

Catalytic combustion of natural gas as the role of on-site heat supply in rapid catalytic CO_2 – H_2O reforming of methane

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Abstract

Development in highly active catalysts for the reforming of methane with H_2O , CO_2 , and $\text{H}_2\text{O} + \text{CO}_2$, and partial oxidation of methane was conducted to produce hydrogen with high reaction rates. A Ni-based three-component catalyst such as Ni– La_2O_3 –Ru or Ni– Ce_2O_3 –Pt supported on alumina wash-coated ceramic fiber in a plate shape was very suitable for both reactions. The catalyst composition was set at 10 wt.-% Ni, 5.6 wt.-% La_2O_3 , and 0.57 wt.-% Ru for example, or molar ratios of these components were 1:0.2:0.03. Even with such a low concentration, the precious metal enhanced the reaction rate markedly, and this synergistic effect was ascribed to the hydrogen spillover effect through the part of precious metal and it resulted in a more reduced surface of the main catalyst component. In particular, a marked enhancement in the reaction rate of CO_2 -reforming of methane was observed by the modification of a low concentration Rh to the Ni– Ce_2O_3 –Pt catalyst. Very high space–time yields of H_2 (i.e., 8300 mol/l h in partial oxidation of methane at 600°C with a methane conversion of 37.5%, and 3585 mol/l h in CO_2 reforming of methane at 600°C with a methane conversion of 58%) were realized in those reactions. By combining the catalytic combustion reaction, methane conversion to syngas was markedly enhanced, and even with a very short contact time (10 ms) the conversion of methane increased more than that at 50 ms. The space–time yield of hydrogen amounted to 2,780 mol/l h with a methane conversion of 90% at 700°C. Furthermore, in a reaction of CH_4 – CO_2 – H_2O – O_2 on the four components catalyst, an extraordinarily high space–time yield of hydrogen, 12 190 mol/l h, could be realized under the conditions of very high space velocity (5 ms).

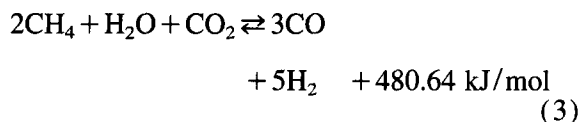
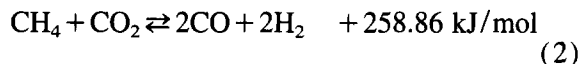
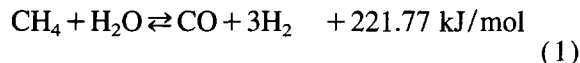
Keywords: Combustion; Natural gas; Methane reforming

1. Introduction

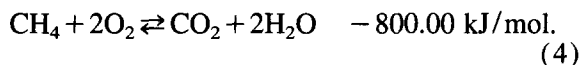
Catalytic hydrogenation of CO_2 is now considered as one of the possible ways to moderate the anxiety on global warming. If CO_2 could be rapidly converted into valuable compounds such as methane, light olefins, and high quality gasoline [1,2], the value of those products would compensate for the cost of expensive hydrogen as the reducing reagent. Hydrogen is now produced on an industrial scale by steam reforming of saturated hydrocarbons, but at a high temperature range

around 900°C; in order to supply the large endothermic reaction heat and to maintain that high temperature, additional CO_2 is evolved by fossil fuel combustion. If a highly active catalyst for methane reforming, which could work at a medium temperature range of around 500–600°C, could be developed, there is a possibility of utilizing the exhaust heat from large scale industries to accelerate the reforming reactions. Another requisite for hydrogen production is that the rate of its production should be comparable to the CO_2 emission from large flues in heavy industries.

Since methane reforming reactions are highly endothermic, expressed as the following Eqs. (1) and (2) or (3) at 500°C,



heat supply to the catalyst bed through the reactor wall cannot follow especially under higher reaction rates. Therefore, in this study, on-site heat supply by combustion of methane using molecular oxygen as in Eq. (4) was tried:



In order to develop novel high active catalysts for the reforming of methane or natural gas not only by H_2O but also CO_2 and/or $\text{CO}_2 + \text{H}_2\text{O}$, the ultra-high active catalyst for oxidation of hydrogen [3] was applied to the standard catalyst for methane reforming reactions. Moreover, modification with a small concentration of Rh was conducted with the expectation of a marked enhancement of the reaction rate through the spillover effect [4].

Much research on CO_2 -reforming has been done recently by many researchers, and reviewed by Nakamura and Uchijima [5] for example. However, many of them [6–11] were concerned with the comparison in catalytic properties of various single component supported metal or metal oxide catalysts and the effect of the sort of support materials upon the performance of catalytic reaction, and the focus was not on the rapid catalytic reaction. As for the rapid catalytic reaction, Schmidt et al. [12] addressed the importance of the experiment and analysis in *ms* order catalytic partial oxidation of methane and light paraffins.

In the present study, the synergistic effect of composite catalysts and the combined reactions to compensate the large amount of endothermic heat

for the rapid synthesis of hydrogen through methane reforming were investigated.

2. Experimental

2.1. Catalyst

In order to reduce the resistance to high flow rates of reaction gases, Fiberfrax (FF), produced by Toshiba Monoflax Co. Ltd., was adopted as the catalysts support. This support is formed in a plate shape of 1 mm thickness with ceramic fibers of 5–10 μm in diameter, and has a void space of 88%. Before impregnation of the catalyst components, Fiberfrax was coated with an alumina layer by 17 wt.-% to increase the surface area as the catalyst support. It was conducted by applying the uniform-gelation method [13], in which a water-methanol solution of $\text{Al}(\text{NO}_3)_3$ was loaded on the support, 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– Ce_2O_3 –Pt–Rh [14] was prepared by the stepwise supporting method [15]. Although the standard composition of the catalyst was set at 10.0 wt.-% Ni, 1/5 atom of Ce, and 1/30 atom of precious metals [16], here, a set of composition 6.6 wt.-% Ni–3.9 wt.-% CeO_2 –2.2 wt.-% Pt–0.20 wt.-% Rh was adopted. On the alumina-coated FF, precious metal, Rh was supported by the incipient impregnation method, followed by reduction with hydrogen to its metallic state, and then Pt was supported in the same way. It was impregnated with a mixed solution of Ni nitrate and Ce nitrate, dried, then thermally decomposed, followed by hydrogen reduction up to 400°C continuing at that temperature for 30 min. In the cases of the other Ni-based three-component catalysts [17] composed of Ni– La_2O_3 and platinum group metals, these were prepared by the same composition method.

2.2. Reaction method

Reactions were carried out under atmospheric pressure by using an ordinary flow type reactor.

Table 1

Effect of Ru combination with Ni–La₂O₃ on catalytic performance in steam reforming of CH₄ and partial oxidation of CH₄

Kind of reaction	Catalyst component	CH ₄ conversion* (%)	Product selectivity (mol.-%)			Space–time yield of H ₂ ** (mol/l h)
			H ₂	CO	CO ₂	
Steam reforming of CH ₄	Ni–La ₂ O ₃	5.5	61.6	0	38.4	13.0
	Ru	5.0	75.2	1.3	23.5	14.5
	Ni–La ₂ O ₃ –Ru	87.3	79.9	13.5	6.61	269
Partial oxidation of CH ₄	Ni–La ₂ O ₃	29.8	0	0	29.8	0
	Ru	16.5	0	0	16.5	0
	Ni–La ₂ O ₃ –Ru	59.2	52.0	40.0	19.1	452

The composition for each catalyst component was as follows: Ni 10.0 wt.-%, La₂O₃ 5.6 wt.-%, Ru 0.57 wt.-%. Feed gas composition: for steam reforming 7.4% CH₄–15.0% H₂O–77.5% N₂; for partial oxidation 28.6% CH₄–14.3% O₂–57.9% N₂. Reaction temperature 600°C, space velocity 115 000 h^{–1}, or contact time 31 ms.

* Equilibrium conversion 87%. ** Moles of hydrogen produced per hour and per liter of the catalyst volume eliminating its super-macro channel space.

The catalyst was punched out in a circular shape of 10 mm diameter, and 1–10 pieces of the catalyst were densely and horizontally packed in a quartz tubular reactor of 10 mm inner diameter. Water vapor as the reaction gas was supplied through a saturator with regulated temperature. Products were analyzed by two sets of gas chromatographs GC-8As and an infrared CO₂ analyzer.

3. Results and discussion

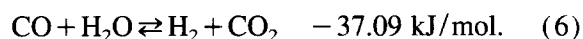
3.1. Effect of precious metal combination with Ni–La₂O₃ on CH₄ reforming reactions

The effect of Ru combination with Ni–La₂O₃ on the steam reforming of methane (Eq. (1)) and partial oxidation of methane (Eq. (5) at 500°C) was



observed at the same reaction temperature, 600°C with a very high space velocity 115 000 h^{–1} or contact time 31 ms. The results are summarized in Table 1 [18]. As the size dimension of the channels in the catalyst belong to a super-macro channel range like ceramic honeycomb matrixes, the inner void of the catalyst was eliminated in the calculation of space velocity (SV) and space–time yield (STY).

As can be clearly seen in Table 1, the activity of the Ni–La₂O₃ catalyst was noticeably low. It was reported that a Ru catalyst supported on Al₂O₃ was highly active in the steam reforming of methane [19], but the quantity of Ru catalyst per unit catalyst volume in this study was very small, and reflecting this, the apparent activity was similar to the Ni–La₂O₃. Furthermore, in the cases of low activity, CO once formed in the steam reforming of methane, successively reacted with water by shift reaction (Eq. (6) at 500°C) producing H₂ and CO₂:



On the other hand, methane conversion on the three-component catalyst markedly increased and reached the equilibrium in this reaction gas composition. Furthermore, selectivity to CO increased and that to CO₂ decreased compared with the Ni–La₂O₃ catalyst and the Ru single component catalyst. The space–time yield of H₂ increased sharply to 269 mol/l h. The reason for this marked difference can be attributed to the state of the catalyst surface, i.e., the surface of Ni–La₂O₃ and Ru was oxidized and resulted in low activity [3]. The Ru parts, which are located in the vicinity but independent of the Ni–La₂O₃ parts, rapidly adsorb hydrogen formed by the reaction. The adsorbed hydrogen is immediately spilt over towards the main catalyst component Ni part, resulting in a

more reduced surface and higher catalytic activity [14].

In the partial oxidation of methane the same effects were seen. On the oxidative surface of Ni–La₂O₃ or Ru, methane could only occasionally burnt catalytically, however, with the combination of Ru, the surface could be maintained in a more reduced state as mentioned above, and the partial oxidation of methane to produce H₂ and CO could predominantly proceed. As a result, STY of H₂ increased suddenly to 452 mol/l h. Part of the CO₂ production could come from CO combustion and/or shift reaction between CO and H₂O. It is also considered that the marked enhancement in the partial oxidation on the three component catalyst attributed to the contribution of the steam reforming by the steam come from the combustion of methane.

The effect of other precious metals on the steam reforming of methane was very similar to the case of Ru [20], and the order of magnitude in enhancing the reaction was as follows:

Rh \approx Pd \approx Ru \approx Ir > Pt.

3.2. Estimation of oxidative-reductive state of catalyst surface during the reaction

In order to evaluate the dynamic state of oxidation-reduction of the catalyst surface during the reaction, partial oxidation of methane was investigated by means of the Forced-oscillating reaction method [21], in which the reaction temperature was increased at a constant heating rate as far as 650°C, and the catalyst then cooled down to 400°C at the same rate.

When the reaction temperature was elevated starting from room temperature, only complete combustion products, CO₂ and H₂O were observed as far as 600°C, and suddenly H₂ and CO were produced above that temperature. When the temperature was decreased, H₂ and CO were produced as far as 400°C. On the other hand, when the feed gas was introduced to the reactor at 300°C, formation of H₂ and CO increased smoothly as far as 650°C, and during the descend-

ing process almost coincided with the ascending process. These results indicate that only the reduced catalyst surface can allow the partial oxidation of CH₄ to form H₂ and CO selectively, and the oxidative surface has little activity and complete oxidation of CH₄ into CO₂ and H₂O occurs. The precious metal assists the reduction of the catalyst surface as the porthole for hydrogen spillover.

3.3. Hydrogen production with extraordinarily high rate through the application of spillover effect in CH₄ partial oxidation

For the rapid conversion of CH₄ to H₂ and CO by partial oxidation on Ni–La₂O₃–Ru catalyst was conducted at a reductive catalytic condition with the maximum space velocity of 575 000 h⁻¹. The feed gas consisted of 86.3% CH₄ and 13.7% O₂ was fed. Space–time yield of H₂ and CO increased approximately in proportion to the space velocity in the range from 57 500 to 575 000 h⁻¹ (or 62.6 ms to 6.26 ms). At 600°C, a surprisingly high space–time yield of H₂, 8300 mol/l h, was obtained.

3.4. Reforming of methane with CO₂ and (H₂O + CO₂)

A reaction gas mixture of 10% CH₄ + 10% CO₂ + 80% N₂ was introduced to the catalyst of Ni–Ce₂O₃–Pt at a space velocity 73 000 h⁻¹ while elevating the reaction temperature from 350°C to 650°C. As shown in Fig. 1, H₂ and CO were formed equally. Both conversions of CH₄ and CO₂ almost coincided with that drawn from the equilibrium, indicating that the reaction progressed stoichiometrically.

In the case of the reaction of CH₄ with CO₂ and H₂O, the result is shown in Fig. 2. The apparent unconverted ratio for CO₂ clearly increased with an increase in the temperature up to ca. 450°C; then decreased sharply above that temperature, and approached the same level as CH₄ at 650°C. The apparent unconverted ratio for methane almost coincided with that drawn from the equi-

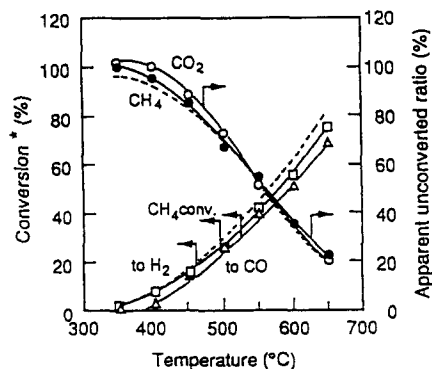


Fig. 1. Effect of temperature on $\text{CH}_4\text{-CO}_2$ reaction. Catalyst, $\text{Ni-Ce}_2\text{O}_3\text{-Pt}$; (10% $\text{CH}_4\text{-10% CO}_2$)/ N_2 ; $\text{SV} = 73\,000\text{ h}^{-1}$. *Conversion was calculated according to the stoichiometry of the reaction: $\text{CH}_4 + \text{CO}_2 \rightleftharpoons 2\text{H}_2 + 2\text{CO} + 258.86\text{ kJ/mol}$. Dotted line: calculated line from the reaction equilibrium.

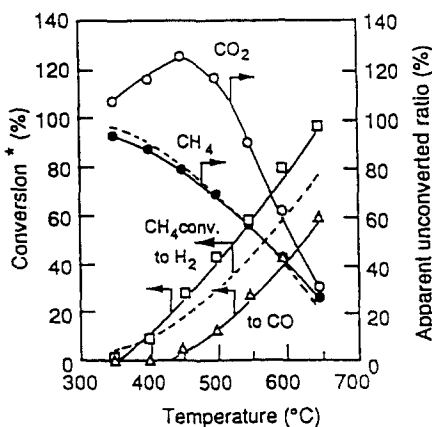


Fig. 2. Effect of temperature on $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ reaction. Catalyst, $\text{Ni-Ce}_2\text{O}_3\text{-Pt}$; (10% $\text{CH}_4\text{-5% CO}_2\text{-7% H}_2\text{O}$)/ N_2 ; $\text{SV} = 73\,000\text{ h}^{-1}$. *Conversion was calculated according to the stoichiometry of the reaction: $2\text{CH}_4 + \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons 5\text{H}_2 + 3\text{CO} + 480.64\text{ kJ/mol}$. Dotted line: calculated line from the reaction equilibrium for the above equation.

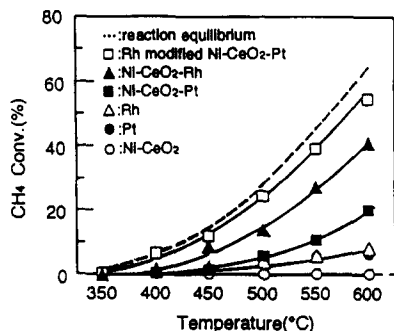
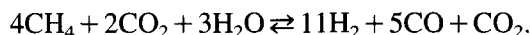


Fig. 3. Effect of Rh modification of the $\text{Ni-Ce}_2\text{O}_3\text{-Pt}$ catalyst on CO_2 reforming of methane. Feed gas: 10% $\text{CH}_4\text{-10% CO}_2\text{-80% N}_2$, $\text{SV} = 730\,000\text{ h}^{-1}$.

librium of the reaction. Compared with the stoichiometry, the H_2 produced was higher and the CO produced was lower. When the amount of H_2O fed in was 1.4 times as much as CO_2 , the following reaction occurred:



This means that by varying the composition of the feed gas in the $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ system, the ratio of H_2 to CO in the produced syngas could be controlled appropriately. It is noteworthy that this kind of control was initially made possible by using a highly active catalyst as presented in this study for both reactions $\text{CH}_4 + \text{CO}_2$ and $\text{CH}_4 + \text{H}_2\text{O}$.

3.5. Marked enhancement of methane reforming reaction by Rh-modification of the catalyst

A prominent enhancement in the methane reforming reaction with CO_2 and H_2O has been observed by modifying the $\text{Ni-Ce}_2\text{O}_3\text{-Pt}$ catalyst with a small amount (0.2 wt.-%) of Rh [14]. As shown in Fig. 3, under a very high space velocity condition, i.e., $\text{SV} 730\,000\text{ h}^{-1}$ ($\text{CT} 4.93\text{ ms}$), an normal decrease in the conversion of reactants occurred on the $\text{Ni-Ce}_2\text{O}_3\text{-Pt}$ catalyst. The conversion of reactants on this catalyst at 600°C , for example, decreased from 65 to 20%, corresponding to the space velocity 73 000 and $730\,000\text{ h}^{-1}$, respectively. On the other hand, the Rh-modified $\text{Ni-Ce}_2\text{O}_3\text{-Pt}$ catalyst exhibited a very high activity, which approached the reaction equilibrium even at such a high space velocity, $730\,000\text{ h}^{-1}$. An extraordinary high space time yield of H_2 , 3585 mol/l h , was achieved at 600°C at a methane conversion of 58%.

3.6. Reaction characteristic of reforming via combustion and direct reaction with H_2O and CO_2

In Fig. 4, the effect of temperature on the CH_4 conversion of each product is shown for the reaction of methane and oxygen on the $\text{Ni-Ce}_2\text{O}_3\text{-Pt-Rh}$ catalyst with a SV of $73\,000\text{ h}^{-1}$. Combustion

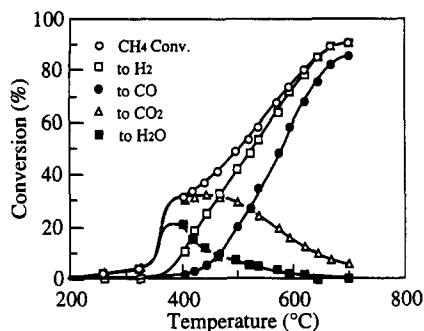


Fig. 4. Effect of temperature on conversion of methane to CO_2 , H_2 , and CO in $\text{CH}_4\text{-O}_2$ feed. Catalyst, supported $\text{Ni-Ce}_2\text{O}_3\text{-Pt-Rh}$; reaction gas, 10% $\text{CH}_4\text{-5% O}_2\text{-85% N}_2$; $\text{SV} = 73\,000\text{ h}^{-1}$ (or $\text{CT } 49.3\text{ ms}$).

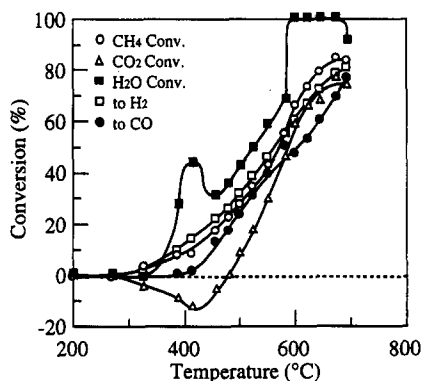


Fig. 5. Effect of temperature on conversion of feed components in $\text{H}_2\text{O-CO}_2$ co-reforming of CH_4 . Reaction gas, 10% $\text{CH}_4\text{-5% H}_2\text{O-5% O}_2\text{-80% N}_2$. Catalyst and SV were the same those as shown in Fig. 4.

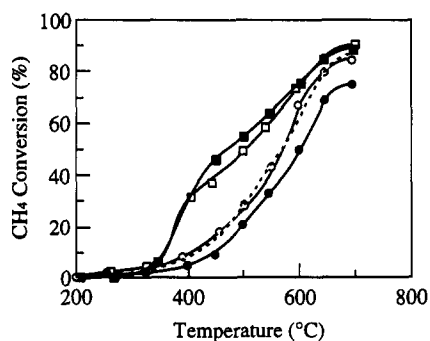


Fig. 6. Comparison of CH_4 conversion under different gas composition and flow rate. Open symbols: $\text{SV} = 73\,000\text{ h}^{-1}$ (49.3 ms). Closed symbols: $\text{SV} = 358\,000\text{ h}^{-1}$ (10.1 ms). Square: 10% $\text{CH}_4\text{-5% O}_2\text{-85% N}_2$. Circular: 10% $\text{CH}_4\text{-5% H}_2\text{O-5% CO}_2\text{-80% N}_2$. Catalyst: $\text{Ni-Ce}_2\text{O}_3\text{-Pt-Rh}$. Dotted line: equilibrium conversion of CH_4 in reaction equation; $2\text{CH}_4 + \text{H}_2\text{O} + \text{CO}_2 \rightleftharpoons 3\text{CO} + 5\text{H}_2 + 480.64\text{ kJ/mol}$.

of methane clearly progressed above 300°C and attained a total conversion of O_2 at around 370°C . Above that temperature the water produced

reacted with methane preferentially and then a methane- CO_2 reaction followed. The feed gas composition is the stoichiometric one for partial oxidation of methane to form syngas having a H_2/CO ratio 2 expressed as Eq. (at 500°C) (5) with a small release of heat.

The equilibrium conversion for the reaction of Eq. (5) is 100% across all temperature ranges, but experimental results clearly indicate that the reaction did not obey that equation but both reforming the reaction expressed as Eqs. (1) and (2) via combustion reaction (Eq. (4)). The hydrogen formed was larger than that expected from Eq. (5) reflecting that steam reforming reaction (Eq. (1)) occurs more easily than CO_2 reforming (Eq. (2)), and the shift reaction expressed as Eq. (6) occurs between the CO formed and the H_2O formed.

On the other hand, as shown in Fig. 5, $\text{H}_2\text{O-CO}_2$ co-reforming of methane without O_2 feed showed a different temperature dependence from that of $\text{CH}_4\text{-O}_2$ feed. Steam reforming of CH_4 (Eq. (1)) occurred preferentially, followed by a shift reaction (Eq. (6)) between the CO and H_2O that were formed, and then CO_2 reforming of CH_4 occurred at a higher temperature range. As a result, the formation of hydrogen in the $\text{CH}_4\text{-O}_2$ reaction was considerably higher than that in the $\text{CH}_4\text{-H}_2\text{O-CO}_2$ reaction across the whole temperature range above ca. 400°C .

3.7. Rapid hydrogen synthesis by combining catalytic combustion of methane

Furthermore, in order to supply the large endothermic heat of the reforming reactions directly to the vicinity of the active sites, the catalytic combustion of methane on the same catalyst was measured. Fig. 6 shows the comparison of methane conversion in both $\text{CH}_4\text{-O}_2$ and $\text{CH}_4\text{-CO}_2\text{-H}_2\text{O}$ reactions under different flow conditions. Conversion of methane in $\text{H}_2\text{O-CO}_2$ co-reforming under a flow condition of $\text{SV } 73\,000\text{ h}^{-1}$ coincided with that expected by the reaction equilibrium. However, at the higher flow rate ($\text{SV } 358\,000\text{ h}^{-1}$) the methane conversion was some-

Table 2
Effect of space velocity on methane reforming reactions with and without O₂

Composition of reaction gas	Space velocity (SV) (h ⁻¹)	Contact time (CT) (ms)	Conversion (%)			Percentage of reaction progress* (%)		Space-time conversion (STC) (mol/l h)	Space-time yield (STY) (mol/l h)	
			CH ₄	CO ₂	H ₂ O	H ₂	CO		H ₂	CO
10% CH ₄ + 10% CO ₂	73 000	49.3	87.4	86.5	84.7	77.8	273	530	520	
+ 80% N ₂	354 000	10.2	87.1	87.3	85.3	80.6	1360	2660	2,690	
(Reaction (2))	730 000	4.93	64.5	69.1	58.8	57.6	1940	3540	3,710	
60% CH ₄ + 10% CO ₂	73 000	49.3	71.2	-31.1	-71.0	57.6	64.2	1240	2,180	1350
+ 10% H ₂ O + 20% O ₂	328 000	11.0	47.8	-49.8	-91.1	35.2	32.5	4226	6,750	3420
(Reaction (7))	730 000	4.93	41.7	-79.8	-93.8	29.3	22.5	7820	12,190	4880

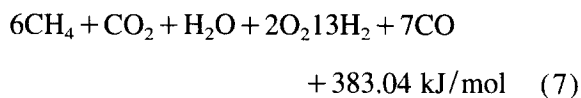
Reaction: 700°C, catalyst: Ni–Ce₂O₃–Pt–Rh/wash-coated Fiberfrax.

* Percentage of the reaction, which progresses obeying each reaction stoichiometry.

what reduced. On the other hand, in CH₄–O₂ reaction even under the higher flow rate the methane conversion increased, indicating that with on-site heat supply by methane combustion, the endothermic reaction of methane reforming was markedly enhanced. The space–time yield of hydrogen under the flow rate of 358 000 h⁻¹ (or contact time of 10 ms) at 700°C achieved a very high level (2780 mol/l h) and a marked enhancement of methane conversion (87%) to syngas was observed even under a very short contact time of ms order [22].

In order to investigate the upper limit of the space–time yield of hydrogen, concentrations of reactants were increased, anticipating that the catalytic combustion and reforming reactions would occur simultaneously. As shown in Table 2 [23], in the case of CO₂-reforming (reaction Eq. (2)), methane conversion was maintained its equilibrium (87%) even with a very short contact time (10 ms). However, when the contact time was halved, the methane conversion decreased 1/1.35, indicating that the mass and heat transfer of the reactants on the catalyst surface in this catalytic reaction environment reached the upper limit. The reaction progressed selectively obeying the reaction stoichiometry of Eq. (2), and hydrogen and carbon monoxide were formed equally. The space–time yield of hydrogen reached 3,540 mol/l h.

In the case of O₂ addition to H₂O–CO₂ co-reforming with molar ratios of CH₄, CO₂, H₂O, and O₂ are 6, 1, 1, and 2, respectively. If the syngas formation progresses selectively, the equation can be written as Eq. (7). Under



conditions of the highest space velocity, 730 000 h⁻¹, an extraordinarily high space–time yield of hydrogen, 12 190 mol/l h was realized. In this case, however, the concentrations of H₂O and CO₂ formed increased more than those of the feed concentrations indicating that H₂O and CO₂ formed by the methane combustion reaction, which occurred in preference to the reforming reactions, remained. However, the space–time yield of hydrogen under the highest space velocity in the reaction expressed as Eq. (7) clearly exceeded well beyond that of the CO₂-reforming mentioned above, and consequently, the acceleration effect of combining the catalytic combustion with the hydrogen formation is evident. Furthermore, it can be pointed out that the reason for this selective formation of hydrogen is due to the retarding effect of CO₂ and H₂O in the feed gas on the successive reaction of syngas such as methanation.

4. Conclusion

The essential feature of the spillover effect must be exhibited under the reaction condition, which is progressing very rapidly. Precious metals such as Ru, Pt, Pd, Ir, and Rh function as a porthole for hydrogen spillover towards the main component catalyst, and keep the catalyst surface a reductive one. This principle was realized in the effective methane reforming reactions on Ni-based composite catalysts to produce hydrogen with very high rates. The combination of methane combustion allows an extraordinarily high formation rate of hydrogen even under high flow rate conditions.

References

- [1] T. Inui, T. Takeguchi, A. Kohama and K. Tanida, *Energy Convers. Mgmt.*, 33 (1992) 513.
- [2] T. Inui, T. Takeguchi, A. Kohama and K. Kitagawa, in L. Gucci et al. (Editors), *New Frontiers in Catalysis, Proc. 10th Intern. Congr. Catal.*, 1992 Budapest, Elsevier 1993, B, p. 1453.
- [3] T. Inui, Y. Miyamoto and Y. Takegami, *Stud. Surf. Sci. Catal.*, 17 (1983) 181.
- [4] T. Inui and K. Mitsuhashi, *Nippon Kagaku Kaishi*, (1977) 1311.
- [5] J. Nakamura and T. Uchijima, *Shokubai (Catalyst)*, 35 (1993) 478.
- [6] Y. Sakai, H. Saito, T. Sodesawa and F. Nozaki, *React. Kinet. Catal. Lett.*, 24 (1984) 253.
- [7] M. Masai, H. Kado, A. Miyake, S. Nishiyama and S. Tsuruya, *Stud. Surf. Sci. Catal.*, 36 (1988) 67.
- [8] O. Tokunaga, Y. Osada and S. Ogasawara, *Fuel*, 68 (1989) 990.
- [9] F. Solymosi, Gy. Kutsán and A. Erdohelyi, *Catal. Lett.*, 11 (1991) 149.
- [10] J. Nakamura, S. Umeda, K. Kubushiro, K. Kunitomi and T. Uchijima, *Sekiyu Gakkaishi*, 36 (1993) 97.
- [11] K. Seshan and A. Lercher, in J. Paul and C-M. Pradier (Editors), *Carbon Dioxide Chemistry, Environmental Issues*, The Royal Soc. Chem., 1994, p. 16.
- [12] M. Huff, P.M. Tornainen, D.A. Hickman and L.D. Schmidt, *Stud. Surf. Sci. Catal.*, 81 (1994) 315.
- [13] T. Inui, M. Suehiro, Y. Saita, T. Miyake and Y. Takegami, *Appl. Catal.*, 2 (1982) 389.
- [14] T. Inui, *Stud. Surf. Sci. Catal.*, 77 (1993) 17.
- [15] T. Inui, K. Ueno, M. Funabiki, M. Suehiro, T. Sezume and Y. Takegami, *J. Chem. Soc. Faraday Trans. 1*, 75 (1979) 1495.
- [16] T. Inui, Y. Miyamoto and Y. Takegami, *Stud. Surf. Sci. Catal.*, 17, 181 (1983).
- [17] T. Inui, M. Funabiki, M. Suehiro and T. Sezume, *J. Chem. Soc. Faraday Trans.*, 1, 75 (1979) 787.
- [18] T. Inui, K. Fujioka, W. Tanakulrengsank and T. Takeguchi, *Stud. Surf. Sci. Catal.*, 77 (1993) 369.
- [19] H. Futami, J. Hashimoto and H. Uchida, *J. Fuel Soc. Jpn.*, 68 (1989) 236.
- [20] T. Inui and K. Fujioka, to be submitted
- [21] T. Inui, H. Wakita and H. Fukuzawa, *Proc. Int. Confer. Advanced Mater.*, 2 (1989) 273.
- [22] T. Inui, K. Saigo, Y. Fujii and K. Fujioka, *Proc. 2nd Int. Workshop on Catalyst Combustion*, 1994, Tokyo, p. 128.
- [23] K. Saigo, Y. Fujii and T. Inui, *Preprints 74th Annu. Meet. Catal. Soc. Japan*, 1994, p. 26.