared by the stepwise supporting method [Inui et al., 1979b]. In this study catalysts having composition of 10.0 wt% Ni-5.6 wt% Ce₂O₃-1.1 wt% Pt-0.2 wt% Rh was used. On the alumina coated FF, Rh was firstly supported by the incipient impregnation method, followed by reduction with hydrogen into its metallic state, and then Pt was supported in the same way. It was impregnated with a mixed solution of $\text{Ni}(\text{NO}_3)_2$ and $\text{Ce}(\text{NO}_3)_3$, dried, then thermally decomposed. This was reduced in hydrogen flow up to 400 °C and at that temperature for 30 min.

2. Reaction Method

Reactions were carried out under atmospheric pressure by using an ordinary flow type reactor. The catalyst was punched out in a circular shape of 10 mm diameter, and horizontally packed in a quartz tubular reactor of 10 mm inner diameter. The reaction gas was allowed to flow with a space velocity (SV) of 730,000 h⁻¹ or contact time (CT) of 4.93 m-sec. In order to examine the reactions at much higher SV con-

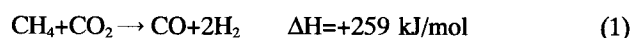
ditions, three catalysts having different shapes, namely doughnut type, rectangular type and cross type, were tested to mitigate the restriction owing to the back pressure. The shapes of the catalysts are depicted in Fig. 1 [Inui et al., 1997]. The reaction gas was allowed to flow for three catalysts with space velocity of 730,000 and 1,095,000 h⁻¹ or contact time of 4.93 and 3.29 m-sec, respectively.

Products were analyzed by two sets of gas chromatographs, Shimadzu GC-8As and an infrared CO₂ analyzer, Shimadzu URA-106. The effect of the catalyst shape was examined using different shapes of the catalyst having a same volume. The space velocity, space-time conversion (STC), and space-time yield (STY) of the products were calculated on the basis of the net catalyst volume subtracted 88 vol% of the channel voids.

RESULTS AND DISCUSSION

1. Effect of Catalytic Combustion with Reforming Reaction

Methane reforming with CO₂ was carried out on the four-components composite catalyst for N₂ diluted and non-diluted reaction gas involving the same molar ratio of CH₄ and CO₂. The results are shown in Fig. 2 by expressing CH₄ conversion as a function of temperature. Evidently, in case of higher concentration of reaction gas, the catalyst-bed temperature was much lower than the furnace temperature owing to the large endothermic reaction as expressed in Eq. (1).



The catalyst exhibited an unusually high activity to the methane reforming with CO₂. Even such a very short contact time, 4.93 m-sec, the reaction progressed according to the reaction stoichiometry, however, of course, at lower temperature range, methane conversion was restricted by the reaction equilibrium.

In order to overcome this situation, the combustion of more easily combustible hydrocarbons such as ethane or propane,

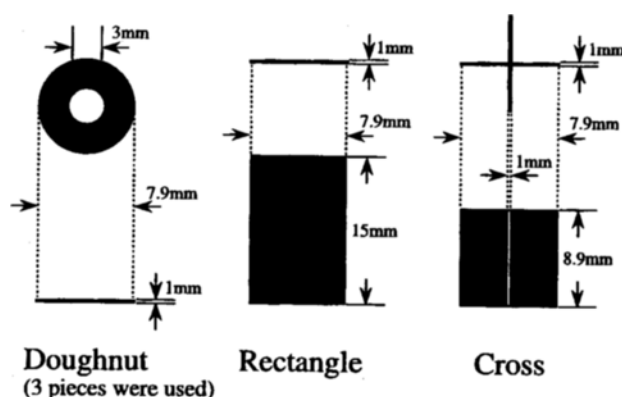


Fig. 1. Shape of the catalysts [catalyst volume (net)=0.01723 ml].

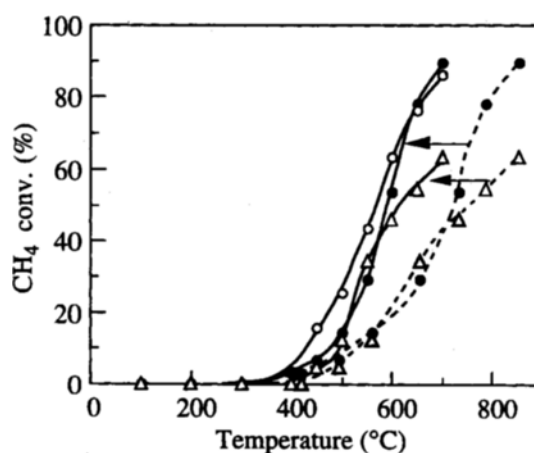


Fig. 2. Change in CH₄ conversion as a function of temperature in CO₂-reforming.

Catalyst: Ni-Ce₂O₃-Pt-Rh; SV: 730,000 h⁻¹; CT: 4.93 m-sec. Dotted line: furnace temperature; Solid line: catalyst-bed temperature. Reaction gas: ○: 10 % CH₄-10 % CO₂-80 % N₂, ●: 35 % CH₄-35 % CO₂-30 % N₂, △: 50 % CH₄-50 % CO₂

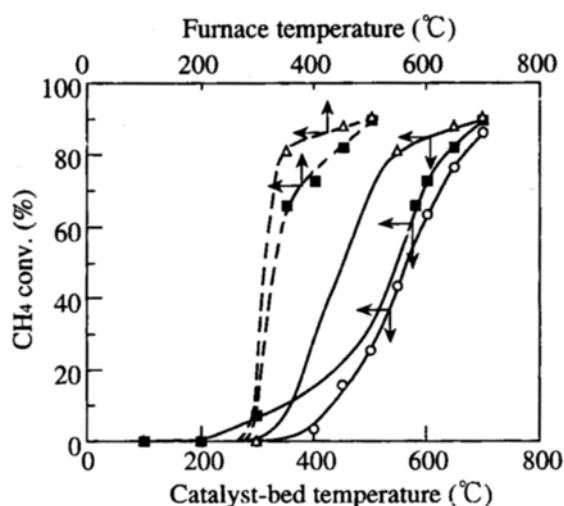
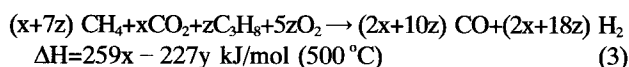
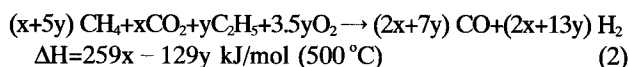


Fig. 3. Effect of combination of ethane- and propane-combustion on the CO_2 -reforming of methane.

SV: 730,000 h^{-1} ; CT: 4.93 m-sec. \circ : without addition 10 % CH_4 -10 % CH_2/N_2 , \blacksquare : ethane added 10 % CH_4 -10 % CO_2 -5 % C_2H_6 -17.5 % O_2/N_2 , \triangle : propane added 10 % CH_4 -10 % CO_2 -3.3 % C_3H_8 -16.5 % O_2/N_2

which are involved in natural gas, was combined by adding these hydrocarbons and oxygen. The aimed reactions to produce only syngas are expressed as the following reaction Eqs. (2) and (3), including heat generation and consumption by combustion and reforming, respectively.



where, elementary reactions for combustion of ethane and propane are as follows;



The results of ethane or propane addition in the CO_2 -reforming of methane are shown in Fig. 3. In contrast with Fig. 2, at very lower furnace temperature such as below 400 $^\circ\text{C}$, the catalyst temperature rose and is maintained at much higher one than the furnace temperature, indicating that by

Table 2. Space-time yield (STY) of hydrogen for the three kinds of catalyst shapes at different space velocities

Packing way of catalyst	SV: 730,000 h^{-1} (CT 4.93 m-sec)		SV: 1,095,000 h^{-1} (CT 3.29 m-sec)	
	CH_4 Conv. (%)	H_2 STY (mol/h·l)	CH_4 Conv. (%)	H_2 STY (mol/h·l)
Rectangle	84.7	8,280	60.8	8,920
Doughnut	77.6	7,590	68.2	10,000
Cross	89.4	8,740	76.4	11,200

Reaction gas: 15% CH_4 -7.5% O_2 -77.5% N_2 at 700 $^\circ\text{C}$.

the on-site heat supply by the combustion, methane conversion was eventually induced at very lower temperature range.

As summarized the results in Table 1, an extraordinary high space-time yield of syngas, as high as 25,000 mol/l·h was obtained.

2. Effect of Catalyst Shape for Ultra-rapid Reforming Reaction

In order to examine the catalyst for the reaction at much higher SV conditions, the shape of catalyst bed was varied to monolithic ones as shown in Fig. 1, and the partial oxidation reforming of methane was carried out as the test reaction. The feed gas composed of 15 % CH_4 and 7.5 % O_2 diluted with N_2 was allowed to flow at space velocities of 730,000 and 1,095,000 h^{-1} or contact times of 4.93 and 3.29 m-sec, respectively. The reaction proceeded stoichiometrically and produced hydrogen and carbon monoxide with an equivalent molar ratio. As summarized in Table 2, the cross type catalyst exhibited the highest conversion of methane among the three kinds of catalyst shape. This results is consistent with the results in which the methanation from CO_2 - H_2 was investigated using three catalysts having different shapes as mentioned above [Inui et al., 1983]. The pressure drop was very small upon using rectangular type or crass type. Therefore, the higher conversion on the cross type catalyst was ascribed to that the mixing diffusion takes place more efficiently and accelerates the reaction. This result suggests the importance of the catalyst shape in rapid reaction and also the potential of this four-components catalyst for super rapid reforming reaction in practical use.

CONCLUSION

The Rh-modified Ni-based four-components composite cat-

Table 1. Effect of added hydrocarbons and space velocity in CO_2 -reforming of methane (catalyst-bed temperature: 700 $^\circ\text{C}$)

Reaction	SV (h^{-1})	Conv. (%)		Reaction degree* (%)		STC (mol/l·h)	STY (mol/l·h)	
		CH_4	CO_2	H_2	CO	CH_4	H_2	CO
Without addition	73,000	66.2	95.7	62.8	41.3	730	1,380	910
	730,000	36.2	98.4	32.9	47.1	3,820	6,920	9,920
Ethane added	73,000	82.2	69.7	73.1	71.3	970	1,720	1,680
	730,000	47.8	44.7	47.5	42.0	5,440	10,800	9,560
Propane added	73,000	80.8	80.0	68.4	70.5	920	1,560	1,600
	730,000	57.3	58.9	56.2	57.5	6,260	12,290	12,580

Reaction gas: without addition 35 % CH_4 -10 % CO_2/N_2 , ethane added 35 % CH_4 -10 % CO_2 5 % C_2H_6 -17.5 % O_2/N_2 , propane added 35 % CH_4 -10 % CO_2 -3.3 % C_3H_8 -16.5 % O_2/N_2 , *calculated based on the reaction of $\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2$.

alyst exhibited a high performance for both CO₂-reforming of methane and combustion of light hydrocarbons. By combining the catalytic combustion of ethane or propane, highly endothermic reforming reaction of methane was markedly induced even at a very low furnace temperature below 400°C, and an extraordinary high space-time yield of syngas was achieved. Furthermore, the way of catalyst packing having a channel structure allowed to progress the reforming reaction in a very high space velocity operation, such as 3 m-sec of contact time. Especially, the cross type catalyst in shape exhibited a higher activity due to the mixing diffusion effect.

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