[Regular Paper]

Partial Oxidation of Methane to Synthesis Gas over Oxidized Diamond Supported Catalysts—Catalytic Behavior of Nickel and Cobalt Species—

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(Received December 7, 2004)

Characterization of nickel and cobalt catalysts supported on oxidized diamond (O-dia) in the partial oxidation of methane to synthesis gas was carried out by X-ray photoelectron spectroscopy (XPS) and the transient response pulse technique. Carbon deposition occurred on nickel/O-dia, but not on cobalt/O-dia catalyst at 873 K throughout prolonged reaction. XPS analyses observed partially reduced nickel oxides on nickel/O-dia catalyst after reaction with methane/oxygen (5/1) at 873 K. Co(0), partially reduced cobalt oxide, and Co(III) oxide phases were found on cobalt/O-dia catalyst after reaction at 873 K. Transient response methane/oxygen (2/1) pulse studies found a large amount of hydrogen production occurred immediately at 873 K over the nickel/O-dia catalyst. However, a very small amount of hydrogen production was seen over the cobalt/O-dia catalyst, indicating that nickel and cobalt species supported on O-dia exhibited different behavior. Transient response of the catalyst bed temperature found that endothermic reaction occurred on the nickel/O-dia catalyst at 873 K, but exothermic reaction proceeded on the cobalt/O-dia catalyst. These results suggest that methane decomposition to hydrogen is the primary reaction path over nickel/O-dia catalyst, whereas complete oxidation is the primary reaction followed by steam and carbon dioxide reforming to produce synthesis gas over the cobalt/O-dia catalyst.

Keywords

Partial oxidation, Diamond, Methane, Synthesis gas, Pulse method

1. Introduction

Partial oxidation of methane to synthesis gas is an energy saving exothermic process that is currently attracting much attention, after the re-evaluation by Aschcroft *et al.*¹⁾, and several review articles have summarized the research in this field^{2),3)}. Two reaction courses have been proposed: direct conversion of methane to hydrogen and carbon monoxide on the catalyst surface (reaction 1), and sequential reaction paths involving complete oxidation (reaction 4) followed by steam and carbon dioxide reforming (reactions 5 and 6) with unreacted methane⁴⁾. Most investigations have dealt with sequential reaction paths⁴⁾. Direct paths to give hydrogen and carbon monoxide, more accurately reactions (2) and (3), were proposed for Pt-loaded monolith catalyst under very high space velocity⁵⁾. We have summarized our research on nickel or cobalt loaded catalyst for the partial oxidation of methane⁶⁾.

We are interested in the unique properties of the diamond surface, and have developed various reactions using catalysts supported on oxidized diamond (O-dia)^{7)~11)}. Diamond surface is easily oxidized by oxidative acids such as HNO₃, HClO₄, H₂O₂, etc., and is also oxidized by O₂ at high temperatures to form C–O–C ether type structures and C=O carbonyl type structure¹²⁾. Transition metals loaded on various metal oxide supports exhibit metal support interactions and sometimes form binary oxides^{13)~16)}. In contrast, O-

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dia cannot form complex oxides with the loaded metal or metal oxide, or may not have strong interactions with loaded species. Therefore, the characteristic features of the loaded species will be preserved.

Previously, we reported that nickel and cobalt catalyst supported on O-dia exhibited high catalytic activity for the partial oxidation of methane⁶⁾ and carbon dioxide reforming of methane¹¹⁾ at the low temperature of 873 K. Nickel O-dia catalyst developed considerable carbon deposition during the partial oxidation reaction at 873 K. However, no carbon deposition was seen at 973 K. Cobalt O-dia catalyst showed slightly lower activity compared to nickel catalyst, but no carbon deposition was observed in the temperature range investigated. Product distributions were different for the nickel and cobalt O-dia catalysts, indicating that different reaction mechanisms occurred.

We proposed the transient response of temperature jump technique to evaluate exothermic (1, 4) and endothermic (2, 5, 6) reactions by measuring the catalyst bed temperature response to methane/oxygen pulse injection^{17),18)}. Iridium titania catalyst exhibited a very large temperature increase at the front edge of the catalyst bed with the introduction of the methane/oxygen (2/1) pulse, suggesting that highly exothermic complete oxidation proceeded as the first step, followed by endothermic reactions (5) and (6). In contrast, rhodium titania catalyst exhibited a temperature decrease at the front edge of the catalyst bed with the introduction of the methane/oxygen (2/1) pulse, suggesting a direct pathway to synthesis gas through reactions (2) and (3)^{17),18)}.

In this paper, we will deal with X-ray photoelectron spectroscopy and the temperature jump technique, to investigate the reaction pathways of nickel and cobalt-loaded O-dia catalysts.

2. Experimental

2.1. Catalyst Preparation and Partial Oxidation Reaction

Commercial fine powdered diamond (General Electric Co., particle diameter less than 0.5 mm) was first hydrogenated at 1173 K for 1 h under a pure hydrogen stream to prepare homogeneous surface conditions. The hydrogenated diamond powder was then oxidized at 723 K for 1 h under an oxygen stream (oxygen/argon = 1/4) to prepare the O-dia. The supported metal catalysts were prepared by impregnating an aqueous solution of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, $\text{RuCl}_3 \cdot n\text{H}_2\text{O}$, $\text{Pd}(\text{CH}_3\text{COO})_2$, $\text{IrCl}_4 \cdot \text{H}_2\text{O}$, $(\text{NH}_3)_2\text{Pt}(\text{NO}_2)_2$, and $\text{RhCl}_3 \cdot \text{H}_2\text{O}$ (Mitsui Pure Chemicals Co.), $\text{Fe}(\text{CO})_5 \cdot 9\text{H}_2\text{O}$, and $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Wako Pure Chemical Industries, Ltd.). After evaporating excess water, the catalyst was calcined in air at 723 K for 1 h.

2.2. Partial Oxidation Reaction

Partial oxidation of methane was carried out with a micro fixed bed flow reactor made of quartz (i.d. 8 mm $\times$ 350 mm) operated at atmospheric pressure. The catalyst (60 mg) was maintained at temperatures of 673–973 K and a flow of 25 ml/min of methane and 5 ml/min of oxygen was passed. Products were analyzed with an online high speed gas chromatograph equipped with CP-Sil 5 and Mol-plot columns (PC-Chrom, M200 Chromato Analyzer).

2.3. Transient Response Measurement

Transient response measurement of the catalyst bed temperature to pulsed reactions was carried out using a fixed bed quartz reactor (4 mm i.d. $\times$ 200 mm). Thin wall sheathed thermocouples were positioned in the front edge of the catalyst bed, and the catalyst (100 mg) was charged. A pulse of methane/oxygen (2/1) was introduced with a 6-port gas sampling valve equipped with measuring tubes (1.0 and 3.0 ml) in a stream of argon carrier gas (50 ml/min). Before the reaction, the catalyst was reduced under a hydrogen flow for 1 h at 873 K. The reaction temperature was controlled with a programmable controller by monitoring the outside temperature of the reactor wall. Analyses of the effluent gases during the pulsed reaction of methane and oxygen were made using an on-line quadrupole mass spectrometer (HAL201, Hiden Analytical Ltd.). The mass spectrometer scanned the parent peaks of the 5 compounds (hydrogen, carbon monoxide, carbon dioxide, oxygen, and methane) within 1 s, and repeated scans were collected in a personal computer.

Methane decomposition was carried out under the same conditions as the pulsed temperature jump measurement, by changing the steady flow of argon (10 ml/min) to a constant flow of pure methane (10 ml/min).

2.4. Characterization

X-Ray photoelectron spectroscopy (XPS) of the catalyst used a JEOL model JPS-9000MX with Mg K α radiation as the energy source. The spectrum was calibrated with Pt4f_{1/2} at 70.9 eV. Reduced or used catalyst samples were placed in a platinum boat under an inert atmosphere and transferred into the XPS instrument using a transfer vessel.

3. Results and Discussion

3.1. Activity of Nickel and Cobalt-loaded O-dia Catalysts

Partial oxidation of methane was carried out using various group VIII metal O-dia catalysts as shown in **Table 1**. Nickel and cobalt catalysts showed high activity for synthesis gas formation. Second row group 15–17 transition metals are highly active for this reaction²⁾, but exhibited only moderate to low activity when supported on O-dia. Carbon deposition was

Table 1 Activity of Various O-dia Supported Transition Metal Catalysts for the Partial Oxidation of Methane^{a)}

Entry	Catalyst	Conversion [%] CH ₄	Selectivity [%]			H ₂ /CO (ratio)	Carbon deposition
			CO	CO ₂	H ₂		
1	Nickel/O-dia	26.2	72.5	27.5	87.3	2.4	○
2	Nickel/O-dia ^{b)}	30.3	86.2	13.7	72.6	1.7	—
3	Cobalt/O-dia	22.9	68.0	32.1	77.6	2.3	—
4	Cobalt/O-dia ^{b)}	29.3	79.8	20.5	79.8	1.8	—
5	Ruthenium/O-dia	19.3	62.5	37.5	76.6	2.4	—
6	Rhodium/O-dia	14.2	52.9	47.1	78.7	2.5	—
7	Palladium/O-dia	13.8	50.9	49.1	77.6	3.1	○
8	Iridium/O-dia	9.4	30.1	69.9	57.1	4.6	—
9	Iron/O-dia	8.7	4.7	95.4	—	—	—
10	Platinum/O-dia	7.9	—	100	—	—	—
11	O-dia	6.1	—	100	—	—	—

a) 873 K, Flow rate: 30 ml/min (CH₄/O₂ = 5), Space velocity: 30,000 h⁻¹·ml/g-catalyst, Catalyst: 60 mg (as prepared catalyst), Metal loading level: 3 wt%.

b) at 973 K.

Table 2 Activity of Reduced and as Prepared Cobalt Catalysts for the Partial Oxidation of Methane^{a)}

Entry	Support	Conversion [%] CH ₄	Selectivity [%]			H ₂ /CO (ratio)
			CO	CO ₂	H ₂	
12	Al ₂ O ₃ (H ₂ reduced)	24.6	74.1	25.9	79.6	2.2
13	Al ₂ O ₃ (no reduction)	3.1	—	100.0	—	—
14	O-dia (no reduction)	22.1	64.1	35.9	75.6	2.4
15	La ₂ O ₃ (no reduction)	9.4	—	100	1.5	—
16	MgO (no reduction)	8.2	—	100	8.4	—
17	TiO ₂ (no reduction)	7.6	13.4	86.6	4.4	0.7
18	Graphite (no reduction)	7.2	—	100	—	—
19	SiO ₂ (no reduction)	0.4	—	100	—	—
20	SiO ₂ (H ₂ reduced)	1.0	0.0	100	—	—
21	Active carbon (no reduction)	—	—	—	—	—
22	Ni/SiO ₂ ^{b)} (no reduction)	0.0	—	—	—	—
23	Ni/SiO ₂ ^{b)} (H ₂ reduced)	27.2	74.6	26.3	76.5	2.6

a) 873 K, Flow rate: 30 ml/min (CH₄/O₂ = 5), Catalyst: 60 mg, Cobalt loading level: 3 wt%, H₂ reduction: H₂ = 10 ml/min (873 K, 1 h).

b) Ni/SiO₂ catalyst.

observed on nickel or palladium catalyst under methane/oxygen (5/1) flow at 873 K after 2 h. Carbon deposition on O-dia catalysts was measured during isothermal reaction at 873 K with hydrogen/argon mixed gas after hydrogen pre-treatment at the same temperature using thermogravimetry (TG). However, no carbon deposition was observed at 923 and 973 K. Cobalt catalyst showed no carbon deposition irrespective of the reaction temperature. The activity of nickel and cobalt O-dia catalysts for the partial oxidation of methane was described previously⁶⁾. Ni/O-dia catalyst provided high methane conversion of 30% into carbon monoxide and hydrogen with selectivity of over 72% at 973 K. No deactivation of the nickel/O-dia catalyst was observed by carbon deposition during the reaction at 973 K for 10 h. Cobalt/O-dia catalyst showed similar but slightly lower activity for the partial oxidation of methane.

Freshly prepared (without hydrogen reduction) nickel

and cobalt silica catalysts achieved very low methane conversion at 873 K (Table 2). Silicone is located below carbon in group 14 of the Periodic Table, and is frequently used as a support material for catalysts. O-dia was employed as pseudo solid carbon oxide phase^{6)~11)}. Such large differences in the effect of silica and O-dia surfaces on partial oxidation is difficult to explain at present. The interaction between metal oxide and the O-dia surface seems to be weak, and consequently the oxide could be easily reduced to lower valence species. Therefore, XPS was performed to obtain information about the nickel and cobalt valence states.

3.2. Active Form of Nickel on the Nickel/O-dia Catalyst

Nickel/O-dia catalyst exhibited high activity for the partial oxidation of methane at 873 K, whereas nickel/silica catalyst had no activity (Table 2). The XPS differences in nickel/O-dia and nickel/silica cata-

a) Fresh catalyst calcined in air at 723 K for 1 h.
 b) Catalyst reduced with H_2 at 873 K for 1 h.
 c) Catalyst (a) after the reaction with CH_4/O_2 at 973 K for 2 h.
 d) Catalyst (b) after the reaction with CH_4/O_2 at 973 K for 2 h.

Fig. 1 X-Ray Photoelectron Spectra of Ni $2p_{3/2}$ on Nickel/O-dia Catalyst

lysts were compared. **Figure 1** shows the nickel species on O-dia in the fresh and reduced catalysts. Fresh calcined nickel/O-dia catalyst showed two peaks at 854.8 and 853.1 eV, which were ascribed to Ni_2O_3 and NiO, respectively¹⁹⁾ (**Fig. 1-a**). The catalyst reduced with hydrogen at 873 K for 1 h (**Fig. 1-b**) had a strong peak at 851.6 eV, shifting from 854.8 and 853.1 eV, indicating that the nickel was reduced to metallic nickel. The binding energy of NiO is 854.0 eV for bulk NiO, and 856.7 eV for nickel oxide supported on alumina²⁰⁾. Our finding is close to that for bulk NiO. The active form of supported nickel catalyst in partial oxidation is reported to be metallic

nickel²¹⁾.

XPS analysis of fresh nickel/O-dia catalyst used for the partial oxidation of methane found two nickel species, probably partially reduced oxides of Ni_2O_{3-x} and NiO_{1-y} (**Fig. 1-c**). Peaks at 854.8 and 853.1 eV of Ni(III) and Ni(II) (**Fig. 1-a**) shifted to slightly lower binding energy of 854.5 and 852.7 eV (**Fig. 1-c**). XPS analysis of nickel/O-dia catalyst reduced under a hydrogen flow for 1 h at 873 K, and used for the partial oxidation of methane at 973 K for 2 h showed the peaks at 854.8 and 853.1 eV of Ni(III) and Ni(II) observed in **Fig. 1-a** had shifted to 853.8 and 852.0 eV (**Fig. 1-d**). These peaks were ascribed to Ni_2O_{3-x} and NiO_{1-y} , which are slightly lower valence state oxides compared to those observed in **Fig. 1-c**. Therefore, partial oxidation of methane oxidized metallic nickel on the surface to nonstoichiometric nickel oxides, such as Ni_2O_{3-x} and NiO_{1-y} . Only a small portion of nickel oxide supported on magnesia was reduced to Ni(0). Similar findings were reported for nickel/alumina²²⁾. Such non-stoichiometric nickel oxide species seem to be the active forms of the nickel catalyst in partial oxidation. Except for the nickel/O-dia catalyst reduced with hydrogen, the half height width of the spectra varied, indicating that nickel oxides were present in different oxidation states. The reaction at 873 K resulted in considerable carbon formation, which prevented XPS measurement with a good signal to noise ratio.

XPS of the fresh and used nickel/silica catalysts are shown in **Fig. 2**. Fresh calcined nickel/silica catalyst showed two peaks at 855.0 and 853.2 eV, which were ascribed to Ni_2O_3 and NiO, respectively, (**Fig. 2-a**), as in the case of Ni/O-dia catalyst. Catalyst reduced with hydrogen at 873 K for 1 h showed two peaks at 854.4 and 851.4 eV, ascribed to slightly reduced Ni_2O_3 and metallic nickel, respectively (**Fig. 2-b**). Compared with the spectrum shown in **Fig. 1-b**, a much larger peak was seen at 854.5 eV in the nickel/silica catalyst, indicating that the stronger interaction between the nickel oxide and silica surface suppresses complete reduction of the oxide to metallic form. Such a difference in the reducibility of nickel oxide over different supports is also seen in nickel oxide on magnesia, calcium oxide, and cerium dioxide²²⁾.

XPS analysis of fresh nickel/silica catalyst after partial oxidation of methane exhibited two peaks at 854.9 and 853.1 eV (**Fig. 2-c**). The binding energies of the two peaks did not change after the reaction (compare **Fig. 2-a** and **Fig. 2-c**). In addition, partial oxidation of methane did not proceed at 973 K over nickel/silica catalyst without pretreatment with hydrogen. XPS analysis of nickel/silica catalysts reduced with hydrogen at 873 K for 1 h, and after partial oxidation of methane at 973 K for 2 h, found the peaks at 855.0 and 853.2 eV (**Fig. 2-a**) shifted to slightly lower binding energy at 854.5 and 852.8 eV (**Fig. 2-d**). These find-

a) Fresh catalyst calcined in air at 723 K for 1 h.
b) Catalyst reduced with H_2 at 873 K for 1 h.
c) Catalyst (a) after the reaction with CH_4/O_2 at 973 K for 2 h.
d) Catalyst (b) after the reaction with CH_4/O_2 at 973 K for 2 h.

Fig. 2 X-Ray Photoelectron Spectra of Ni $2p_{3/2}$ on Nickel/SiO₂ Catalyst

ings indicate that nickel oxide on silica could not be reduced to the metallic form or slightly reduced oxides in a flow of methane and oxygen. In addition, metallic nickel was oxidized during the reaction and appeared as higher binding energy oxide phases, compared to those observed in nickel species on O-dia. One possibility is that nickel oxide supported on O-dia is easily reduced to lower valence states as evidenced by the result in Fig. 1-b, due to weak interaction between the nickel oxide and O-dia surface.

3.3. Active Species of Cobalt in the Cobalt/O-dia Catalyst

Cobalt/O-dia catalyst exhibited high catalytic activity

a) Fresh catalyst calcined in air at 723 K for 1 h.
b) Catalyst reduced with H_2 at 873 K for 1 h.
c) Catalyst (a) after the reaction with CH_4/O_2 at 873 K for 2 h.
d) Catalyst (b) after the reaction with CH_4/O_2 at 873 K for 2 h.

Fig. 3 X-Ray Photoelectron Spectra of Co $2p_{3/2}$ on Cobalt/O-dia Catalyst

for the partial oxidation of methane at 873 K, but cobalt/silica and cobalt/alumina catalysts showed no activity at 873 K⁶⁾. The cobalt species on both fresh and used catalysts were examined using XPS of cobalt/O-dia and cobalt/alumina catalyst and compared in Figs. 3 and 4. Cobalt/silica catalyst should be used for direct comparison, but cobalt/silica catalyst had no activity even after hydrogen reduction (Table 2). Fresh calcined cobalt/O-dia catalyst showed a peak at 779.6 eV, assignable to Co_3O_4 (Fig. 3-a), since the catalyst was prepared by calcination at 723 K under an air flow²³⁾. After reduction with hydrogen at 873 K for 1 h (Fig. 3-b), the peak appeared at 776.5 eV, a shift from

a) Fresh catalyst calcined in air at 723 K for 1 h.
 b) Catalyst reduced with H_2 at 873 K for 1 h.
 c) Catalyst (a) after the reaction with CH_4/O_2 at 873 K for 2 h.
 d) Catalyst (b) after the reaction with CH_4/O_2 at 873 K for 2 h.

Fig. 4 X-Ray Photoelectron Spectra of Co $2p_{3/2}$ on Cobalt/ Al_2O_3 Catalyst

the higher binding energy of 779.6 eV, indicating that oxidic cobalt was reduced to metallic cobalt. This value is slightly lower compared to the reported values for metallic cobalt^(24),25). The weak broad peak at 778.7 eV could be ascribed to slightly reduced cobalt oxide (CoO_{1-x}). XPS analysis of the fresh cobalt/O-dia catalyst after partial oxidation of methane showed the skewed peak was deconvoluted into three cobalt species, Co_3O_4 (779.0 eV), slightly reduced CoO_{1-x} (778.6 eV), and metallic cobalt (776.4 eV) (Fig. 3-c). However, the intensity of the metallic cobalt species was weak. XPS analysis of the cobalt/O-dia catalyst reduced with hydrogen flow for 1 h at 873 K, and after partial oxidation of methane at 873 K for 2 h detected two cobalt species Co_3O_4 (779.1 eV), and metallic

cobalt (Fig. 3-d). When the reduced catalyst was used, metallic cobalt species remained during the reaction. However, conversion of methane with fresh and reduced catalyst was of the same order of magnitude (conversion, fresh catalyst: 22.9%; hydrogen reduced catalyst: 21.2%). Therefore, the XPS analyses suggest that the active species of cobalt/O-dia catalyst is both metallic cobalt and low valence state cobalt oxide (surface oxygen deficient species).

XPS analysis of fresh calcined cobalt/alumina catalyst showed a broader peak at 779.6 eV ascribed to Co_3O_4 (Fig. 4-a), as for the cobalt/O-dia catalyst. After reduction of the catalyst with hydrogen at 873 K for 1 h (Fig. 4-b), a strong peak appeared at 776.5 eV, shifted from the higher binding energy of 779.6 eV (Fig. 4-a), indicating that oxidic cobalt was reduced to metallic cobalt, and the peak at 777.2 eV (Fig. 4-b) was ascribed to slightly reduced CoO_{1-x} oxide. Broader overlapping peaks indicated that reduction to metallic cobalt was not complete, compared to the cobalt/O-dia catalyst. The used cobalt/alumina catalyst showed almost the same spectrum as that of fresh catalyst, indicating that cobalt oxide was not reduced to low valence state cobalt oxides and metallic cobalt, in the course of the reaction with methane/oxygen mixture. Therefore, freshly prepared cobalt/alumina catalyst did not exhibit catalytic activity for the partial oxidation of methane at 873 K (Table 1). Such behavior is quite different from that of the cobalt/O-dia catalyst. XPS analysis of the cobalt/alumina catalyst reduced with hydrogen for 1 h at 873 K, after partial methane oxidation at 873 K for 2 h exhibited two peaks at 777.3 and 776.4 eV, which were ascribed to oxygen deficient CoO_{1-x} and metallic cobalt (Fig. 4-d). Therefore, the reduced cobalt/alumina catalyst exhibited high catalytic activity for the partial oxidation of methane at 873 K (Table 2). Metallic or partially reduced CoO dispersed on rare earth oxide support is apparently the active site for the partial oxidation of methane²⁷⁾. These results suggest that cobalt/O-dia catalyst is reduced more easily than cobalt/alumina catalyst during the reaction with methane/oxygen.

The binding energy of metallic cobalt was lower than the reported value of 778.1 eV in both catalysts^{16),23)–25)}. As seen in Figs. 3 and 4, the binding energy of Co_3O_4 was the same value as reported. One possible explanation for our results is that a lower loading level of the cobalt was employed in our study (5 wt%). The reduced catalysts did not show any XRD peaks of cobalt species, indicating that both the surface cobalt and the bulk cobalt species were fully reduced. In contrast, the fresh cobalt/O-dia catalyst showed diffraction peaks ascribed to Co_3O_4 species. No significant shake-up peak was observed in the XPS analyses, indicating that pure $Co(II)$ species was not formed.

(a) Reaction at 873 K, (b) reaction at 973 K.
CH₄ flow rate = 10 ml/min, Catalyst: 100 mg.

Fig. 5 Transient Response Profile against Argon Flow to the Reaction of Methane over Nickel/O-dia Catalyst

3.4. Transient Response Studies on Nickel/O-dia Catalyst

The transient response reaction of methane was examined to obtain more information about the reaction pathway of synthesis gas production over nickel/O-dia catalyst. Before the reaction, the nickel/O-dia catalyst was reduced with hydrogen at 873 K for 1 h, since nickel oxide on the catalyst surface could not be reduced with a pulse of methane/oxygen (2/1) mixed gas. **Figure 5** shows hydrogen formation at 873 and 973 K when the flowing gas was switched from argon to pure methane (reaction 2). Hydrogen and unreacted methane were the only gaseous products observed. Rapid and continued production of hydrogen with a small response of methane was observed over nickel/O-dia catalyst at 873 K (**Fig. 5-a**). On the other hand, only a very low concentration of hydrogen appeared instantaneously when methane was supplied to the nickel/O-dia catalyst at 973 K (**Fig. 5-b**). This is quite unusual for a chemical reaction to proceed less rapidly at a higher temperature. The reason seems to be different types of carbon formed on the nickel surface. The behavior shown in **Fig. 5-b** is quite similar to the result obtained for iridium/titania catalyst¹⁷⁾.

Previously we demonstrated that reaction paths in

Reaction conditions: Ar carrier = 50 ml/min, Mixed gas: CH₄/O₂ = 2 (1 ml or 3 ml), Furnace temperature: 873 K.

Fig. 6 Temperature Profiles at the Front Edge of the Catalyst Bed and Products after Pulsed Injection of CH₄/O₂ over Nickel (3 wt%)/O-dia Catalyst at 873 K

the partial oxidation of methane can be evaluated by the temperature changes at the catalyst bed during the methane/oxygen pulsed reaction^{17),18)}. A rapid temperature rise in the front edge of the iridium/titania catalyst bed was observed with the injection of a methane/oxygen (2/1) pulse. On the other hand, a small but distinct temperature decrease was observed on the rhodium/titania catalyst bed at methane/oxygen pulse injection. These observations suggest that iridium/titania catalyzed, partial oxidation predominantly proceeds by sequential steps involving reactions (4), (5), and (6). In contrast, direct decomposition of methane occurs over rhodium/titania catalyst to hydrogen and carbon monoxide^{17),18)}.

The temperature at the front edge of the catalyst bed slightly decreased upon introduction of the methane/oxygen pulse at 873 K as shown in **Fig. 6**. The synthesis gas production reactions (2), (5), and (6) are endothermic. Therefore, the above results (**Figs. 5-a**, and **6**) suggest that hydrogen formation probably proceeded *via* methane decomposition (reaction 2), and then CH_x species generated on the nickel surface were oxidized to CO_x with either surface oxygen or vapor phase oxygen. The products were hydrogen and car-

Reaction conditions: Ar carrier = 50 ml/min, Mixed gas: CH₄/O₂ = 2 (1 ml or 3 ml), Furnace temperature: 973 K.

Fig. 7 Temperature Profiles at the Front Edge of the Catalyst Bed and Products after Pulsed Injection of CH₄/O₂ over Nickel (3 wt%)/O-dia Catalyst at 973 K

bon monoxide as seen in Fig. 6-b. These results are consistent with the findings of continuous flow partial oxidation of methane with oxygen, in which considerable amount of carbon formation was observed during reaction at 873 K⁶.

Methane decomposition on the nickel surface is the most important key reaction in the direct oxidation of methane to form synthesis gas. Nickel catalysts are very active for methane decomposition^{27)~29)}. Moreover, direct formation of carbon monoxide and hydrogen formation from methane without intermediate total oxidation using nickel-containing catalysts is possible³⁰⁾. Therefore, partial oxidation of methane *via* the direct path is not peculiar to the nickel/O-dia catalyst.

Figure 7 shows the transient temperature responses of the nickel/O-dia catalyst during pulsed injection of methane/oxygen (2/1) at 973 K. A small sudden rise in temperature at the front edge of the catalyst bed was observed at the methane/oxygen (2/1) pulse. This temperature increase can be ascribed to the exothermic complete oxidation reaction (4). Carbon monoxide and hydrogen were obtained together with a small amount of carbon dioxide (pulse size 3 ml). These results strongly suggest that synthesis gas formation over nickel/

H₂ reduction: H₂ = 10 ml/min, 873 K, 1 h, Temperature: 873 K, Catalyst: 100 mg, CH₄ flow rate = 10 ml/min.

Fig. 8 Transient Response against Reaction of Methane over Cobalt/O-dia Catalyst

O-dia catalyst at 973 K may proceed *via* a two-step pathway: total oxidation of methane to carbon dioxide and water (reaction 4), followed by reforming to synthesis gas (reactions 5 and 6), as indicated previously for the iridium/titania catalyst^{17),18)}. Carbon dioxide is produced by complete oxidation of methane, whereas the slower carbon dioxide reforming reaction of methane forms unreacted carbon dioxide. Our results showed that higher carbon dioxide selectivity was obtained at 973 K, although the equilibrium is less favorable for carbon dioxide (Table 1).

3. 5. Transient Response Studies on Cobalt/O-dia Catalyst

Cobalt/O-dia catalyst shows slightly different behavior compared to nickel/O-dia catalyst⁶⁾. Methane conversion was higher at lower temperature and no carbon deposition was seen after the reaction at any temperature. The transient pulse method was used to investigate the differences in the nickel/O-dia catalyst and cobalt/O-dia catalyst.

Figure 8 shows hydrogen formation over the cobalt/O-dia catalyst when the flowing gas was switched from argon to methane at 873 K (reaction 2). Before the reaction, the cobalt/O-dia catalyst was reduced with hydrogen at 873 K for 1 h. When methane was supplied to the cobalt/O-dia catalyst, only a small hydrogen response appeared and then decreased to a low concentration. This behavior is quite different from that observed for the nickel/O-dia catalyst at 873 K, indicating that only slight methane decomposition occurred. This behavior was the same as that observed in the reaction with nickel/O-dia at 973 K.

A sudden rise in temperature at the front edge of the cobalt/O-dia catalyst bed was observed at methane/oxygen pulses (Fig. 9). The temperature rise increased with larger pulse size from 1.0 to 3.0 ml. The temper-

Reaction conditions: Ar carrier = 10 ml/min, Mixed gas: CH₄/O₂ = 2 (1 ml or 3 ml), Furnace temperature: 873 K.

Fig. 9 Temperature Profiles at the Front Edge of the Catalyst Bed and Products after Pulsed Injection of CH₄/O₂ over Cobalt (3 wt%)/O-dia Catalyst at 873 K

ature increase in the front edge of the catalyst bed can be ascribed to the exothermic complete oxidation reaction. As in the case of the nickel/O-dia catalyst at 973 K, carbon monoxide and hydrogen together with a considerable amount of carbon dioxide were obtained from the methane/oxygen pulse. These results strongly suggest that synthesis gas formation over cobalt/O-dia catalyst may proceed *via* two-step pathways, as for the iridium/titania catalyst¹⁷⁾. Carbon dioxide and water were produced by the complete oxidation reaction in the front edge of the catalyst bed. Slower carbon dioxide and steam reforming reactions followed to form hydrogen and carbon monoxide. The reaction of carbon dioxide with methane over nickel and cobalt/O-dia catalysts was discussed previously¹¹⁾. A large amount of unreacted carbon dioxide was observed, whereas almost no carbon dioxide was detected from the nickel/O-dia catalyst in the pulsed reaction at 873 K (Fig. 6). All these results suggest that different reaction pathways occur over the nickel/O-dia catalyst at 873 K and the nickel/O-dia catalyst at 973 K and cobalt/O-dia catalyst at any temperature.

Catalyst: 50-150 mg, Reaction temperature: 973 K.
○: H₂, □: CO, △: CO₂.

Fig. 10 Effect of Space Velocity on CH₄ Conversion and Product Selectivities over Nickel (3 wt%)/O-dia Catalyst

3.6. Effect of Space Velocity in the Partial Oxidation of Methane on the Product Distribution over Ni and Co/O-dia Catalysts

Among the reactions involved in the partial oxidation of methane, complete oxidation is the fastest, and carbon dioxide reforming is the slowest. The effect of the space velocity on the product distribution gives information about the reaction course. Figure 10 shows the conversion of methane and selectivities for carbon monoxide, hydrogen and carbon dioxide as a function of the space velocity over nickel/O-dia catalyst at 973 K. The methane conversion and the carbon monoxide and hydrogen selectivities decreased with increasing space velocity. On the other hand, the carbon dioxide selectivity increased. These results suggest that two-step reaction pathways are important in synthesis gas formation. If the partial oxidation proceeds *via* the one-step process (reaction 1), an increase in the space velocity would decrease the conversion of methane without changing the hydrogen and carbon monoxide selectivities.

Similarly with cobalt/O-dia catalyst, the space velocity was varied by increasing the feed rate at 873 K. Figure 11 shows the methane conversion and selectiv-

Catalyst: 50-150 mg, Reaction temperature: 873 K, CH₄/O₂ = 5, Flow rate: 30 ml/min. ○: H₂, □: CO, △: CO₂.

Fig. 11 Effect of Space Velocity on CH₄ Conversion and Product Selectivities over Cobalt (3 wt%)/O-dia Catalyst

ities for carbon monoxide, hydrogen and carbon dioxide as a function of the space velocity. Exactly the same behavior was observed, indicating that the two-step pathway occurs in partial oxidation over cobalt/O-dia catalyst.

These results show that carbon deposition behavior during partial oxidation of methane at 873 K over nickel/O-dia is due to the decomposition of methane to carbon and hydrogen (reaction 2). The reason why no carbon deposition was observed on the same catalyst at 973 K is the change in the reaction mechanism from methane decomposition to complete oxidation (reaction 4). The reason for such a change in mechanism could not be interpreted in this study. Thermodynamic calculation shows that ΔG for reaction (2) is negative at 873 K and becomes more negative with higher reaction temperature. Higher activation energy of complete oxidation may be one of the reasons for the change in reaction mechanism. The weak capability for the decomposition of methane (reaction 2) and higher oxidation ability of cobalt/O-dia catalyst resulted in the two-step reaction pathway, irrespective of the reaction temperature.

4. Conclusion

The active forms of nickel and cobalt species on O-dia catalyst in the partial oxidation of methane were examined by XPS and compared to inactive catalysts. Reduced forms of both nickel oxide and cobalt oxide phases were found to be the active phases. The presence of the metallic form is not essential to the catalytic activity. Reduction of oxides did not proceed in methane and oxygen flows over nickel/silica and cobalt/alumina catalysts.

Reaction mechanisms of the partial oxidation of methane with nickel/O-dia catalyst and cobalt/O-dia catalyst to give synthesis gas differ at 873 K, as the reaction proceeded through the direct path to give hydrogen and carbon on the nickel/O-dia catalyst surface, whereas two-step complete oxidation followed by reforming occurred over cobalt/O-dia catalyst, irrespective of the temperature.

Acknowledgment

This work was financially supported by a Grant-in-Aid for Scientific Research (10555283 and 14350429). We thank Professor S. Nishiyama of Kobe University for his interpretation of X-ray photoelectron spectra.

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要 旨

酸化ダイヤモンド担持触媒を用いたメタンの部分酸化反応による合成ガス生成 — ニッケルおよびコバルトの触媒挙動 —

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メタンの部分酸化反応における酸化ダイヤモンド担持ニッケルおよびコバルト触媒 (Ni/O-dia触媒およびCo/O-dia触媒) のキャラクタリゼーションをXPS (X-ray photoelectron spectroscopy) およびtransient response法を用いて行った。

873 Kでのメタンの部分酸化反応において, Co/O-dia触媒を用いたときには触媒表面上への炭素析出は見られなかったが, Ni/O-dia触媒を用いたときには炭素が析出した。各反応後の触媒をXPSで分析すると, Ni/O-dia触媒では部分的に還元された酸化ニッケル種が認められ, Co/O-dia触媒では0価のコバルト, 部分的に還元された酸化コバルト種および酸化コバルト (III) の存在が確認された。一方, 873 Kに保持した触媒にメタンの

みを供給したところ, Ni/O-dia触媒ではメタン供給と同時に多量の水素が生成したが, Co/O-dia触媒ではわずかな量の水素しか生成しなかった。さらに, メタン/酸素混合ガス (2:1) をパルスで供給したところ, Ni/O-dia触媒では吸熱が起こり, Co/O-dia触媒では発熱が起こった。以上のことを考え合わせると, Ni/O-dia触媒ではまずメタンの分解によって水素が生成し, 残った炭素種が酸素と反応し一酸化炭素が生成するものと考えられる。Co/O-dia触媒ではメタンの完全酸化が起こり, 生成した水および二酸化炭素によるメタンの改質反応によって合成ガスが生成するものと考えられる。