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Partial oxidation of CH_4 with air to produce pure hydrogen and syngas

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ABSTRACT

The gas–solid reaction between methane and the lattice oxygen of Ni, Co, and Fe-oxides loaded on various support materials produced a synthesis gas (hydrogen and carbon monoxide) at 600–800 °C. Metal oxides were reduced to metals or lower valence oxides, and they were re-oxidized to oxides by introducing air after the reaction. Thus, production of hydrogen or synthesis gas free from nitrogen can be achieved alternatively without using pure oxygen. As a metal oxide, Fe_2O_3 and Rh_2O_3-loaded on Y_2O_3 exhibited the highest H_2 selectivity of 60.1% with a moderate CH_4 conversion of 54% and a high lattice oxygen utilization of 84% at 800 °C.

1. Introduction

Hydrogen production from natural gas has generally been conducted by steam reforming (SR) (reaction (1)) [1].

$$CH_4 + H_2O \rightarrow 3H_2 + CO \quad \Delta H^{\circ}_{298} = +206\,kJ/mol \tag{1}$$

Since reaction (1) is highly endothermic and runs at high temperatures above 1073 K, the reaction necessitates a large amount of energy, and as a result a large amount of CO_2 is emitted into the atmosphere.

In contract, the catalytic partial oxidation of CH_4 (POM) (reaction (2)) is an exothermic reaction and has the advantage that it is performed at relatively lower temperatures. Since Ashcroft et al. recalled attention to this reaction in 1990 [2], this field of chemistry has attracted much interest of many researchers [2–5].

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow 2H_2 + CO \quad \Delta H^{\circ}_{298} = -36\,kJ/mol \tag{2}$$

Application of Ni-loaded catalysts used to steam reforming has been investigated. However, in the catalytic partial oxidation, the catalysts have suffered from sintering of Ni and carbon deposition [6,7]. Nearly all the noble metal catalysts can produce syngas, showing superior advantages to Ni-loaded catalysts with regard to both activity and carbon resistance [8]. However, noble metals are very costly and their reserves are limited in the world. Thus, it may be somewhat difficult to apply them to industrial processes. To overcome this problem, Takehira et al. [9] have applied a solid-phase crystallization method to Ni-loaded MgO-Al_2O_3 catalyst. This catalyst has highly dispersed Ni metal and high durability against coke formation. However, pure oxygen is typically required for POM, and in the commercial operation of POM, a costly oxygen plant must be installed [10,11].

As an alternative process, in order to obtain pure hydrogen from CH_4, catalytic decomposition of CH_4 over Ni/SiO_2 is proposed (reaction (3)), and carbon formed could potentially be removed by introducing steam to give H_2 and CO (reaction (4)) [12].

$$\text{Step 1} \quad CH_4 + \text{Cat.} \rightarrow \text{C/Cat.} + 2H_2 \quad \Delta H^{\circ}_{298} = +75\,kJ/mol \tag{3}$$

$$\text{Step 2} \quad \text{C/Cat.} + H_2O \rightarrow \text{Cat.} + CO + 2H_2 \quad \Delta H^{\circ}_{298} = +131\,kJ/mol \tag{4}$$

However, such a process yields a large amount of carbon on the catalyst bed, which causes a large pressure drop between the front end and the bottom of the bed, making operation difficult in a fixed bed reactor. In addition, if steam is used to re-generate the carbon-formed catalyst, the advantage of such a process against steam reforming would be diminished.

The redox properties of NiO (reactions (5) and (6)) dispersed with different inorganic binders including MgO, Y-SZ and Ni–Mg–Al mixed oxides have been investigated [13–15]. The reactions have been studied by means of thermogravimetric measurement during redox cycles at a constant temperature. Ni–Mg–Al mixed oxides have been reported to exhibit excellent regenerability in cyclic use [15].

$$\text{Step 1} \quad NiO + CH_4 \rightarrow Ni + CO + 2H_2 \quad \Delta H = +205\,kJ/mol \tag{5}$$

$$\text{Step 2} \quad Ni + \tfrac{1}{2}x\text{Air}(O_2 + N_2)NiO_x + \tfrac{1}{2}xN_2 \quad \Delta H = -241\,kJ/mol \tag{6}$$

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Recently, the gas–solid reaction between methane and lattice oxygen of oxides to give synthesis gas was reported by Otsuka et al. (reactions (7)–(9)) [16].

$$\text{Step 1}\quad CeO_2 + xCH_4 \rightarrow CeO_{2-x} + xCO + 2xH_2 \tag{7}$$

$$\text{Step 2}\quad CeO_{2-x} + xCO_2 \rightarrow CeO_2 + xCO \tag{8}$$

$$CeO_{2-x} + xH_2O \rightarrow CeO_2 + xH_2 \tag{9}$$

Similarly, the redox cycle, the reduction of Fe_2O_3 with CH_4 (reaction (10)) and the subsequent oxidation of iron metal with H_2O (reactions (11) and (11′)) or CO_2 has been proposed [17–23].

$$\text{Step 1}\quad Fe_2O_3 + 3CH_4 \rightarrow 2Fe + 3CO + 6H_2 \quad \Delta H = +239.1\ \text{kJ/mol} \tag{10}$$

$$\text{Step 2}\quad 3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2 \quad \Delta H = +151.2\ \text{kJ/mol} \tag{11}$$

$$2Fe + 3H_2O \rightarrow Fe_2O_3 + 3H_2 \quad \Delta H = +99.4\ \text{kJ/mol} \tag{11′}$$

The studies have shown that the lattice oxygen of iron oxide or cerium oxide exhibits high activity for methane oxidation to give synthesis gas, and that there is no danger of an explosion occurring with pure oxygen. However, these reactions with H_2O or CO_2 are highly endothermic and consume a large amount of energy, necessitating a higher reaction temperature.

Shikong et al. have reported that $La_{0.9}Sr_{0.1}FeO_3$ catalyst shows high catalytic activity for the redox cycle between reaction (12) and reaction (13) by using air at 900 °C [24]. Wei et al. have reported that CeO_2 catalyst exhibits high catalytic activity in the same reaction by using air above 865 °C [25]. In addition, reduction of metal oxides such as WO_3 [26] and $LaFeO_3$ perovskite [27,28] with CH_4 and oxidation of the reduced metal oxide has been reported.

$$\text{Step 1}\quad C_aH_b + M_cO_d \rightarrow aCO + \tfrac{b}{2}H_2 + cM \tag{12}$$

$$\text{Step 2}\quad M + \tfrac{1}{2}m\text{Air}(O_2 + 4N_2) \rightarrow MO_m + 2mN_2 \tag{13}$$

However, the gas–solid reaction between methane and the lattice oxygen of oxides to the synthesis gas runs at a high temperature of nearly above 865 °C and consumes a large amount of energy. Metal oxides are rapidly deactivated by repeated runs of the reduction of oxide and re-oxidation of metal due to metal sintering.

This paper deals with the oxidation of CH_4 using lattice oxygen of transition metal oxides and re-oxidation of reduced metals by air in order to develop a process that can be carried out at a lower temperature. We found in particular that Fe_2O_3-loaded catalysts with a small amount of co-loaded Rh_2O_3 exhibit high and constant catalytic activities for repeated reduction and oxidation cycles.

2. Experimental

2.1. Catalyst preparation

The catalyst supports used in this study were CeO_2, Y_2O_3, SiO_2 (Wako Pure Chemical Industries Ltd.), Al_2O_3 (Sumitomo Chemical Co.), MgO (1000A; Ube Industries Ltd.), TiO_2 (P25; Japan Aerosil Co.), and La_2O_3 (Nacalai Tesque, Inc.). CeO_2 and Y_2O_3 were prepared by thermal decomposition of $Ce(NO_3)_3{\cdot}6H_2O$ and $(CH_3COO)_3Y{\cdot}4H_2O$ (Wako Pure Chemical Industries Ltd.) at 600 °C under air for 5 h, respectively.

The supported Fe_2O_3-Rh_2O_3/Y_2O_3 catalyst was prepared by impregnating the suspended Y_2O_3 with an aqueous solution of $Fe(NO_3)_3{\cdot}9H_2O$ (Wako Pure Chemicals Ltd.) and $RhCl_3{\cdot}3H_2O$ (Mitsuwa Pure Chemicals), followed by evaporation-to-dryness. The prepared catalyst precursors were calcined at 600 °C for 5 h in air prior to the reaction.

2.2. Catalytic reaction

The partial oxidation of methane was carried out with a fixed bed flow-type quartz reactor (8 mm i.d. × 350 mm *L* and 4 mm i.d. × 200 mm *L*) at a temperature range of 500–800 °C under atmospheric pressure. After placing 0.5 g of the catalyst in the reactor, the catalyst was heated to the desired temperature. The partial oxidation of CH_4 was carried out under 10 mL/min of CH_4 and 40 mL/min of Ar, and re-oxidation of the reduced catalyst was carried out with 10 mL/min of O_2 and 40 mL/min of Ar at a temperature range of 500–800 °C. Products were analyzed with an on-line gas chromatograph and a quadrupole mass spectrometer. Selectivities to CO, CO_2, and carbon were calculated from the absolute amounts of produced CO, CO_2, and carbon against converted CH_4. H_2 selectivity was calculated from the absolute amounts of produced H_2 and H_2O against converted CH_4.

2.3. Catalyst characterization

Temperature-programmed reaction with methane (TPR) was carried out by an on-line quadrupole mass spectrometer (HAL201, Hiden Analytical Ltd.) fitted with an outlet of a fixed bed quart reactor (i.d. 4 mm × 200 mm). After placing 100 mg of catalyst into the reactor, 10 mL/min of CH_4 and 20 mL/min of Ar were introduced. A mass spectrometer was used to scan the corresponding parent peaks of the following 6 compounds, H_2, H_2O, CH_4, CO, CO_2, and O_2, within 1 s, and repeated scans were collected on a personal computer.

Powder X-ray diffraction (XRD) patterns were obtained with a Shimadzu XRD-6000 using monochromatized Cu Kα radiation.

Surface areas of the support and catalyst were measured by the BET method using N_2 at −197 °C with an automatic Micromeritics Gemini 2375.

A scanning electron microscope (SEM), JEOL JSM5410, was employed to evaluate the catalyst surface.

3. Results and discussion

3.1. Effects of metal oxide and support material on the reduction behavior with methane

Previous studies of the reduction of Fe_2O_3 with CH_4 were carried out with a bulk iron oxide with small amounts of additives [19]. The amount of lattice oxygen utilized to oxidize CH_4 could be maximized without any additives. In this simple system, the reaction with methane would proceed at a higher temperature, and bulk oxides tend to aggregate when they are reduced metallic species. In addition, bulk oxide generally has a small surface area.

Supports having high surface areas are commonly used to disperse active species on them, resulting in an increase in the number of active site. In addition, prevention of the sintering of active sites could be expected. In order to lower the reaction temperature of an oxide with methane, use of a support was examined. At first, selection of active metal oxides was performed with a typical support, Al_2O_3. As active oxides, less expensive iron group metal oxides were selected. Fig. 1 shows the temperature-programmed reaction of CH_4 with NiO, Co_3O_4, and Fe_2O_3 on Al_2O_3. From the H_2 production behavior, NiO afforded the lowest reaction temperature of 430 °C, and Co_3O_4 reacted at 670 °C. Fe_2O_3 was not reduced below 800 °C and was reduced after 10 min on holding at 800 °C. In TPR runs, a holding time of 40 min was applied at 800 °C. After the TPR run on NiO-loaded Al_2O_3, ca. 1.3 mmol of carbon

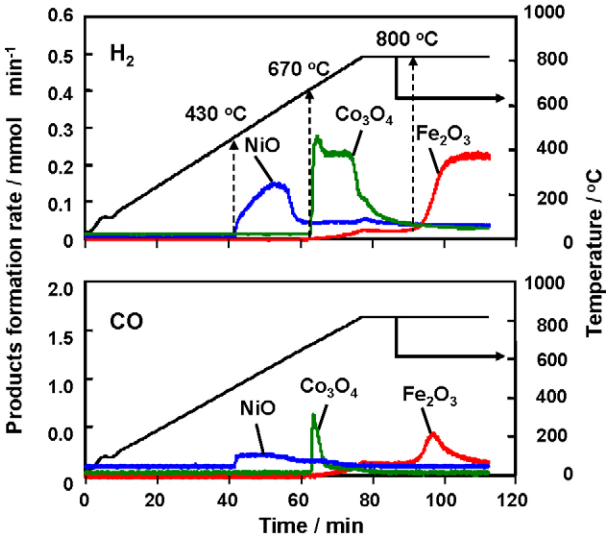

Fig. 1. CH_4-TPR patterns of iron group metal oxide-loaded Al_2O_3. Upper trace, H_2 formation rate; lower trace, CO formation rate. Catalyst: 0.1 g, 20 mmol of metal oxide/1 g of Al_2O_3, heating rate: 10 °C/min, CH_4/Ar = 10/20 (mL/min).

formed on the catalyst; in contrast, no carbon formation was observed on Fe_2O_3-loaded catalyst. Bulk Co_3O_4 reacted at a moderate reaction temperature with a small amount of deposited carbon.

From these results, Fe_2O_3 was selected as a metal oxide and an optimal support material was then looked for. Selection was carried out by TPR, and the results are summarized in Table 1. Initial temperature indicates the temperature at which H_2 production started, and the numerals in the parentheses [800 °C (7 or 16 min)] indicate that H_2 production started 7 or 16 min after reaching 800 °C. Except for Y_2O_3, on all other support materials, the reaction of CH_4 with Fe_2O_3 occurred at or above 800 °C and no carbon formation was observed. However, only a small amount of carbon was detected on Y_2O_3-supported catalyst, which is likely due to the higher conversion of CH_4 on this support. Further studies were carried out with Fe_2O_3 loaded on Y_2O_3.

The ratios of H_2/CO were very high in all the support materials, showing that complete oxidation of CH_4 to CO_2 and H_2O did occur (reaction (5)), and that reforming of CH_4 with H_2O and CO_2 occurred slightly, with a considerable extent of CH_4 decomposition to H_2 (reaction (14)). Low activity of iron catalyst on the reforming is consistent with reported results [9]. In general, CO_2 reforming is a slower reaction than H_2O reforming, which also contributes to the higher H_2/CO ratio.

$$Fe + xCH_4 \rightarrow FeCx + \tfrac{x}{2}H_2 \quad (14)$$

It is desirable to use a composite oxide containing higher amounts of Fe_2O_3 to obtain a maximum amount of H_2 and CO from a unit mass of composite catalysts. The loading level of Fe_2O_3 over Y_2O_3 was examined, and the results are summarized in Table 2. The highest amount of H_2 was obtained on Fe_2O_3 (50 mmol)/Y_2O_3 (g) catalyst, and a large amount of carbon formed with a low CO selectivity. A catalyst Fe_2O_3 (20 mmol)/Y_2O_3 (g) afforded a high selectivity to CO with low carbon formation. This result is attributed to the higher feed ratio of CH_4 to lattice oxygen of iron, resulting in CH_4 decomposition (reaction (14)).

3.2. Effects of additive on Fe_2O_3/Y_2O_3 catalyst

As discussed above, Fe_2O_3/Y_2O_3 reacted with CH_4 to give H_2 and CO in the TPR runs. However, the initial temperature was still high (722 °C), and considerable carbon formation was observed. In addition, the activities of steam and CO_2 reforming were low. To overcome these points, the effects of additives were examined, and the results are shown in Fig. 2 and Table 3. The initial reduction temperature decreased below 700 °C with the addition of a small amount of Rh and Pt. However, addition of Ru, Pd, and Ir only slightly decreased the initial temperature, and no rapid increases in the reaction rate were observed with increases in the reaction temperature. Table 3 illustrates the results of the reaction of CH_4 at a constant temperature of 800 °C, where much smaller H_2/CO

Table 1
Effect of the support on Fe_2O_3-loaded catalyst in the partial oxidation of methane

Support	Initial temperature[a] (°C)	Fe (mmol)	Lattice O (mmol)	Product (mmol)				Lattice O conversion (%)	Carbon (mmol)
				H_2	CO	CO_2	H_2O		
MgO	800 (after 7 min)	0.41	0.62	0.78	0.17	0.09	0.04	62.0	0.00
Al_2O_3	800 (after 16 min)	0.21	0.35	2.22	0.17	~0	0.37	154.3	0.00
TiO_2	No reaction	0.25	0.38	0.15	0.17	0.02	0.20	100.0	0.00
Y_2O_3	722	0.06	0.09	1.20	0.09	0.01	0.05	177.8	0.08
La_2O_3	800	0.07	0.11	0.65	0.02	0.01	0.05	72.7	0.00
CeO_2	800	0.13	0.2	0.84	0.33	0.06	0.05	220.0	0.00
None	No reaction			0.23	0.05	0.05	0.40		0.00

Catalyst: Fe_2O_3 10 mol% in the catalyst, 0.1 g, CH_4/Ar = 3/27 (mL/min), catalysts were heated at a rate of 10 °C/min until 800 °C and maintained at 800 °C for 40 min.
[a] Initial H_2 formation temperature; after *xx* min indicates reaction started after reaching 800 °C.

Table 2
Effect of Fe_2O_3 loading level in Fe_2O_3/Y_2O_3 on the partial oxidation of methane

Fe loading level[a] (mmol/1 g Y_2O_3)	Metal (mmol)	Lattice O[b] (mmol)	Product (mmol)					Seletivity (%)			H_2/CO ratio
			H_2	H_2O	CO	CO_2	Carbon	H_2	CO	CO_2	
90	1.10	1.65	6.42	1.09	0.54	0.22	2.83	85.5	15.1	6.2	11.8
50	1.00	1.50	18.74	0.78	0.60	0.23	3.12	96.0	15.2	5.9	31.2
20	0.75	1.13	6.32	0.61	0.53	0.15	0.85	91.1	34.7	9.9	11.9
10	0.56	0.83	6.37	0.27	0.34	0.07	1.01	96.0	24.1	5.1	18.6
5	0.35	0.53	5.12	0.34	0.36	0.03	1.54	93.7	18.7	1.4	14.2

Catalyst: 0.1 g, CH_4/Ar = 3/27 (mL/min), catalysts were heated at a rate of 10 °C/min until 800 °C and maintained at 800 °C for 40 min.
[a] *x* mmol of Fe_2O_3/1 g Y_2O_3.
[b] Lattice oxygen in Fe_2O_3.

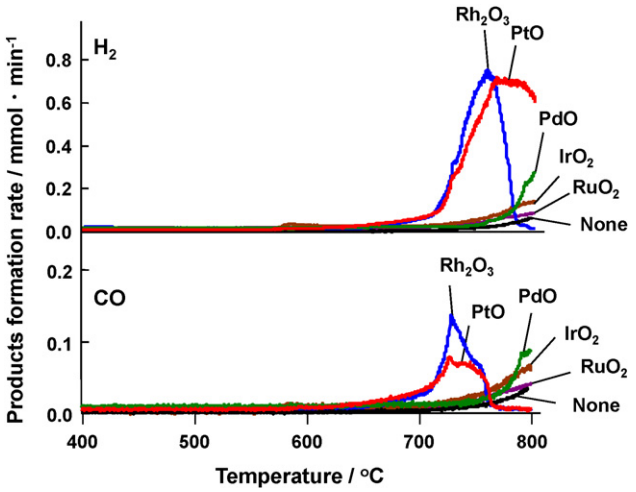

Fig. 2. Effect of additive metal to Fe-loaded catalysts on the initial reduction temperature. Upper trace, H_2 formation; lower trace, CO formation. Catalyst: 0.1 g, Fe_2O_3 20 mmol; additive 0.5 mmol/1 g of Y_2O_3, heating rate: 10 °C/min, CH_4/Ar = 10/20 (mL/min).

ratios were observed. Fe_2O_3-Rh_2O_3/Y_2O_3 afforded the highest CH_4 conversion with a low H_2/CO ratio compared to the TPR results. A low H_2/CO ratio correlates with decreases in both the decomposition of CH_4 and carbon formation. With regard to the H_2/CO ratio, large differences in the TPR run and the constant temperature run were observed. This result is partly due to differences in the feed to the lattice oxygen ratio. Namely, in the constant temperature run, a limited amount of CH_4 was supplied to the catalyst bed during a short period at 800 °C. In contrast, in the TPR run, the reaction time was longer than that of the constant temperature run. Thus on the active catalyst, CH_4 decomposition did occur to give H_2 and carbon (reaction (14)).

For the practical operation of this process, it is preferable to completely use the lattice oxygen of Fe_2O_3. Under such conditions, however, there is also undesired CH_4 decomposition. Therefore, it is desirable to limit the CH_4/lattice oxygen ratio below stoichiometric levels. The role of Rh_2O_3 could be ascribed to promotion of the reforming reaction of CH_4 with H_2O and CO_2. Although no information regarding Rh species was obtained, metallic Rh would be formed during the reaction with CH_4, which is well known to be an active phase in the reforming reaction [3,4].

3.3. Re-generation of used Fe_2O_3-Rh_2O_3/Y_2O_3 catalyst with Ar-O_2 mixed gas

Fig. 3 shows the products for three successive series of reactions and regeneration cycles under constant temperature. With the introduction of CH_4, a rapid response of H_2 was observed, followed by an increase in the CO formation rate and a gradual decrease in the unreacted CH_4 concentrations. After sweeping off CH_4, Ar–O_2 (4:1) mixed gas was introduced. Here, detection of the effluent was

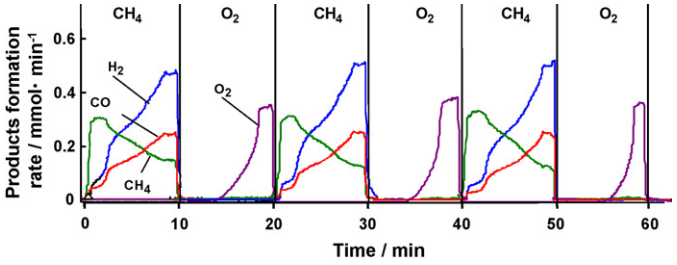

Fig. 3. Change in the product formation rates over Fe_2O_3(20)-Rh_2O_3(0.5)/Y_2O_3 in the repeated reaction and regeneration cycle. Catalyst: 0.5 g, reaction temperature: 800 °C, re-oxidation temperature: 800 °C, reaction time: 10 min, re-oxidation time: 10 min, CH_4 or O_2/Ar = 10/40 (mL/min), CH_4/Fe_2O_3 = 2.1.

made possible by a mass spectrometer, and air could not be utilized to detect CO. No response of O_2 was observed just after the O_2 introduction, and after ca. 5 min, O_2 gradually began to appear and reached original concentrations with small responses to CO and CO_2 (very low concentration).

The same reaction behavior was observed in the second and the third reaction stages with CH_4, indicating that oxidation of the reduced catalyst with O_2 for 10 min is sufficient to complete regeneration. The fact that only trace amounts of CO and CO_2 were observed in the oxidation stage clearly shows that carbon formation during the reaction stage is negligible.

Reaction and regeneration cycles were further repeated, and the results are shown in Fig. 4. Gradual decreases in the CH_4 conversion were initially observed. However, as seen in Fig. 4, after the sixth cycle, almost constant conversion of CH_4 and H_2 and CO selectivities was obtained. The reason for the initial decrease in activity was ascribed to a decrease in the surface area of the catalyst after the first oxidation stage (24.0–4.4 m^2/g).

Fig. 5 shows changes in the reaction products during the reaction and oxidation stages with different lattice oxygen to feed ratios (0.1 g catalyst), as shown in the conditions applied to those applied to Fig. 3 (0.3 g catalyst), together with the changes in the catalyst bed temperature. With the introduction of CH_4, a prompt response of CO_2 was observed and it decreased to a certain level, where a higher CH_4 concentration was fed against the catalysts (CH_4/Fe_2O_3 = 0.4). The response of H_2 and CO gradually increased together with a decrease in the response of unreacted CH_4. During the reaction stage (Fig. 5a and b), a decrease of ca. 15 °C in the catalyst bed temperature was observed, seeming to indicate that the heat of exothermic CH_4 oxidation almost compensated for the endothermic reforming reactions.

After sweeping off CH_4 and product gases by Ar, an Ar–O_2 mixture was introduced to regenerate the catalyst. A large and rapid increase in the catalyst bed temperature was observed without leaking of O_2 into the effluent. The bed temperature decreased to the prefixed furnace temperature after reaching the maximum of 980 °C, followed by an O_2 response. No CO or CO_2 formation was observed, indicating that O_2 was consumed to oxidize reduced iron species to Fe_2O_3.

Table 3
Effect of additive metal to Fe_2O_3/Y_2O_3 catalysts on the partial oxidation of methane[a]

Additive	Product (mmol)					Conversion (%)		Selectivity (%)			H_2/CO ratio
	H_2	H_2O	CO	CO_2	Carbon	CH_4	Lattice O[a]	H_2	CO	CO_2	
Rh_2O_3	1.84	0.55	0.85	0.64	0.04	35.4	46.6	77.0	55.8	41.5	2.2
PtO	1.04	0.96	0.49	0.44	0.05	20.2	41.9	52.0	49.8	44.7	2.1
None	0.48	0.82	0.32	0.32	0.23	14.8	31.0	36.8	36.7	36.8	1.5

[a] Fe2O3 20 mmol; additive 0.5 mmol/1 g of Y2O3. Catalyst: 0.5 g, reaction temperature: 800 °C, reaction time: 10 min, CH4 or O2/Ar = 10/40 (mL/min), CH4/Fe2O3 = 2.1.

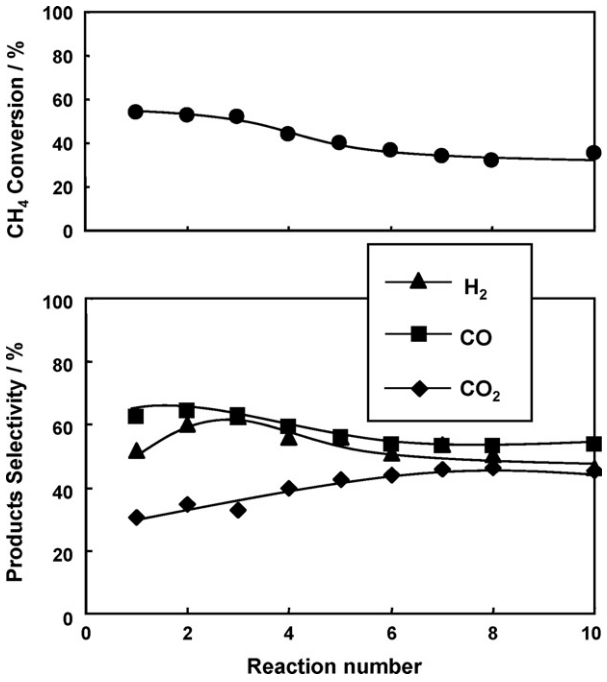

Fig. 4. Catalyst life time test of $Fe_2O_3(20)$-$Rh_2O_3(0.5)/Y_2O_3$. Catalyst: 0.5 g, reaction temperature: 800 °C, re-oxidation temperature: 800 °C, reaction time: 10 min, re-oxidation time: 10 min, CH_4 or O_2/Ar = 10/40 (mL/min), CH_4/Fe_2O_3 = 2.1.

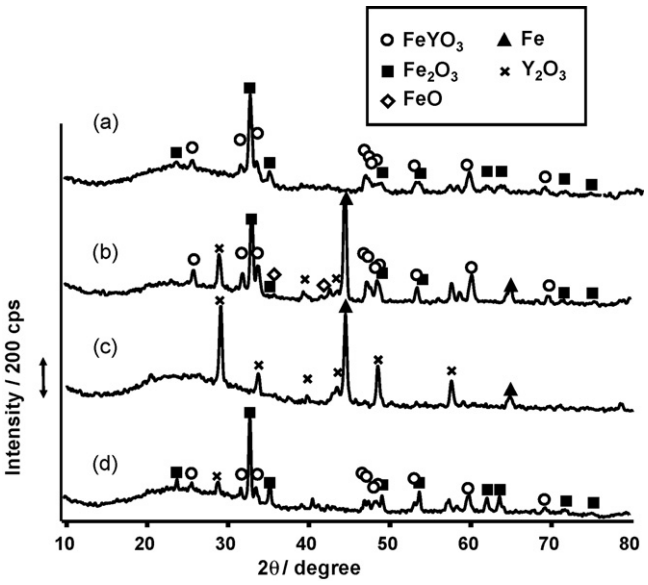

Fig. 6. XRD patterns of $Fe_2O_3(20)$-$Rh_2O_3(0.5)/Y_2O_3$ catalyst. CH_4 or O_2/Ar = 10/20 (mL/min). (a) Fresh catalyst, (b) after CH_4 flow 10 min (CH_4/lattice O = 1.08) at 800 °C, (c) after CH_4 flow 20 min (CH_4/lattice O = 2.16) at 800 °C and (d) catalyst after the 10th re-oxidation.

Similar behavior was observed in the run for 7 min (Fig. 5b), where the amount of feed CH_4 increased to the amount of lattice oxygen (CH_4/Fe_2O_3 = 1.5). Then, a certain amount of iron oxide was reduced to metallic iron, leading to CH_4 decomposition to give H_2 and carbon (reaction (14)). This corresponds to the steep increase in the H_2 response and decrease in the response of unreacted CH_4, in the later stage of the reaction (after 5 min from the introduction of CH_4). Carbon formation was confirmed by the large response of CO in the oxidation stage together with the temperature increase in the catalyst bed.

3.4. Catalyst characterization

In order to confirm the above-mentioned redox cycles of Fe_2O_3 and metallic Fe or FeOx, XRD of fresh and reacted catalysts were examined. Fig. 6 shows diffraction patterns of a fresh Fe_2O_3–Rh_2O_3/Y_2O_3 (Fig. 6a), catalysts after the reaction with CH_4 for 10 min (Fig. 6b), 20 min (Fig. 6c), and that after the 10th reaction-re-generation cycle (Fig. 6d). In the fresh and regenerated catalysts, diffraction peaks of strong Fe_2O_3 and minor iron yttrium complex oxide phases ($FeYO_3$) were observed. After the reaction with CH_4 for 10 min (Fig. 6b), in addition to the above phases, diffraction peaks of FeO and metallic iron could be detected. The sample, after the reaction with CH_4 for 20 min (Fig. 6c), afforded only diffraction peaks ascribed to metallic iron and Y_2O_3.

These results clearly indicate that the redox cycles between Fe_2O_3 and Fe occurred to give H_2 and CO with the reaction of CH_4.

Fig. 7 shows SEM images of fresh and regenerated catalyst. No significant increase in particle size was observed before and after the 10th re-oxidation cycle, indicating that sintering of oxides was small.

Although CH_4 conversion did not reach 100% in these experiments, a smaller SV could be applied to obtain complete conversion of CH_4. Heat required for the reaction of CH_4 with the

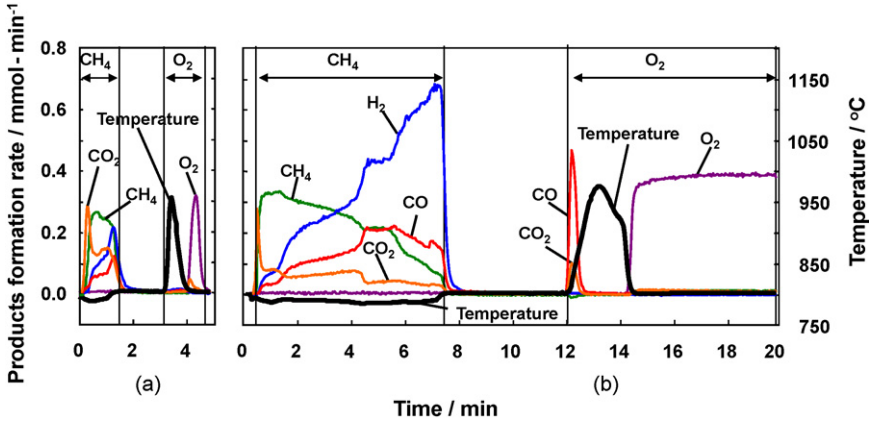

Fig. 5. Change of product formation rates and catalyst bed temperature over $Fe_2O_3(20)$-$Rh_2O_3(0.5)/Y_2O_3$ at 800 °C. Catalyst: 0.1 g, reaction temperature: 800 °C, re-oxidation temperature: 800 °C, CH_4 or O_2/Ar = 10/20 (mL/min). (a) Reaction time: 2 min, re-oxidation time: 2 min, CH_4/Fe_2O_3 = 0.4 and (b) reaction time: 7 min, re-oxidation time: 7 min, CH_4/Fe_2O_3 = 1.5.

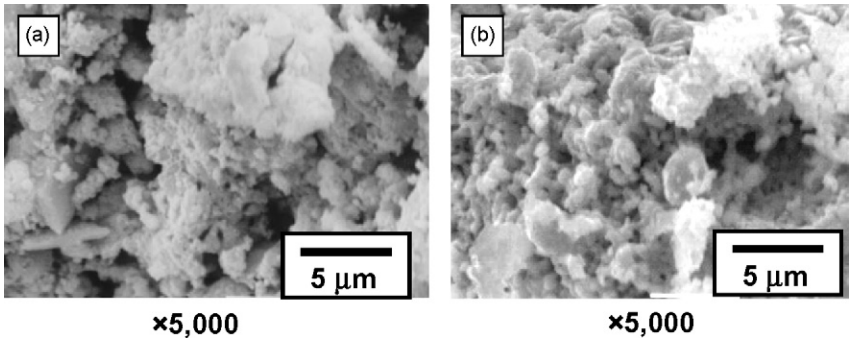

Fig. 7. SEM images of Fe_2O_3(20)-Rh_2O_3(0.5)/Y_2O_3 catalyst. (a) Fresh and (b) after 10th re-oxidation.

oxide could be supplied by the heat generated in the oxidation stage by continuously switching two or more reactors to produce H_2.

4. Conclusion

Fe_2O_3-loaded Y_2O_3 catalyst promoted with a small amount of Rh_2O_3 produced H_2 and CO by the reaction with CH_4, and reduced iron was regenerated by air ($Ar:O_2$ = 4:1). Thus, without using pure oxygen, H_2 or synthesis gas free from nitrogen could be produced.

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