Partial oxidation of methane to synthesis gas over Ru-loaded Y_2O_3 catalyst

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Ru-loaded Y_2O_3 catalyst was investigated for the partial oxidation of methane to synthesis gas. Ru(0.5 wt%)/Y_2O_3 catalyst afforded a high CH_4 conversion of 27% at a $CH_4:O_2$ ratio of 5 to give nearly a 1 : 2 ratio of CO and H_2 with a selectivity of 75% at 873 K. Ru(0.5 wt%)/Y_2O_3 catalyst maintained high catalytic activity over 10 h in the partial oxidation of methane. Carbon deposition of the catalyst surface in the reaction of CH_4 was examined by thermogravimetric analyses, and it was found that no carbon deposition occurred on the Ru(0.5 wt%)/Y_2O_3 catalyst. The synthesis-gas production proceeded basically *via* a two-step reaction consisting of methane combustion to give H_2O and CO_2, followed by the reforming of methane from CO_2 and steam.

KEY WORDS: methane; thermogravimetric; carbon deposition.

1. Introduction

Recently, natural gas has been given much attention as a fossil fuel resource. Due to its high hydrogen:carbon ratio, natural gas is able to mitigate CO_2 emission. Although its use as fuel is of interest, its use as a hydrogen source for fuel cells is an additional important aspect of natural gas. In order to convert the natural gas into raw material for chemical reactions, conversion of natural gas into synthesis gas (H_2, CO) must first be accomplished by reforming reactions using H_2O (reaction 1) or CO_2 (reaction 2), and also a partial oxidation reaction (reaction 3). The three reactions proceed as follows.

The steam reforming reaction of methane

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

The CO_2 reforming reaction of methane

$$CH_4 + CO_2 \rightleftharpoons 2CO + 2H_2 \qquad \Delta H^{\circ}_{298} = +247\,\mathrm{kJ/mol}. \tag{2}$$

The partial oxidation reaction of methane

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2 \qquad \Delta H^{\circ}_{298} = -36\,\mathrm{kJ/mol}. \tag{3}$$

Steam reforming is an industrially established process for converting natural gas into synthesis gas; highly efficient plants have been constructed, but with large investment costs. The partial oxidation of methane is an exothermic reaction. Recently, this reaction has been re-examined from the viewpoint of saving energy. A characteristic feature of this reaction is to obtain synthesis gas with a H_2/CO ratio of 2. This ratio is adequate for methanol synthesis or for synthesis of higher hydrocarbons by the Fischer–Tropsch reaction. One of the major problems involved in the commercialization of this process is to avoid carbon deposition during the partial oxidation of methane. In addition, the high cost of an oxygen plant is a hindrance to commercialization.

The group VIII transition elements of noble metals (Ru, Rh, Ir, Pt, Pd) and non-noble metals (Co, Ni, Fe) have been reported as active catalysts for the partial oxidation of methane. We have reported that Ir/TiO_2 showed high activity without carbon deposition for the partial oxidation of methane [1–3]. Dissanayake *et al.* [4] carried out the partial oxidation of methane over a Ni/Al_2O_3 catalyst and obtained high selectivities of the synthesis gas. NiO/MgO solid solution catalyst [5] and LiLaNiO/γ-Al_2O_3 catalyst [6] were reported to be active catalysts for the partial oxidation of methane. Hickman and Schmidt [7] investigated Al_2O_3 monolith-supported Rh and Pt catalysts for the partial oxidation of methane. It has also been reported that the Rh/MgO catalyst was a highly active and selective catalyst in the partial oxidation of methane [8].

Noble metals are too expensive for large-scale commercial use. However, Ru and Rh have been shown to be carbon resistant, whereas non-noble metals are prone to deactivation by coke [9,10]. Although Rh is a highly active metal, it is one of the most expensive materials that can be used as a catalyst. Therefore, we focused on the less expensive Ru as a catalyst.

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Studies have already been published on the partial oxidation of methane with a Ru-loaded catalyst. Ashcroft *et al.* [11] reported that CO and H_2 are obtained from CH_4 and O_2 at 1050 K by using Ln_2RuO_7 (Ln = lanthanide) catalyst with high yield and high selectivity. Poirier *et al.* [12] examined the same reaction by using Ru/Al_2O_3 as a catalyst, while Moffat and Matsumura [13] employed the Ru/SiO_2 catalyst. Partial oxidation of methane is believed to proceed in two steps, as shown in reactions (4), (1), and (2) [2].

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H^\circ_{298} = -801\,\mathrm{kJ/mol}. \tag{4}$$

We have carried out the CO_2 reforming of methane with the Ru/La_2O_3 catalyst. In the course of CO_2 reforming (reaction (2)), several lanthanoid-loaded Ru catalysts afforded high activity for the partial oxidation of methane [14]. Thus, Ru/Ln_2O_3 catalysts are candidates as an active catalyst for the partial oxidation of methane. In this paper, we consider Ru/Ln_2O_3 catalysts for the partial oxidation of methane. In particular, we focus on detailed studies of the Ru/Y_2O_3 catalyst, in which active and stable oxide forms have been obtained.

2. Experimental

2.1. Catalyst preparation

The catalyst supports used in the present study were Al_2O_3 (JRC-ALO-4), SiO_2 (Merck), MgO (500A; Ube Industries, Ltd.), TiO_2 (P25; Japan Aerosil Co.), Sm_2O_3, Eu_2O_3 (Anan Chemicals), Pr_6O_{11} (Santoku Metal Industry), Nd_2O_3 (Nacalai Tesque, Inc.), CaO (Wako Pure Chemical Industry), Y_2O_3-stabilized ZrO_2 (Strem Chemicals), Y_2O_3, La_2O_3, CeO_2, and ZrO_2. The catalyst supports of Y_2O_3, La_2O_3, CeO_2, and ZrO_2 were prepared by the thermal decomposition of $Y_2(C_2O_4)_3{\cdot}4H_2O$, $La(CH_3COO)_3{\cdot}\frac{3}{2}H_2O$, $Ce(NO_3)_3{\cdot}6H_2O$, and $ZrO_2{\cdot}nH_2O$ (Wako Pure Chemical Industry) at 873 K in air at atmospheric pressure for 5 h.

Group VIII metal-loaded catalysts were prepared by impregnating an aqueous solution of $RuCl_3{\cdot}nH_2O$, $Pd(CH_3COO)_2$, $IrCl_4{\cdot}H_2O$, $(NH_3)_2Pt(NO_2)_2$, $Co(NO_3)_2{\cdot}6H_2O$, $RhCl_3{\cdot}H_2O$ (Mitsuwa Pure Chemicals), $Fe(NO_3)_3{\cdot}9H_2O$, $Ni(NO_3)_2{\cdot}6H_2O$ (Wako Pure Chemical Industry) onto metal oxides. Water was removed by evaporation under reduced pressure. Dried catalysts were calcined at 873 K in air for 5 h.

2.2. Catalytic reaction

The reaction was carried out with a fixed-bed flow-type quartz reactor (i.d. 8 × 350 mm) at atmospheric pressure. Using 60 mg of catalyst, 25 ml/min of CH_4 and 5 ml/min of O_2 were introduced at a temperature range of 673–973 K. Before the reaction, the catalysts were reduced with H_2 for 1 h at 873 K with a heating rate of 30 K/min from room temperature. Products were analyzed with an online high-speed gas chromatograph (PC-Chrom, M200 Chromato Analyzer).

2.3. Characterization

X-ray photoelectron spectra (XPS) of the catalyst were obtained on a Jeol model JPS-9000MX using Mg K_α radiation as the energy source.

Carbon deposition behavior was achieved by using a thermogravimetric analyzer (Shimadzu, TGA-50). A 13 mg sample was placed on the TG pan. Heating was programmed at a rate of 20 K/min to a prescribed temperature under an Ar atmosphere. After reaching the desired temperature, the Ar flow was switched to a CH_4–air ($CH_4 = 15$, air = 15 ml/min) mixture, and the catalyst weight increase in the sample was monitored.

Transient response measurement of the catalyst bed temperature in the pulsed reactions was carried out using a fixed-bed quartz reactor (i.d. 4 mm × 200 mm). In the front edge of the catalyst bed, thin wall sheathed thermocouples were set and 100 mg of the catalyst was charged. A pulse of CH_4 and O_2 (2 : 1) mixed gas was introduced with a six-port gas-sampling valve equipped with measuring tubes, under a steam of Ar carrier gas [3,19]. Before the reaction, the catalysts were reduced under H_2 flow for 1 h at 873 K.

The reaction temperature was controlled by monitoring the outside temperature of the reactor wall by using a programmable controller. Analyses of the gases during the methane decomposition were made using an online quadrupole mass spectrometer (HAL201, Hiden Analytical Ltd.). The mass spectrometer scanned the parent peaks of the five compounds (H_2, CO, CO_2, O_2 and CH_4) within 1 s, and repeated scans were collected in a personal computer.

3. Results and discussion

3.1. Effect of support on the activity of Ru-loaded catalysts

Table 1 shows the specific surface area of the catalysts and the conversion of methane as well as CO, CO_2 and H_2 selectivities in the partial oxidation of methane over Ru(0.5 wt%) loaded catalysts. The order of the catalytic activity in the different supports at 873 K was $La_2O_3 > Y_2O_3 > CeO_2 > ZrO_2 > SiO_2 > TiO_2 > Al_2O_3 > Pr_6O_{11} > Nd_2O_3 > Sm_2O_3 > Eu_2O_3 > MgO > YSZ > CaO$. When La_2O_3, Y_2O_3 and CeO_2 were used for support, these catalysts afforded high CH_4 conversion into CO and H_2 with selectivities of over 75% and a H_2 : CO ratio of 2, as was expected from the stoichiometry of the reaction (reaction (3)). On these supports, higher CH_4 conversions were obtained than those observed in studies

Table 1
Activity of supported Ru(0.5 wt%) catalysts for the partial oxidation of methane

Catalyst	Surface area (m^2/g)	Conversion (%) CH_4	Selectivity (%)			H_2/CO (ratio)
			CO	CO_2	H_2	
Ru/La_2O_3	19.1	29.0	79.9	20.1	78.9	2.0
Ru/Y_2O_3	13.7	27.5	78.9	21.1	79.2	2.0
Ru/CeO_2	70.2	27.3	81.7	18.3	79.5	2.0
Ru/ZrO_2	40.0	23.5	79.8	20.2	82.1	2.1
Ru/SiO_2	399	16.5	59.9	40.4	76.8	2.6
Ru/TiO_2	37.8	15.9	72.3	27.7	61.8	1.7
Ru/Al_2O_3	176	14.3	62.4	37.6	63.9	2.1
Ru/Pr_6O_{11}	1.7	10.1	8.6	91.4	23.9	5.6
Ru/Nd_2O_3	3.3	9.7	12.0	88.0	19.5	3.4
Ru/Sm_2O_3	4.6	9.4	8.1	91.9	19.1	4.6
Ru/Eu_2O_3	8.1	7.6	37.9	62.1	–	–
Ru/MgO	37.4	3.6	15.0	85.0	3.9	0.6
Ru/YSZ	n.d.	1.6	–	100	–	–
Ru/CaO	11.5	–	–	–	–	–

Note: Catalyst: 60 mg. Flow rate: 30 ml/min ($CH_4/O_2 = 5$). Reaction temperature: 873 K. n.d.: not determined.

of Ru supported on Al_2O_3 or SiO_2 catalyst. If the partial oxidation of methane (reaction (3)) was assumed to be the main reaction path of synthesis-gas production, CH_4 conversion would be expected to be limited to 40%, due to the smaller $CH_4:O_2$ ratio (5:1). Complete oxidation (reaction (4)) gave a CH_4 conversion of 10%. The characteristic feature of Ru/Pr_6O_{11}, Ru/Nd_2O_3 and Ru/Sm_2O_3 is the high catalytic activity, affording the complete oxidation of methane (reaction (4)) and CO_2 as a major product.

In the case of CO_2 reforming of methane using the La_2O_3-supported catalyst, catalytic activity varied considerably during the reaction, and La_2O_3 was transformed into $La_2O_2{\cdot}CO_3$ or $La(OH)_3$. Thus, the La_2O_3-supported catalyst showed changes in structure during the reaction, as has been described previously in the case of CO_2 reforming [14]. To avoid such changes in the support structure, further studies were carried out using a Y_2O_3-supported catalyst.

3.2. *Effect of the Ru loading level on the partial oxidation of methane*

The effect of the Ru loading level on the partial oxidation of methane using Ru/Y_2O_3 catalyst is shown in figure 1. The reaction occurred with a loading level as low as 0.1 wt%, and ~25% CH_4 conversion and a synthesis gas selectivity of ~70% were obtained with a loading level of 0.5 wt%. Further increases in the loading level to 5 wt% only slightly increased CH_4 conversion, to 30%.

3.3. *Effect of reaction temperature of Ru/Y_2O_3 catalyst on the partial oxidation of methane*

Figure 2 shows the temperature dependence of the partial oxidation of methane over $Ru(0.5\,wt\%)/Y_2O_3$ catalyst. The reaction did not proceed at 673 K, and methane conversion occurred above 773 K. The amounts of CO and H_2 increased and the amount of CO_2 decreased with increasing reaction temperatures. At 973 K, $Ru(0.5\,wt\%)/Y_2O_3$ catalyst afforded a methane conversion of 35%. The ratio of H_2 to CO at 973 K decreased to less than 2. The reason for this effect seems to be a reverse water–gas shift reaction (5), where H_2 was consumed to give CO and H_2O. It seems reasonable to assume that the reaction proceeded favorably at a higher temperature due to the endothermic nature of the reaction.

$$H_2 + CO_2 \rightleftharpoons CO + H_2O \qquad \Delta H^{\circ}_{298} = +41\ \mathrm{kJ/mol}. \tag{5}$$

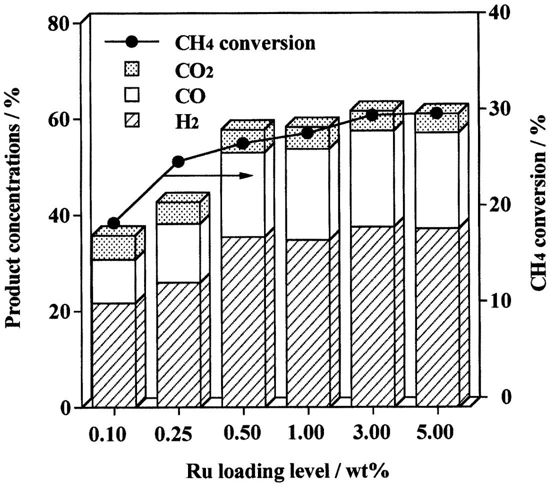

Figure 1. Effect of Ru-loading level of Y_2O_3 catalyst on the partial oxidation of methane. Flow rate: 30 ml/min ($CH_4/O_2 = 5$). Reaction temperature: 873 K. Catalyst: 60 mg.

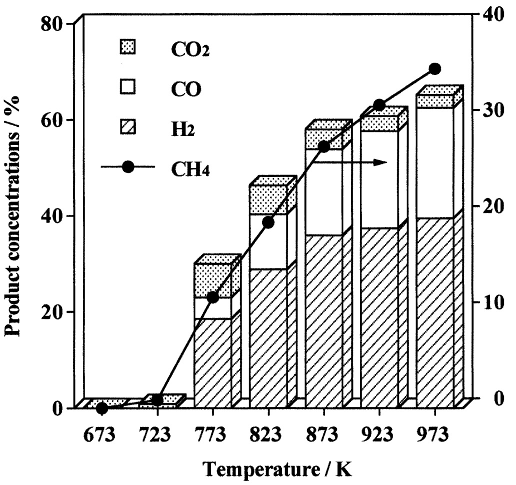

Figure 2. Effect of temperature on the CH_4 conversion and product concentrations over Ru/Y_2O_3. Flow rate: 30 ml/min ($CH_4/O_2 = 5$). SV = 30 000 h^{-1} ml/g-catalyst. Catalyst: 60 mg.

3.4. Active form of ruthenium in the Ru/Y_2O_3 catalyst

In order to determine the characteristics of the ruthenium species on Y_2O_3, the fresh and the used catalysts were examined with XPS, and the results are shown in figure 3. The fresh calcined Ru/Y_2O_3 catalyst showed two peaks at 464.0 and 462.8 eV, which were ascribed to Ru(IV)O_2 and Ru(II)O (a), respectively, since the catalyst was prepared by calcination under air flow at 873 K. When the catalyst was reduced with hydrogen at 873 K for 1 h (f), the strong peak shifted to a lower binding energy, indicating that oxidic ruthenium was reduced to metallic ruthenium. After the reaction at 723 K for 2 h, the catalyst was subjected to XPS analysis; the spectrum is shown in (b). Before the reaction, the Ru/Y_2O_3 catalyst was reduced under H_2 flow for 1 h at 873 K, and the reduced catalyst was used for the reaction at 723 K. After the reaction, the used catalyst was subjected to XPS analysis (c). Peaks at 462.8 eV of RuO observed in the spectrum shown in (a) shifted to 462.4 eV (b) and 462.2 eV (c), and almost the same spectra as those observed on (b) and (c) were obtained. It appears that RuO was reduced slightly. Although RuO (c) was reduced to Ru metal by H_2 reduction, Ru metal was oxidized again under the CH_4–O_2 flow. The observed peak at 464.0 eV (a) of RuO_2 did not alter the reaction (spectrum (b) and spectrum (c)). The partial oxidation reaction did not proceed at 723 K using both reduced Ru/Y_2O_3 and unreduced Ru/Y_2O_3 catalysts. These results demonstrate that only RuO of the Ru/Y_2O_3 catalyst was reduced at 723 K. The partial oxidation of methane did not proceed, even when only RuO was reduced.

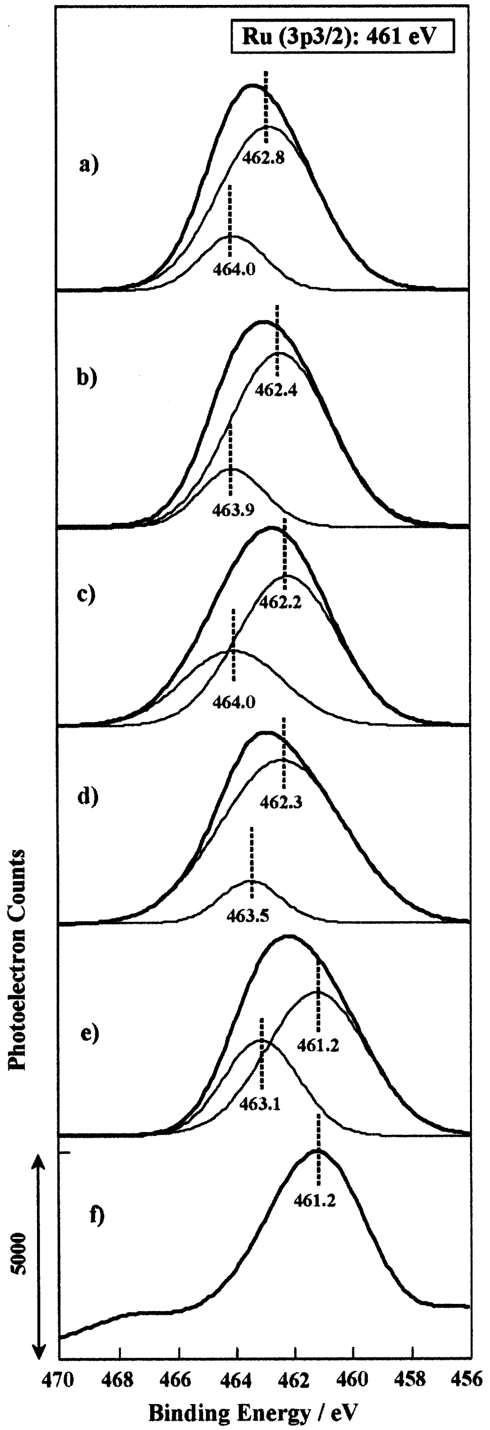

Figure 3. XPS spectra of Ru($3p_{3/2}$) on Ru/Y_2O_3 catalyst. (a) Fresh catalyst. (b) Catalyst after the reaction with CH_4/O_2 at 723 K for 2 h. (c) H_2 reduced catalyst after the reaction with CH_4/O_2 at 723 K for 2 h. (d) Catalyst after the reaction with CH_4/O_2 at 873 K for 2 h. (e) H_2 reduced catalyst after the reaction with CH_4/O_2 at 873 K for 2 h. (f) H_2 reduced catalyst at 873 K for 1 h.

After the reaction at 873 K, the Ru/Y_2O_3 catalyst was subjected to XPS (d). Again prior to the reaction, the Ru/Y_2O_3 catalyst had been reduced under H_2 flow for 1 h at 873 K, and the catalyst after the reaction at 873 K for 2 h was subjected to XPS analysis; the spectrum is shown in (e). At 873 K, the Ru-supported Y_2O_3 catalyst produced synthesis gas for the partial oxidation of methane. Peaks at 464.0 eV and 462.8 eV of the oxidic form (a) shifted slightly to a lower binding energy side of 463.5 eV and

462.3 eV (d). The results shown in spectrum (d) indicate that both RuO and RuO_2 were reduced slightly. Peaks at 464.0 eV and 462.8 eV of the oxidic form observed in spectrum (a) shifted to 463.1 = eV and 461.2 eV (e). It appears that RuO_2 was reduced slightly to a lower valency state of oxides, and RuO was reduced to metallic ruthenium. When both RuO and RuO_2 were reduced, the synthesis gas was produced. Active species of the Ru/Y_2O_3 catalyst appear to be species observed in spectra (d) and (e). These results clearly show that the active species of the Ru/Y_2O_3 catalyst for the partial oxidation of methane to synthesis gas were in the reduced RuO and in the reduced forms of RuO_2.

The XRD pattern of fresh catalyst showed diffraction peaks assignable to RuO_2. In a previous paper [15], we elucidated that Ru/La_2O_3 catalyst afforded both RuO_2 and metallic Ru after CO_2 reforming of methane.

3.5. *Effect of group VIII metal on the performance of the partial oxidation of methane*

Figure 4 shows CH_4 conversion and product distribution in the partial oxidation of group VIII metal (0.5 wt%) supported Y_2O_3 catalysts. The order of the catalytic activity of the group VIII transition metals loaded on Y_2O_3 in the partial oxidation of methane was unusual. CH_4 conversion and selectivities to CO and H_2 were the highest with the Ru/Y_2O_3 catalyst. Although just above Ru in the periodic table, Fe did not show activity. Co and Rh did not show activity, but Ir exhibited high activity. Choudhary *et al.* [16] reported that metallic cobalt or partially reduced CoO dispersed on the rare earth oxide seemed to be active phases of partial oxidation. However, Co supported on Y_2O_3 catalyst did not produce synthesis gas, and even the hydrogen-treated Co/Y_2O_3 did not afford synthesis gas. These results seem to suggest that Co_2O_3 or CoO, when on Y_2O_3, cannot be reduced to metallic cobalt under H_2 at 873 K. Only the lowest of the transition elements, Ni, showed high catalytic activity. Pd and Pt, the 2nd and 3rd lowest elements, exhibited moderate activity. These findings cannot be presented here.

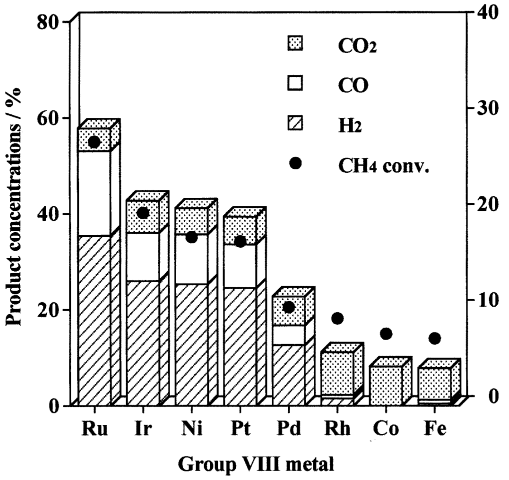

Figure 4. Partial oxidation of methane over Y_2O_3-supported transition metals. Flow rate: 30 ml/min ($CH_4/O_2 = 5$). Reaction temperature: 873 K. Catalyst: 60 mg.

Table 2
Thermogravimetric analyses of Y_2O_3-supported catalysts for CH_4 decomposition at 873 K [a]

Catalyst	Carbon deposition rate	Carbon deposition
	C μmol/g-cat./min	C μmol
Ni/Y_2O_3	108.7	84.8
Rh/Y_2O_3	34.9	27.3
Pd/Y_2O_3	25.1	19.6
Ru/Y_2O_3	n.d.	n.d.
Ir/Y_2O_3	n.d.	n.d.
Co/Y_2O_3	n.d.	n.d.
Pt/Y_2O_3	n.d.	n.d.
Fe/Y_2O_3	n.d.	n.d.

[a] Prior to the reaction, catalysts were reduced with H_2 at 873 K for 1 h. Flow rate = 15 ml/min (CH_4/air = 1). Reaction time: 1 h. n.d.: not determined.

Ni, Rh and Pd catalysts showed gradual deactivation during the partial oxidation reaction. Carbon deposition on group VIII (Ni, Ru, Rh, Pd, Ir, Pt, Fe, Co) metal-loaded Y_2O_3 catalysts were measured under an isothermal reaction at 873 K using a thermogravimetric analysis; the results are shown in table 2. Carbon deposition was not detected with Ru, Ir, Pt, Fe and Co catalysts in reaction with CH_4 for 1 h. In contrast, rapid carbon deposition occurred on Ni, Rh and Pd catalysts in the initial stage of the reaction, indicating that these catalysts would be deactivated by carbon deposition.

3.6. *Stability of the Ru/Y_2O_3 catalyst*

Figure 5 shows the effect of time-on-stream on the partial oxidation of methane at 873 K over Ru(0.5 wt%)/Y_2O_3 and Ni/Y_2O_3 catalysts. The Ru(0.5 wt%)/Y_2O_3 catalyst maintained initial catalytic activity for 10 h with a high CH_4 conversion of about 28%. On the other hand, the Ni/Y_2O_3 catalyst showed gradual deactivation over a period of 10 h and carbon deposition was observed after the reaction. The details of the carbon deposition are described in the following section. The problem with using Ni catalysts is formation of whisker carbon deposition on the catalysts, which may lead to plugging of the reformer tubes.

3.7. *Comparison of Ru/Y_2O_3 and Rb catalysts in the partial oxidation of methane*

It has been reported that $Rh/A1_2O_3$ catalyst exhibits high activity in the partial oxidation of methane [17,18]. The differences between several Rh catalysts and Ru/Y_2O_3 catalyst are compared in figure 6. The Ru/Y_2O_3 catalyst showed the same activity as Rh/Al_2O_3,

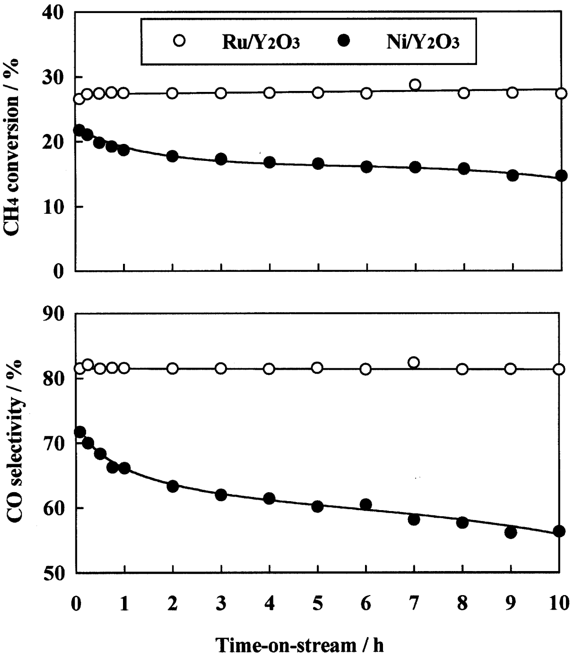

Figure 5. Effect of time-on-stream on the conversion of methane and CO selectivity over Ru/Y_2O_3 and Ni/Y_2O_3 catalysts. Flow rate: 30 ml/min ($CH_4/O_2 = 5$). Reaction temperature: 873 K. Catalyst: 60 mg.

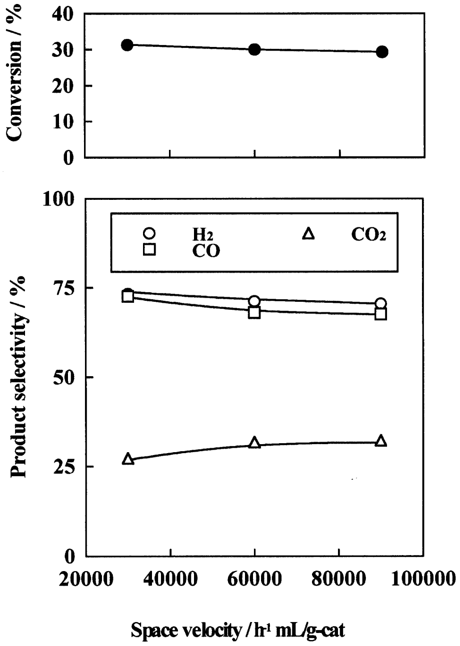

Figure 7. Effect of space velocity on the CH_4 conversion and product selectivities over Ru(0.5 wt%)/Y_2O_3. Flow rate: 30 ml/min ($CH_4/O_2 = 5$). Reaction temperature: 873 K. Catalyst: 60 mg.

the activity of which was higher than that of both Rh/TiO_2 and Rh/SiO_2. However, the Rh catalysts showed carbon deposition after 2 h of reaction. The Ru/Y_2O_3 catalyst was highly active, without carbon deposition, in the partial oxidation of methane. These results seem to suggest Ru/Y_2O_3 as an excellent catalyst.

3.8. Reaction mechanism of Ru/Y_2O_3 catalyst

In order to obtain more detailed information on the reaction pathways of synthesis-gas production over Ru/Y_2O_3 catalyst, the space velocity was varied by increasing the feed rate at a reaction temperature of 873 K. Figure 7 shows CH_4 conversion and selectivies to CO, H_2 and CO_2 as a function of space velocity, but the H_2O selectivity was not determined. The CH_4 conversion and the CO and H_2 selectivities decreased with increasing space velocity. On the other hand, the CO_2 selectivity increased. These results seem to support the two-step reaction mechanism, that the Ru/Y_2O_3 catalyst might have promoted the reaction sequence of total oxidation of methane to CO_2 and H_2O (reaction (4)), and the reforming reactions to synthesis gas (reactions (1), (2)) [2]. If the partial oxidation of methane to synthesis gas is a one-step process (reaction (3)), then the CH_4 conversion would decrease without changing the H_2/CO ratio.

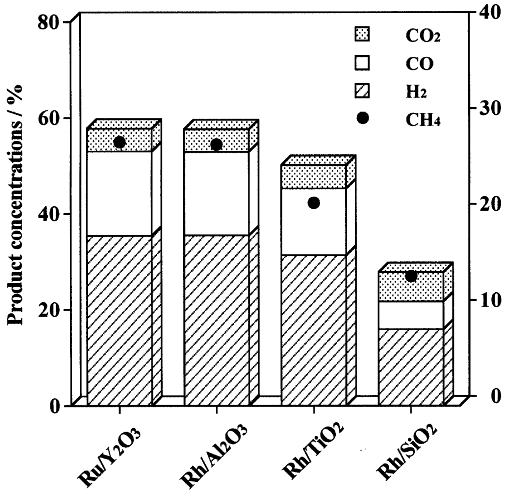

Figure 6. Activity of Ru/Y_2O_3 and various Rb catalysts for the partial oxidation of methane. Flow rate: 30 ml/min ($CH_4/O_2 = 5$). Reaction temperature: 873 K. Catalyst: 60 mg.

Moreover, in order to investigate the reaction pathways over the Ru/Y_2O_3 catalyst, a pulsed reaction technique was employed to measure transient temperature changes in the catalyst bed [3,19]. Among the four reactions, (1) and (2) were highly endothermic, (3) was moderately exothermic, and (4) was highly exothermic. In this reaction feature, observation of the catalyst bed temperature by means of injecting a pulse of reactants may provide information about the initial reaction that takes place at the catalyst bed [3,19].

Figure 8 shows the transient temperature responses of Ru/Y_2O_3 catalyst against a pulsed injection of CH_4/O_2 (2:1). A sudden rise in the temperature at the front edge of the catalyst bed was observed upon introduction of the pulse of the CH_4 and O_2 mixture (2:1) at 873 K. The temperature increase at the front edge of the catalyst bed could reasonably be ascribed to the exothermic

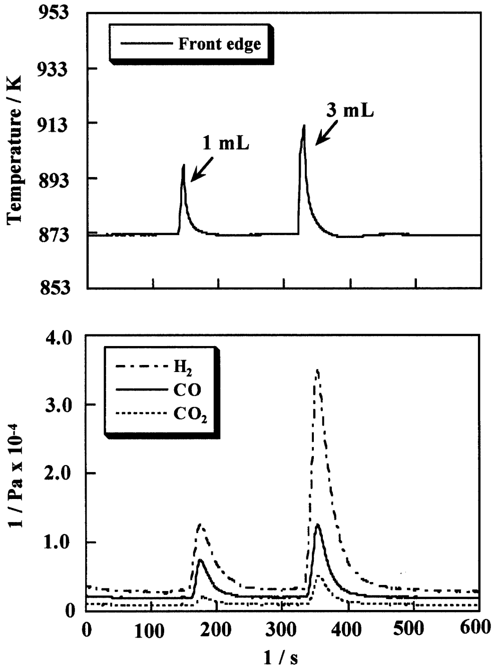

Figure 8. Temperature profile at the front edge of catalyst bed and partial pressure variations with time of the fragments over Ru(0.5 wt%)/Y_2O_3 catalyst. Reaction conditions: Ar carrier = 10 ml/min. Mixed gas: $CH_4/O_2 = 2$ (1 ml or 3 ml). Furnace temperature: 873 K.

complete oxidation reaction, since the absolute amounts of the increase in temperature are much larger than those observed for the temperature drop in reaction (2). It seems that CO_2 is produced by the complete oxidation reaction (4). The synthesis gas was formed *via* a two-step reaction pathway using the Ru/Y_2O_3 catalyst in this CH_4–O_2 reaction.

4. Conclusions

In the case of the Ru/Y_2O_3 catalyst, a low loading level of Ru(0.5 wt%) on Y_2O_3 exhibited very high catalytic activity for the partial oxidation of methane to synthesis gas at 873 K. Moreover, a synthesis gas ratio of $H_2/CO = 2$ was obtained, and the initial activity was maintained in a 10 h reaction. It is thought that the synthesis-gas production *via* the partial oxidation of methane proceeded basically by means of a two-step path consisting first of complete oxidation to give CO_2 and H_2O, followed by the methane reforming with both CO_2 and H_2O.

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