Partial Oxidation of Methane over Ni/Ce-ZrO₂/θ-Al₂O₃

Zhong-Wen Liu, Hyun-Seog Roh, Ki-Won Jun†, Sang-Eon Park† and Taek-Yong Song*

Chemical Technology Division, Korea Research Institute of Chemical Technology,
P. O. Box 107, Yuseong, Daejeon 305-600, Korea
*LNG Technology Research Center, Korea Gas Corporation, 973 Dongchun-Dong, Yeonsu-Ku, Incheon 406-130, Korea
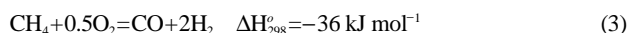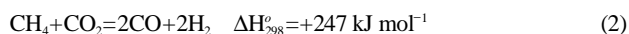(*Received 17 April 2002 • accepted 23 May 2002*)

Abstract−The catalytic behavior of Ni/Ce-ZrO₂/θ-Al₂O₃ has been investigated in the partial oxidation of methane (POM) toward synthesis gas. The catalyst showed high activity and selectivity due to the heat treatment of the support and the promotional effect of Ce-ZrO₂. It is suggested that the support was stabilized through the heat treatment of γ-Al₂O₃ and the precoating of Ce-ZrO₂, on which a protective layer was formed. Moreover, sintering of the catalyst was greatly suppressed for 24 h test. Pulse experiments of CH₄, O₂ and/or CH₄/O₂ with a molar ratio of 2 were systematically performed over fresh, partially reduced and well reduced catalyst. Results indicate that CH₄ can be partially oxidized to CO and H₂ by the reactive oxygen in complex NiO$_x$ species existing over the fresh catalyst. It is demonstrated that POM over Ni/Ce-ZrO₂/θ-Al₂O₃ follows the pyrolysis mechanism, and both the carbonaceous materials from CH₄ decomposition over metallic nickel and the reactive oxygen species present on NiO$_x$ and Ce-ZrO₂ are intermediates for POM.

Key words: Partial Oxidation of Methane, Ni Catalyst, Ce-ZrO₂, θ-Al₂O₃, Characterization, Pulse Reaction, Mechanism, Synthesis Gas

INTRODUCTION

Methane utilization has received much attention in the past decades. Although the direct use of CH₄ as a feedstock to produce valuable chemicals such as methanol and ethane is more effective, it has been limited because of the low reactivity of CH₄ [Anderson, 1989]. Nevertheless, CH₄ can be reformed to syngas, which is the feedstock to produce methanol and other hydrocarbons by methanol synthesis and Fischer-Tropsch synthesis, through steam reforming of methane (SRM, reaction 1), CO₂ reforming of methane (CDR, reaction 2), and catalytic partial oxidation of methane (POM, reaction 3) [Armor, 1999; Nam et al., 2000].

$$CH_4 + H_2O = CO + 3H_2 \quad \Delta H^o_{298} = +206 \text{ kJ mol}^{-1} \quad (1)$$

$$CH_4 + CO_2 = 2CO + 2H_2 \quad \Delta H^o_{298} = +247 \text{ kJ mol}^{-1} \quad (2)$$

$$CH_4 + 0.5O_2 = CO + 2H_2 \quad \Delta H^o_{298} = -36 \text{ kJ mol}^{-1} \quad (3)$$

A large amount of energy is consumed because both SRM and CDR are highly endothermic processes. On the other hand, POM which is a mildly exothermic process, offers the greatest potential for a fast, efficient, and economical conversion of CH₄, due to the high conversion, high selectivity, suitable H₂/CO ratio, and very short residence time [Tsang et al., 1995].

The supported transitional metals and precious metals have been reported as active catalysts for POM [Tang et al., 1998; Buyevskaya et al., 1996; Boucouvalas et al., 1996; Fathi et al., 2000]. However, the nickel-based catalyst is the most investigated because of its low cost and high activity. The modification, characterization and mechanistic studies on POM over nickel-based catalysts have become

one of the most active topics in catalysis [Tang et al., 1998; Tsipouriari et al., 1998; Takeguchi et al., 2001; Choudhary et al., 1997; Au et al., 1996; Hu and Ruckenstein 1998a, b, c; Lu et al., 1998].

Two mechanisms have been proposed for POM [Dissanayake et al., 1991; Jin et al., 2000; Heitnes et al., 1995]: (1) the combustion-reforming mechanism, in which CH₄ is completely oxidized to CO₂+H₂O, and CO is a result of the reforming of H₂O and CO₂ with the residual CH₄; (2) the pyrolysis mechanism, in which CH₄ pyrolyzed over the catalyst to produce CO directly without the preformation of CO₂. Although the mechanism of POM over nickel-based catalysts is still debatable, it seems that the mechanism is closely related to the oxidation state of nickel. Based on the results of pulse reaction and isotopic GC-MS studies, Hu and Ruckenstein [Hu and Ruckenstein, 1998a] demonstrated that POM follows different mechanisms over reduced and unreduced Ni/SiO₂ catalyst. In combination with in situ HTXRD, semi-in situ XPS techniques, van Looij and Geus [van Looij and Geus, 1997] concluded that the partially oxidized nickel is responsible for the combustion reaction and the reforming of CH₄ calls for metallic nickel sites. Choudhary et al. [Choudhary et al., 1997] found that the activity of POM over Ni/(SiO₂)$_x$ (Al₂O₃)$_{1−x}$ can be greatly enhanced by precoating of the support with MgO, CaO, Yb₂O₃, Sm₂O₃. They attributed it to the elimination or drastic reduction in the formation of catalytically inactive NiAl₂O₄ spinel and/or NiSiO₄ phases from the chemical interactions between NiO and Al₂O₃ and/or SiO₂ from support at high temperatures. Miao et al. [Miao et al., 1997] have studied the promotional effects of alkali metal (Li, Na, K) oxides and rare-earth metal (La, Ce, Y, Sm) oxides on the Ni/Al₂O₃ catalysts for POM. Their results indicated that the modification with the oxides improves the ability of the catalysts to suppress carbon deposition over the catalyst during POM.

In previous studies [Roh et al., 2001a, b], we have successfully

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developed Ni/Ce-ZrO$_2$ catalyst for SRM, POM and Oxy-SRM. The addition of ceria proved to enhance CH$_4$ dissociation, to improve oxygen capacity, and to promote carbon elimination during POM reaction. However, Ce-ZrO$_2$ is a quite expensive ingredient as a support from the practical viewpoint. At the same time, our preliminary results indicate that θ-Al$_2$O$_3$ is a stable support for POM [Roh et al., 2001c; Liu et al., 2002]. These results motivated us to precoat θ-Al$_2$O$_3$ support with Ce-ZrO$_2$ to improve the performance and to reduce the cost of the catalyst.

In this paper, activity, selectivity and stability of Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ for POM were investigated in an experimental fixed-bed reactor. XRD and XPS were used to characterize the catalyst. Pulse experiments of CH$_4$, O$_2$ and mixed gas of CH$_4$ and O$_2$ were carried out to study the performance of the catalyst at transient state and to probe the mechanism of POM.

EXPERIMENTAL

1. Catalyst

The support used in this study was prepared as follows. The solution of mixed Ce-acetate/Zr-nitrate (CeO$_2$/ZrO$_2$=0.20 w/w) was impregnated on γ-Al$_2$O$_3$ (CONDEA Chemie GmbH) at room temperature for 12 h. The precoated sample was calcined at 1,173 K for 6 h with a heating rate of 1 K per minute. During the heat treatment, γ-Al$_2$O$_3$ was transferred to θ-Al$_2$O$_3$. Nickel was loaded by impregnating appropriate amount of Ni(NO$_3$)$_2$·6H$_2$O on the support and dried at 373 K. After drying, the sample was calcined in air at 823 K for 6 h. The nickel loading was 12 wt%. Hereafter, the catalyst means Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ with 12 wt% Ni loading if it is not specified.

2. Reaction Procedure

A steady state experiment of POM was carried out in a fixed-bed reactor system. The reactor (Incolloy 800H) with an inner diameter of 18 mm was heated in an electric furnace. The bed temperature was monitored by a K-type thermocouple placed in the catalyst bed with a thermowell. Before reaction, two grams of catalyst with a particle size of 16-20 mesh were loaded and reduced at 973 K for 3 h with 5% H$_2$ in N$_2$. At the desired temperature, feed gases [CH$_4$/O$_2$=1.95, N$_2$/(CH$_4$+O$_2$)=1], which were separately fed and controlled by mass flow controller, were mixed in a mixer before the reactor. A cold trap at the outlet of the reactor was used to condense any water from the product gas stream. The products were analyzed by an on-line GC equipped with a TCD and a Carbosphere packed column (Alltech). The operating conditions were GHSV=27,600 ml/(g$_{cat}$ h), reaction pressure P=1 atm, T=1,018 K, and time on stream (TOS) of 24 h.

Pulse experiments using CH$_4$, O$_2$ and/or CH$_4$/O$_2$ with a molar ratio of 2 were performed in a quartz micro-reactor. Prior to each reaction, 30 mg catalyst (20-45 mesh) was loaded in the reactor and treated at the desired temperature in He (30 ml/min) for 90 min to remove any residual gases in the system, then exposed to pulses of CH$_4$, O$_2$ and/or CH$_4$/O$_2$. During each pulse, the exit gas was analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with a TCD (Carbosphere column, 353 K, helium as carrier gas). The conversion and selectivity were calculated on the basis of carbon contents in the products and 100% carbon and oxygen balances.

3. Characterization of the Catalyst

The reduced and used samples were passivated by much diluted oxygen of 0.5% O$_2$ in N$_2$ for 30 min at room temperature before unloading. The unloaded samples were transferred in atmosphere and stored for test in a dry room with inert gas of Ar.

The XRD patterns of fresh, reduced, and used samples were recorded with a Rigaku 2155D6 diffractometer using a copper target at 40 kV×50 mA and scanning speed of 2° (2θ) per minute. Surface analysis of the catalyst was performed at room temperature on a VG ESCALAB 210 spectrometer with an Al Kα radiation generated at 300 watts. The analysis was operated at pass energy of 20 eV and a step size of 0.1 eV. Binding energies were adjusted relative to adventous carbon at 284.6 eV. The specific surface area of the samples, which were evacuated at 473 K, was measured by BET nitrogen adsorption method in a volumetric equipment Micromeritics ASAP-2400. The procedure for the characterization of the samples by TPR was described elsewhere [Roh et al., 2001d].

RESULTS

1. Catalytic Performance at Steady State

The catalytic performance as a function of time on stream is presented in Fig. 1. The average CH$_4$ conversion during 24 h test was 88.9% while the O$_2$ was completely consumed. The CO selectivity and H$_2$/CO ratio were about 97% and 2.1, respectively. There was
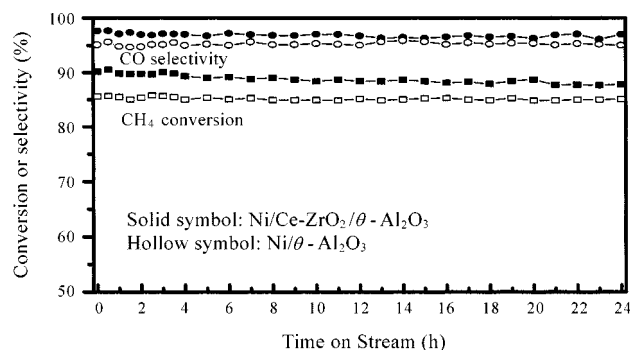

Fig. 1. CH$_4$ conversion and CO selectivity as a function of time on stream (Reaction conditions: P=1 atm, T=1,018 K, CH$_4$/O$_2$=1.95, N$_2$/[CH$_4$+O$_2$]=1, GHSV=27,600 ml/(g$_{cat}$ h)].
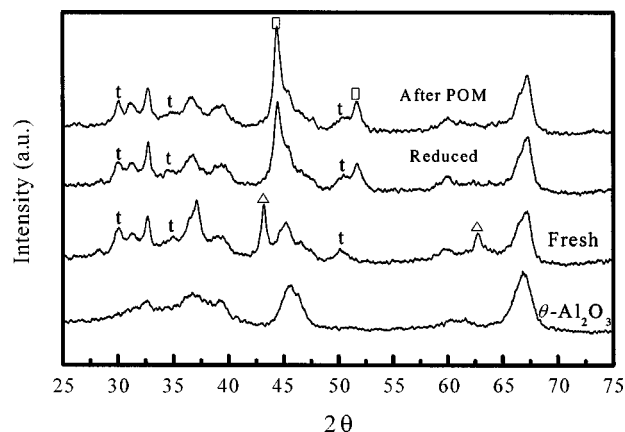

Fig. 2. XRD patterns of the fresh, reduced, used catalyst and θ-Al$_2$O$_3$ support (□: Ni, △: NiO, t: tetragonal Ce-ZrO$_2$).
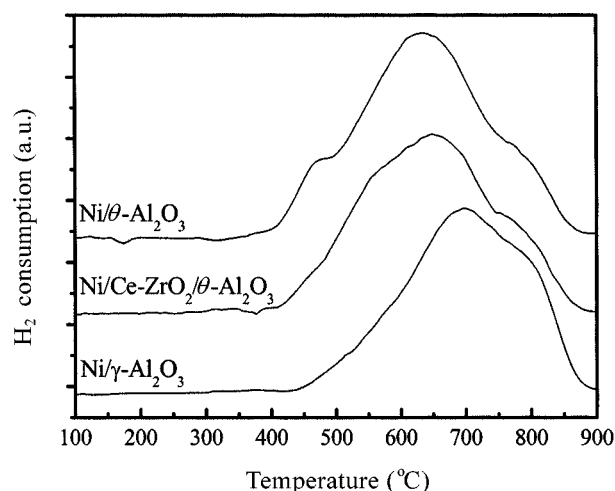
Fig. 3. TPR patterns of Ni/γ-Al₂O₃, Ni/θ-Al₂O₃ and Ni/Ce-ZrO₂/θ-Al₂O₃ catalysts.

no obvious deactivation based on CH_4 conversion during TOS of 24 h. In comparison, the results over Ni/θ-Al₂O₃ catalyst are also given in Fig. 1. It is clear that the Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst exhibited higher activity and CO selectivity towards POM. This must be related to the promotional effect of Ce-ZrO₂ and will be discussed later.

2. Catalyst Characterization

2-1. XRD, TPR and BET Analysis

The XRD patterns of the catalyst at different state are given in Fig. 2. The phases of NiO and support were clearly shown for the fresh sample. The XRD lines of NiO and Ni were diffused, which is ascribed to the smaller crystallite size of nickel or nickel oxide on the support. The precoated Ce-ZrO₂ solid solution was indexed as a tetragonal phase. There is no NiAl₂O₄ spinel phase detected by XRD for all the samples. It is likely that the content of the spinel phase is too low to be detected by XRD, but it is confirmed from TPR results (Fig. 3).

According to the TPR results, the formation of NiAl₂O₄ species is retarded through heat treatment and precoating of Ce-ZrO₂. For Ni/γ-Al₂O₃ catalyst, there were two peaks at the peak maximum about 963 K and 1,073 K, which can be assigned to the reduction of NiO$_x$ species with strong interaction with γ-Al₂O₃ and highly dispersed NiAl₂O₄ species, respectively. However, for Ni/Ce-ZrO₂/θ-Al₂O₃ as shown in Fig. 3, only a very small shoulder peak at peak maximum about 1,073 K was observed. Comparing the peak area at 1,073 K for the three samples, it can be seen that the amount of NiAl₂O₄ species in the catalysts is in the order of Ni/γ-Al₂O₃>Ni/θ-Al₂O₃>Ni/Ce-ZrO₂/θ-Al₂O₃. Therefore, the spinel phase over Ni/Ce-ZrO₂/θ-Al₂O₃ catalyst was successfully decreased.

The NiO phase was not detected for the samples reduced and used in POM for 24 h although these samples were passivated with diluted oxygen at room temperature before unloading and transferred in the atmosphere. This suggests that the bulk phase of the nickel was not oxidized under the passivation conditions. The interaction of oxygen with nickel surfaces has been studied intensively and the oxidation of metallic nickel at room temperature brings about the formation of a two-dimension oxide with a thickness of 2 to 3 NiO layers [van Looij and Geus, 1997]. So, this low NiO content

Table 1. The BET surface areas of the catalysts

Samples	BET surface area (m²/g)	
	Reduced	Used
Ni/Ce-ZrO₂/θ-Al₂O₃	76	75
Ni/θ-Al₂O₃	101	96

cannot be detected by XRD. No observable phase transformation occurred after POM by comparing the XRD patterns of the reduced and used samples. Therefore, the support is stabilized by heat treatment and precoating of Ce-ZrO₂.

From the BET results listed in Table 1, within the test error, there is only negligible difference of BET surface area for the reduced and used catalyst. It is concluded that there is no obvious sintering of the catalyst after use in POM for 24 h. However, it is obvious that there exists an observable difference (~5%) of BET surface area for the reduced and used Ni/θ-Al₂O₃ catalyst. This will be discussed later.

2-2. XPS Analysis

To obtain information on the surface state of the catalyst, XPS was performed for the fresh, reduced and used samples. From the XPS spectra at Ni 2p region (not shown), it is clear that both Ni and NiO were present on the surface of reduced and used samples although they were passivated by diluted oxygen and transferred in atmosphere. This confirms that the oxidation of Ni is very limited at room temperature.

To further probe the surface composition of the samples, surface Ni/Al ratio was calculated based on the XPS results and given in Table 2. At the same time, bulk Ni/Al ratio is also provided, which was calculated according to the nickel loading. For comparison, the results for Ni/θ-Al₂O₃ catalyst are provided in Table 2. It is worth noting that the change of the Ni/Al ratio for the two catalysts follows the same trend. The surface Ni/Al molar ratio for fresh sample was much higher than those of the reduced and used samples. The loss of surface Ni/Al molar ratio for the used sample may be from the fact that the surface nickel is partly covered by the carbonaceous materials deposited during POM. However, it is not the case for the reduced sample because there was no carbon deposition over the catalyst during reduction process. It was reported that a significant loss of surface Ni/Zr molar ratio occurred after reduction of Ni/ZrO₂ catalysts [Montoya et al., 2000]. The authors [Montoya et al., 2000] explained this observation on the basis that nickel particles are covered or occluded by the support. In the present case, the great loss of surface Ni/Al molar ratio may be ascribed to the decoration of Ni by the support, which caused the change of the surface composition after reduction of the catalyst. Both the carbon coverage and support decoration of nickel are responsible for

Table 2. Summary of the Ni/Al ratios of the catalysts

Samples		Fresh	Reduced	Used
Ni/Ce-ZrO₂/θ-Al₂O₃	Surface Ni/Al ratio	0.191	0.043	0.030
Ni/θ-Al₂O₃		0.178	0.032	0.023
Ni/Ce-ZrO₂/θ-Al₂O₃	Bulk Ni/Al ratio		0.129	
Ni/θ-Al₂O₃			0.123	

the significant loss of surface Ni/Al molar ratio of the used catalyst.

3. Pulse Study

To further probe the performance of the catalyst, pulse experiments of CH$_4$, O$_2$ and/or the mixture of CH$_4$ and O$_2$ with a molar ratio of 2 were performed. At the same time, fresh catalyst, partially reduced catalyst, which was reduced in situ from room temperature to 923 K at a 10 K/min rate in 5% H$_2$/N$_2$, and well reduced catalyst, which was reduced in situ in 5% H$_2$/N$_2$ at 973 K for 2 h, were systematically investigated to obtain mechanistic information on POM.

3-1. Pulse Study over Well Reduced Catalyst

To investigate the activity of CH$_4$ decomposition and carbon elimination by O$_2$, an ordinal pulse of CH$_4$, O$_2$ and CH$_4$ over well reduced catalyst was performed at 1,023 K and 923 K and the results are given in Fig. 4 and Fig. 5, respectively.

As illustrated in Fig. 4, the catalyst showed high activity for CH$_4$ decomposition and the CH$_4$ conversion decreased slowly for the first four pulses, and then decreased rapidly to about 44% at the fifth pulse. At the same time, CO was the main gaseous carbon-containing product and the selectivity of CO$_2$ was very low and there was no CO$_2$ detected from the second pulse onward. The oxygen species for the production of CO and CO$_2$ must come from the support and promoter which existed as reactive oxygen since the cat-

Fig. 4. Sequential pulse results of CH$_4$, O$_2$ and CH$_4$ over well reduced catalyst at 1,023 K.

Fig. 5. Sequential pulse results of CH$_4$, O$_2$ and CH$_4$ over well reduced catalyst at 923 K.

alyst was well reduced before CH$_4$ pulses and there was no gas-phase oxygen present in the system. This can be confirmed from TPR results of the Ce-ZrO$_2$/θ-Al$_2$O$_3$ support in which an obvious reduction peak at about 973 K was observed [Roh, 2001d]. As the activity of the catalyst for CH$_4$ decomposition can be restored to its initial value after removal of the carbon species deposited on the catalyst and the replenishment of the lattice oxygen in the following O$_2$ pulses, it can be concluded that the decrease of CH$_4$ conversion can be ascribed to both the deposition of carbon species on the active sites for CH$_4$ decomposition and the consumption of the reactive oxygen species present on the catalyst.

To investigate the reaction between O$_2$ and the carbonaceous materials, which deposited on the catalyst during CH$_4$ pulses, O$_2$ was pulsed after 5 pulses of CH$_4$. A large amount of CO and CO$_2$ was produced for the first three O$_2$ pulses, indicating that the carbonaceous materials reacted quickly with oxygen species to form carbon-containing products. So, it is reasonable to propose that the surface carbonaceous materials are intermediates for POM.

Furthermore, the selectivity of CO was much higher than that of CO$_2$ for the first O$_2$ pulse and the difference between the selectivities of CO and CO$_2$ decreased for the second pulse. However, the selectivity of CO$_2$ was much higher than that of CO for the third pulse. This phenomenon can be explained based on the ratio of surface carbon to oxygen species both present on the catalyst and in the system (C/O) as discussed in our previous study [Dong et al., 2002]. It is believed that the C/O ratio is a crucial factor to determine the selectivities of CO and CO$_2$ [Au et al., 1996]. The higher C/O ratio is more favorable for the production of CO. In the present case, as the pulse volume of O$_2$ and the initial amount of carbon species over the catalyst were fixed, the increase of the CO$_2$ selectivity with repeating of O$_2$ pulses can be ascribed to the consumption of carbon on the catalyst during the previous O$_2$ pulses. As a part of carbon was consumed during the first pulse of O$_2$, the C/O ratio for the second O$_2$ pulse became lower, which resulted in the increase of CO$_2$ selectivity and the decrease of CO selectivity.

In order to investigate the oxygen species with different sources involved in POM, CH$_4$ was reintroduced after O$_2$ pulses. It was observed that CH$_4$ conversion for the first pulse was higher than that of the first pulse before O$_2$ pulses. This implies that the activity for CH$_4$ decomposition was enhanced after O$_2$ pulses. Moreover, a large amount of CO and CO$_2$ was produced, which suggests that a tremendous amount of reactive oxygen species was present on the catalyst after O$_2$ pulses. For the following pulses, CH$_4$ conversion was stable, and there was no obvious deactivation during the five pulses, which confirms that reactive oxygen is favorable for decomposing CH$_4$.

In comparison with the results at 1,023 K, the CH$_4$ conversion was much lower at 923 K as shown in Fig. 5, which indicates that the decomposition of CH$_4$ is more enhanced at higher temperature. For the O$_2$ pulses after CH$_4$ pulses, it is noteworthy that the selectivity of CO$_2$ was much higher than that of CO, which is different from the results at 1,023 K. This may be caused by the difference of activation energies of CO(s) desorption and oxidation as suggested by Au et al. [Au et al., 1996]. According to the pyrolysis mechanism, surface C species react with surface oxygen species to give out adsorbed CO (s). Then the CO (s) may desorb from the catalyst surface to form gaseous CO or react further with oxygen species to
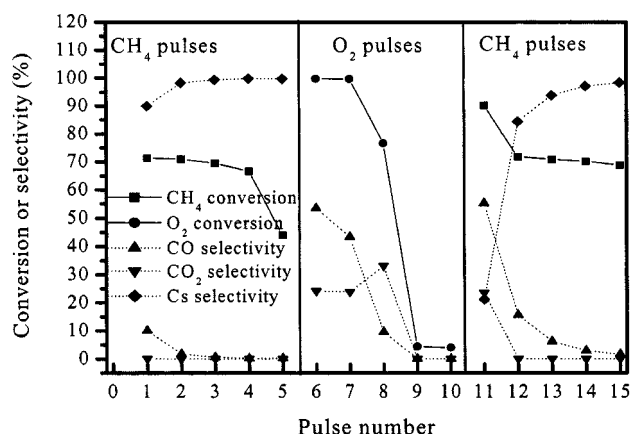
Fig. 6. Pulse results of CH_4/O_2 (=2/1) and CH_4 over well reduced catalyst at 1,023 K.
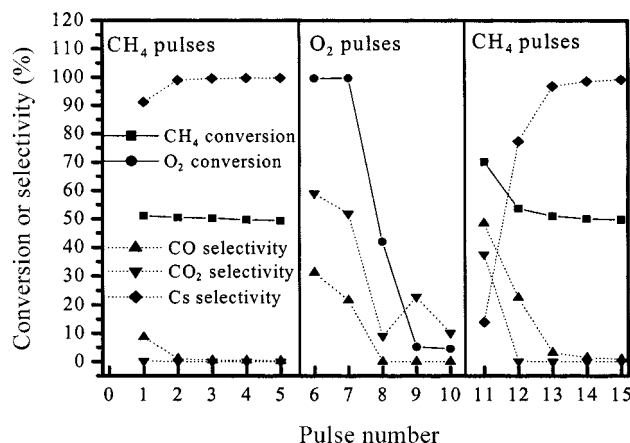

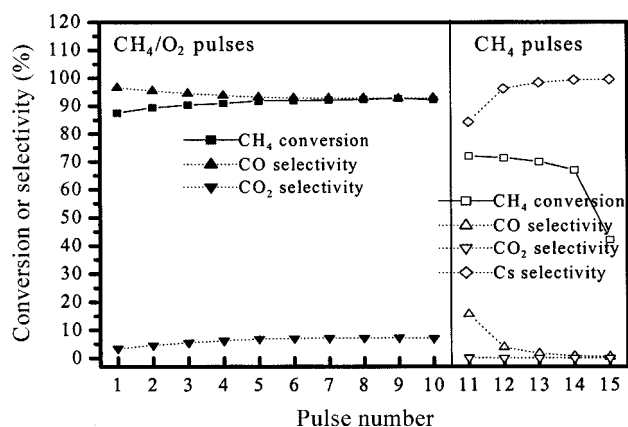Fig. 8. Sequential pulse results of CH_4/O_2 (=2/1) over fresh catalyst at 1,023 K.

produce CO_2 (s). The activation energy of CO (s) desorption on Ni (111) surface (113 kJ/mol) is two times higher than that of CO (s) oxidation (64 kJ/mol). So, higher temperature would rather favor CO (s) desorption than CO (s) oxidation, leading to the increase of CO selectivity.

CH_4/O_2 (=2/1) pulses were also performed over the well reduced catalyst and the results are given in Fig. 6. During the pulse reaction, CH_4 conversion maintained very high while the O_2 was completely consumed. From the product distribution, it is clear that POM was the overwhelming reaction.

After 10 pulses of CH_4/O_2, pure CH_4 was injected. For the first CH_4 pulse, a considerable amount of CO was formed, but only a little amount of CO_2 was detected. The results indicate that a considerable amount of reactive oxygen species still remained on the catalyst after CH_4/O_2 pulses even if it was well reduced before pulse reaction, and these oxygen species are favorable to produce CO rather than CO_2. This clearly suggests that the reactive oxygen species are one of the intermediates for POM.

3-2. Pulse Study over Partially Reduced and Fresh Catalyst

Pulse reaction of CH_4, O_2 and CH_4/O_2 was also performed over partially reduced catalyst. For CH_4 and O_2 pulses at both 1,023 K and 923 K, very similar results to those over the well reduced cat-
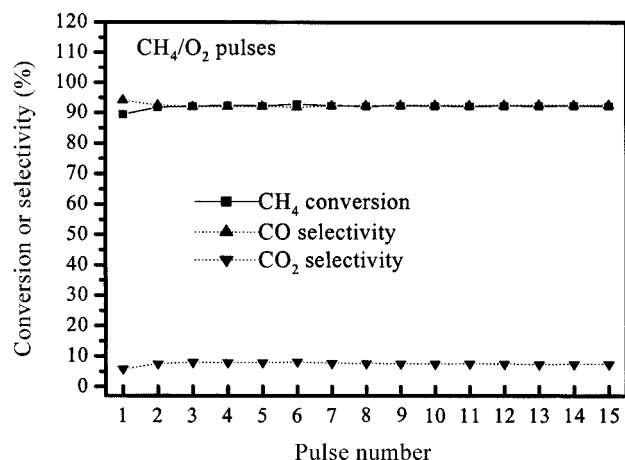
alyst at the same temperature were obtained. From the pulse results of CH_4/O_2 shown in Fig. 7, very high CH_4 conversion and CO selectivity were observed even for the first pulse, which reconfirms that the reactive oxygen species are intermediates for POM.

However, from the pulse results over fresh catalyst illustrated in Fig. 8, it can be seen that CO_2 was the main gaseous carbon-containing product (its selectivity was above 90%) with a CH_4 conversion of about 50% and O_2 conversion of 100% when CH_4/O_2 was pulsed for three times. Moreover, there was no hydrogen detected for the first three pulses. These results suggest that total oxidation of CH_4 was the main reaction. According to oxygen balance, CH_4 conversion should be about 25% based on the oxygen present in the feed. This suggests that a part of oxygen for the production of carbon-containing products was provided by the catalyst, e.g., the reactive oxygen in NiO. So, it can be concluded that metallic nickel was generated and accumulated with an ordinal pulse of CH_4/O_2 until its steady state. From the 6th pulse onward, POM was the overwhelming reaction as reflected from the product distribution. In combination with the results over partially reduced and well reduced catalysts (Fig. 6 and Fig. 7), it can be concluded that the presence of metallic nickel on the catalyst is a prerequisite for POM.

To study the activity of the fresh catalyst for CH_4 decomposition, CH_4 and CH_4/O_2 were sequentially pulsed and the results are given

Fig. 7. Sequential pulse results of CH_4/O_2 (=2/1) over partially reduced catalyst at 1,023 K.

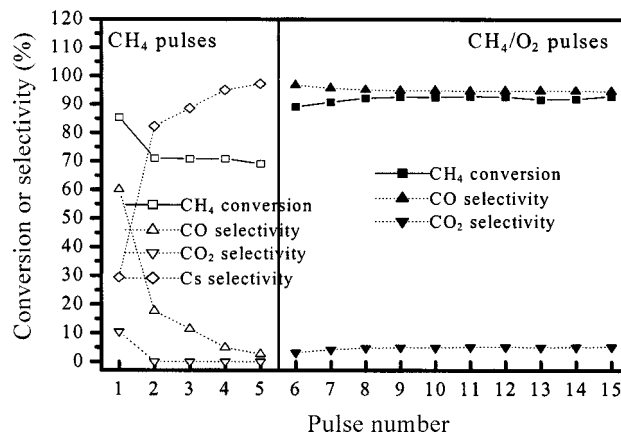Fig. 9. Sequential pulse results of CH_4 and CH_4/O_2 (=2/1) over fresh catalyst at 1,023 K.

in Fig. 9. CO was the main gaseous carbon-containing product and the selectivity of CO$_2$ was low. Meanwhile, hydrogen was detected in the products, but it cannot be quantified because helium was used as a carrier gas. This suggests that CH$_4$ was partially oxidized to CO and H$_2$ by NiO over the fresh catalyst while NiO was reduced to metallic nickel. For the following CH$_4$/O$_2$ pulses, very similar results were obtained to those over the partially reduced and well reduced catalyst (Fig. 6 and Fig. 7), which suggests that carbonaceous materials deposited on the catalyst during CH$_4$ pulses are not poisons for the following CH$_4$/O$_2$ pulses.

DISCUSSION

1. Promotional Effect of Ce-ZrO$_2$

From the above results of POM at steady state, it is clear that the catalyst displayed high activity and selectivity toward POM. From XRD and TPR results, one can see that NiAl$_2$O$_4$ species with low activity for POM are successfully suppressed. In our previous study [Roh et al., 2001c; Liu et al., 2002], heat treatment of γ-Al$_2$O$_3$ was proven to be an effective method for the preparation of Ni/θ-Al$_2$O$_3$ catalyst. From the results shown in Fig. 1, it is clear that Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ catalyst showed higher activity and CO selectivity than that of Ni/θ-Al$_2$O$_3$ catalyst. Furthermore, over Ni/γ-Al$_2$O$_3$, Ni/θ-Al$_2$O$_3$ and Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ with a nickel loading of 3 wt%, the initial CH$_4$ conversion under the operating conditions of T=1,023 K, CH$_4$/O$_2$=1.875 and GHSV=55,200 ml/(g$_{cat}$ h) was about 68%, 77% and 91%, respectively [Roh et al., 2001d]. These observations can be reasonably ascribed to the heat treatment of the support and the promotional effect of Ce-ZrO$_2$.

It is well known that Ni/γ-Al$_2$O$_3$ is unstable at the operating conditions of POM because of thermal deterioration of the support at higher temperatures. Therefore, γ-Al$_2$O$_3$ was pretreated at 1,173 K to make θ-Al$_2$O$_3$ for stabilization. As demonstrated in our previous study, heat treatment is an effective way to stabilize γ-Al$_2$O$_3$ [Roh et al., 2001c; Liu et al., 2002]. At the same time, heat treatment can reduce the reactivity of γ-Al$_2$O$_3$ with NiO as a result of the decrease of the surface area. This was confirmed from the TPR results of Ni/γ-Al$_2$O$_3$ and Ni/θ-Al$_2$O$_3$ shown in Fig. 3. The reduction peak of NiO$_x$ in Ni/γ-Al$_2$O$_3$ was at about 963 K, which was about 50 K higher than that in Ni/θ-Al$_2$O$_3$. Moreover, the peak intensity of the highly dispersed NiAl$_2$O$_4$ species in Ni/γ-Al$_2$O$_3$ was more pronounced than that of Ni/θ-Al$_2$O$_3$. Those observations could be interpreted as the stabilization effect of heat treatment.

In comparison with Ni/(SiO$_2$)$_x$ (Al$_2$O$_3$)$_{1-x}$ catalysts precoated with MgO, CaO, and Yb$_2$O$_3$, the directly supported NiO-MgO, NiO-CaO, and NiO-Yb$_2$O$_3$ on (SiO$_2$)$_x$ (Al$_2$O$_3$)$_{1-x}$ catalysts showed very low activity for POM [Choudhary et al., 1997]. The authors explained their observation on the basis that the formation of a protective layer between the precoated metal oxides and the support is responsible for the high performance of the precoated catalysts. Our present results clearly showed that Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ catalyst has higher activity and CO selectivity than the Ni/θ-Al$_2$O$_3$ catalyst. Moreover, BET results shown in Table 1 indicate that the precoated Ce-ZrO$_2$ is beneficial for suppressing the sintering of the catalyst during POM. Those observations are consistent with the viewpoint of protective layer.

It is well known that the addition of CeO$_2$ into ZrO$_2$ results in a material, which promotes the formation of oxygen vacancies and increases the oxygen mobility [Stagg-Williams et al., 2000]. TPR results indicate that Ce-ZrO$_2$/θ-Al$_2$O$_3$ support showed an obvious peak at about 973 K [Roh, 2001d], which can be assigned to reduction of the coated Ce-ZrO$_2$ while the reduction of CeO$_2$ itself must be at about 1,150 K. This is consistent with the above idea. Our previous results [Roh et al., 2001a, b] also indicate that a synergistic effect exists between CeO$_2$ and ZrO$_2$ that improves the reducibility of the oxide and has a beneficial effect on the long-term activity of the catalyst. Furthermore, comparing the TPR results in Fig. 3, the shoulder peak assigned for relatively free NiO over Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ is much weaker than that over Ni/θ-Al$_2$O$_3$ although the TPR patterns of the two catalysts are very similar. The negligible decrease of the BET surface area of the catalyst after use in POM for 24 h suggests that a long-term stability for POM can be reasonably expected. These observations are closely related to the above mentioned promotional effect of Ce-ZrO$_2$ solid solution.

2. POM Mechanism

Pulse results of CH$_4$ over fresh catalyst clearly showed that CH$_4$ was partially reduced to CO and H$_2$ by NiO supported on Ce-ZrO$_2$/θ-Al$_2$O$_3$. This is really an unexpected result. Previous investigators [Lu et al., 1998; Jin et al., 2000] found that CH$_4$ conversion was low and CO$_2$ and H$_2$O were main products when pure CH$_4$ was pulsed over fresh Ni/γ-Al$_2$O$_3$ and Ni/α-Al$_2$O$_3$ catalysts. As reported in reference [Lu et al., 1998], TPR of fresh Ni/γ-Al$_2$O$_3$ showed only a reduction peak at ~1,073 K, which was ascribed to the reduction of highly dispersed NiAl$_2$O$_4$. However, from TPR results shown in Fig. 3, the largest peak at ~923 K, which can be ascribed to the reduction of complex NiO$_x$ species showing strong interactions with Ce-ZrO$_2$/θ-Al$_2$O$_3$ was observed for fresh Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$. In the present case, we can relate it to that the bond strength of Ni-O of NiO$_x$ species is favorable to the formation of CO when it interacts with CH$_4$ due to the SMSI-like interactions between NiO$_x$ and Ce-ZrO$_2$/θ-Al$_2$O$_3$.

POM was the overwhelming reaction when CH$_4$/O$_2$ was pulsed over partially reduced or well reduced catalyst. Over the fresh catalyst, however, there was no H$_2$ detected and the products were the results of total oxidation of CH$_4$ when CH$_4$/O$_2$ was pulsed. Therefore, it is reasonable to propose that the presence of metallic Ni over the catalyst is a prerequisite for POM. As we suggested above, both carbonaceous materials and reactive oxygen species are intermediates for POM. So, our present results support the pyrolysis mechanism. Based on the above results and discussion, the mechanism of POM over Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ can be summarized as follows. CH$_4$ dissociatively adsorbed on metallic Ni to give out H$_2$ and carbonaceous species. Part of the carbon materials reacts with reactive oxygen species (NiO$_x$), which are activated on metallic Ni by gas phase O$_2$, to produce CO. As a matter of fact, Ce-ZrO$_2$/θ-Al$_2$O$_3$ showed an obvious reduction peak at about 973 K. So, it is reasonable to propose that the reactive oxygen of Ce-ZrO$_2$ also participates in POM. Alternatively, CO can be formed through reduction of Ce-ZrO$_2$ near the metallic Ni by deposited carbon. Moreover, the oxygen vacancies in Ce-ZrO$_2$, which are formed by reaction with carbon, can be replenished by gaseous O$_2$ such that a reduction-oxidation cycle is formed to produce CO continuously. Both routes are responsible for the production of CO. The production of CO$_2$ is from the successive oxidation of CO(s), which is strongly dependent on the reaction temperature and carbon to oxygen ratio.

CONCLUSION

The following are the conclusions drawn from this investigation.

1. Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ catalyst showed high activity and stability for POM during a 24 h test, which benefits from the promotional effect of Ce-ZrO$_2$ and the heat treatment of the support at high temperature.

2. A protective layer between Ce-ZrO$_2$ and θ-Al$_2$O$_3$ is formed to suppress the formation of inactive NiAl$_2$O$_4$ and the heat treatment stabilizes the support and reduces the interaction between NiO and support. Moreover, sintering of the catalyst for 24 h test was greatly suppressed in comparison with ordinary Ni/Al$_2$O$_3$, which gives a reasonable expectation of long-term stability.

3. CH$_4$ can be partially oxidized to CO and H$_2$ by the reactive oxygen in NiO$_x$ species with strong interactions with Ce-ZrO$_2$/θ-Al$_2$O$_3$, but POM still calls for the presence of metallic nickel.

4. Based on the pulse results of CH$_4$, O$_2$ and CH$_4$/O$_2$ over fresh, partially reduced and well reduced catalyst, POM over Ni/Ce-ZrO$_2$/θ-Al$_2$O$_3$ follows the pyrolysis mechanism, and both the carbonaceous materials from CH$_4$ decomposition over metallic nickel and the reactive oxygen species present on NiO$_x$ and Ce-ZrO$_2$ are intermediates for POM.

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