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Pulse study on the partial oxidation of methane over Ni/θ-Al₂O₃ catalyst

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Abstract

Pulse reactions of CH_4, O_2 and mixed gas ($CH_4/O_2 = 2$) over fresh, partially reduced and well reduced Ni/θ-Al₂O₃ catalysts have been carried out at 923 and 1023 K to study the mechanism of CH_4 activation and the catalytic partial oxidation of CH_4. The fresh catalyst showed high activity for the dissociation of CH_4, and CO rather than CO_2 was the main carbon-containing gaseous product while H_2 being detected for the first CH_4 pulse, suggesting that CH_4 can be partially oxidized to CO and H_2 by the lattice oxygen of NiO. The bond strength of Ni–O seems to be favorable to the partial oxidation of CH_4, which is due to the strong interaction between NiO and θ-Al₂O₃. The results of CH_4/O_2 pulses indicate that both metallic nickel and NiO_x ($x < 1.0$) are active phases for partial oxidation of CH_4. It has been demonstrated that both the reaction temperature and the C/O ratio are critical to the selectivities to CO and CO_2. The mechanisms of the oxidation of CH_4 over fresh and reduced catalysts have been proposed.
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Keywords: Ni catalyst; θ-Al₂O₃; Pulse reaction; Partial oxidation of methane; Mechanism

1. Introduction

The reforming of natural gas to syngas is one of the important methods for the effective utilization of natural gas [1]. Particularly, much attention has been paid to the catalytic partial oxidation of CH_4 (POM) [2], which can be expressed as:

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow CO + 2H_2, \quad H^\circ_{298} = -36\,kJ\,mol^{-1} \tag{1}$$
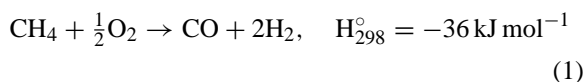
In comparison with steam reforming of methane (SRM), which is a currently industrialized process for the production of hydrogen and syngas, POM has

many advantages such as a mild exothermicity, much higher efficiency, and a suitable H_2/CO ratio of 2 for methanol and Fischer–Tropsch synthesis [3]. Perovskites and supported metals have been reported as active catalysts for POM [2,4–7]. However, the nickel-based catalyst has been the most intensively investigated because of its low cost and high activity. The modification and/or characterization of the nickel-based catalysts and mechanistic studies on POM have become one of the most active topics in catalysis.

Both theoretical and experimental works have been carried out to disclose the mechanism of POM [8–11]. Two mechanisms have been proposed for POM: (1) the combustion-reforming mechanism [12], in which CH_4 is completely oxidized to $CO_2 + H_2O$, and CO is a result of CO_2 and H_2O reforming with the residual

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CH_4; (2) the pyrolysis mechanism [6], in which CH_4 is pyrolyzed on the catalyst to produce CO directly without the preformation of CO_2. To understand the POM mechanism better, CH_4 activation over different catalysts or model catalysts was studied extensively [13–16]. However, to date, the mechanism of POM is still debatable although nickel-based catalysts with high activity and stability have been reported [17,18]. Regarding the active catalytic phase for POM, some researchers believe that metallic nickel is responsible for POM over nickel-based catalysts [17,19,20]. Lu et al. [21] have claimed that the catalyst surface on which both metallic nickel and NiO_x species (reducible at 793–833 K) are coexistent is active and selective for POM. However, Dissanayake et al. [22] have suggested that CH_4 complete oxidation occurs in the region of $NiAl_2O_4$ and/or $NiO + Al_2O_3$ and that the reforming of CO_2 and/or H_2O with CH_4 occurs over Ni/Al_2O_3 by analyzing the used Ni/Al_2O_3 catalyst for POM in different bed locations.

Pulse technique is one of the most effective methods for probing the mechanism of POM without the "hot spot" problem. Both CH_4 activation and the mechanistic studies on POM over different catalysts were intensively investigated by using the pulse method combined with other techniques. It was reported that the only carbon-containing product is CO_2 when CH_4 is pulsed for the first time over the fresh catalyst [11,20]. Other researchers reported that both CO and CO_2 are produced although the selectivity of CO is much lower than that of CO_2 [19,21]. In our previous study [23], $Ni/\theta-Al_2O_3$ catalyst showed high activity and stability in POM. In this work, pulse reactions of CH_4, O_2 and CH_4/O_2 (2/1) were systematically conducted to investigate further the performance of the catalyst with different surface states, e.g. fresh, partially reduced and well reduced. We found that CO rather than CO_2 was the main carbon-containing product while H_2 was detected for the first CH_4 pulse over the fresh catalyst. The results allowed us to verify the active sites or phases responsible for CH_4 activation and POM.

2. Experimental

The catalyst used in this study was $Ni/\theta-Al_2O_3$ (12 wt.% Ni). The detailed procedure for the prepa-

ration of the catalyst was described elsewhere [23].

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 with an inner diameter of 4 mm. Prior to each reaction, 30 mg of each 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 mixed gas of CH_4/O_2 (1 ml pulse, 15–18 min interval). Here, we designate the fresh catalyst as $Ni/\theta-Al_2O_3$ (F), partially reduced catalyst as $Ni/\theta-Al_2O_3$ (P) 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 as $Ni/\theta-Al_2O_3$ (R) which was reduced in situ in 5% H_2/N_2 at 973 K for 2 h. During each pulse, the exit gas was analyzed on-line by a Shimadzu GC-8A gas chromatograph equipped with TCD (carbosphere column, 353 K; helium as carrier gas). The conversion and selectivity were calculated on the basis of carbon contents in the products assuming 100% carbon and oxygen balances.

3. Results and discussion

3.1. Successive CH_4 and O_2 pulses

3.1.1. $Ni/\theta-Al_2O_3$ (F)

The results of CH_4 sequential pulses over $Ni/\theta-Al_2O_3$ (F) catalyst are shown in Fig. 1. It is clear that CH_4 conversion (77.3%) for the first pulse was the highest. At the same time, CO was the main gaseous product with a selectivity of about 65.3% for the first pulse, and the selectivity to CO_2 was low (12.4%). Meanwhile, hydrogen was detected in the products, but it could not be quantified because helium was used as carrier gas. After the second pulse, the selectivity of CO_2 decreased to zero and CO selectivity decreased sharply. Since there was no gas-phase oxygen present in the system and the mobile oxygen from the support was very scarce as shown in the following (Figs. 4 and 5), it suggests that the oxygen was from NiO, which would be reduced to metallic nickel to give carbon-containing products. Based on the initial weight of the catalyst and the amount of CO_2 and CO formed for methane pulses, it is estimated that above 80% of the NiO initially present on the catalyst
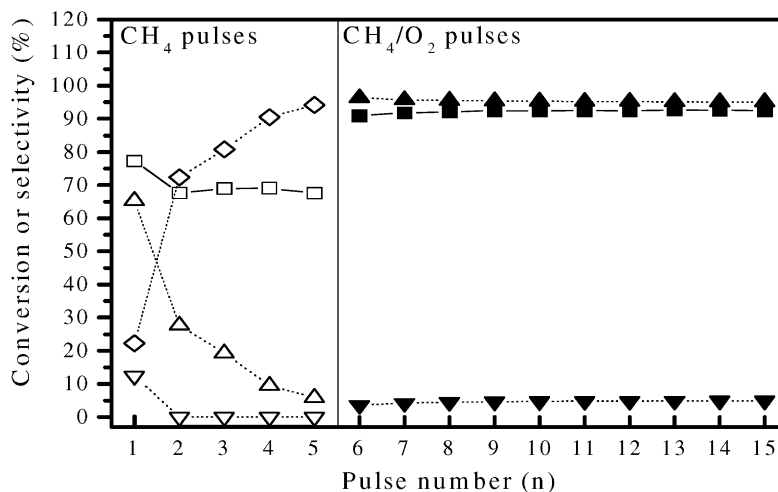
Fig. 1. Sequential pulse reactions of CH_4 and CH_4/O_2 over Ni/θ-Al_2O_3 (F) catalyst at 1023 K (open symbols: CH_4 pulses, solid symbols: CH_4/O_2 pulses; square: CH_4 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity, diamond: Cs selectivity).

has been reduced to metallic Ni. This was a really unexpected result and different from previous investigations [19–21,24]. To the best of our knowledge, CO_2 was the main gaseous product and there was no hydrogen detected when CH_4 was pulsed over the fresh nickel-based catalysts in the literature [20,21]. The importance of this difference is that CH_4 can be partially oxidized to CO and H_2 by lattice oxygen of NiO supported on θ-Al_2O_3.

Assuming the 100% material balance of carbon, the selectivity to carbonaceous material (Cs) deposited on the catalyst during the pulses of CH_4 was calculated. The Cs selectivity increased sharply with the ordinal pulse of CH_4 which implies that metallic nickel forms the active sites for CH_4 decomposition to Cs.

3.1.2. Ni/θ-Al_2O_3 (P)

The results of sequential pulses of CH_4, O_2, and CH_4 over Ni/θ-Al_2O_3 (P) catalyst at 1023 K are given in Fig. 2. For the first pulse of CH_4, CO selectivity was about 29%, and rapidly decreased with the ordinal pulse of CH_4. The selectivity of CO_2 was only 0.9% for the first pulse and there was no CO_2 detected by TCD for the following five pulses.

After six pulses of CH_4, oxygen was pulsed to investigate the reaction between surface carbon and oxygen. A large amount of CO_2 and CO was produced for the first pulse of O_2. At the same time, even for

the first pulse of O_2, CO selectivity plus CO_2 selectivity was less than 100%, revealing that some part of O_2 was consumed to oxidize the catalyst.

In order to investigate the role of the oxygen species involved in POM, CH_4 was reintroduced after the O_2 pulses. It is noticeable that CH_4 conversion (88.3%) for the first pulse was the highest, and then sharply decreased for the second pulse. After that, CH_4 conversion was stable for the following five pulses. From the sixth pulse onward, CH_4 conversion rapidly decreased again until reaching the value of 9.6% at the tenth pulse, which indicates that the catalyst deactivated because of the carbon deposition. This can also be seen from the Cs selectivity curve in Fig. 2. The Cs selectivity was only 23.5% for the first pulse. From the sixth pulse onward, the reaction of the pulsed CH_4 ended up mainly as Cs. In combination with the results of CH_4 pulses over Ni/θ-Al_2O_3 (F), it can be seen that carbon deposition becomes a main reaction only when metallic nickel is present and that there is less reactive oxygen species on the catalyst, which illustrates the importance of the surface state in determining the product distribution.

To study the effect of temperature on the activation of CH_4, the sequential pulses of CH_4, O_2 and CH_4 were delivered at 923 K as shown in Fig. 3. The CH_4 conversion was kept around 45%, which was much lower than that at 1023 K, within the initial five pulses.
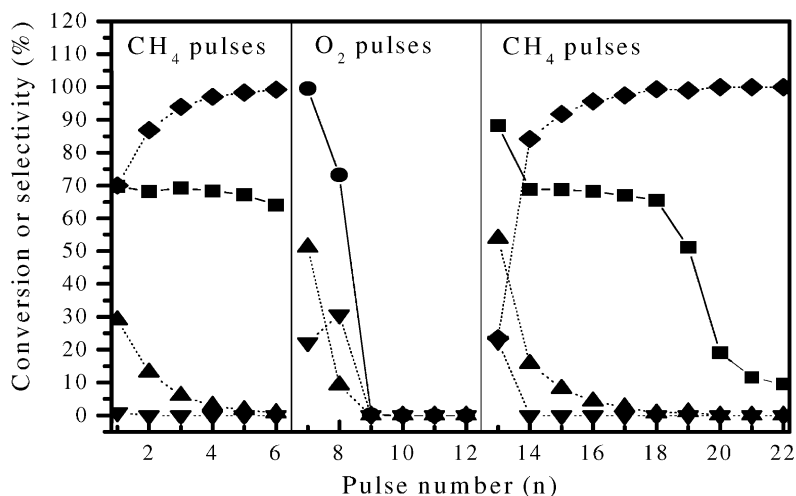
Fig. 2. Sequential pulse reactions of CH_4, O_2 and CH_4 over Ni/θ-Al_2O_3 (P) catalyst at 1023 K (square: CH_4 conversion, circle: O_2 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity, diamond: Cs selectivity).

This indicates that higher temperature favors the activation of CH_4 as reported by others [11]. In the mean time, the selectivity of CO (18%) was lower than that at 1023 K (28%, Fig. 2, first pulse). Moreover, CO was the main carbon-containing gaseous product at both 923 and 1023 K during the CH_4 pulses. However, the selectivity of CO_2 was much higher than that of CO at 923 K for the first O_2 pulse after CH_4 pulses, which was reversed from that at 1023 K. This indicates that

higher temperature suppresses the formation of CO_2. This may be in part explained in terms of the fact that the activation energy of CO (s) desorption is higher than that of its oxidation as suggested by Au et al. [19].

However, the selectivity of CO_2 became higher than that of CO for the second O_2 pulse at 1023 K as presented in Fig. 2. This cannot be explained in terms of the above viewpoint. It is most likely that the ratio of the total carbonaceous materials deposited on the
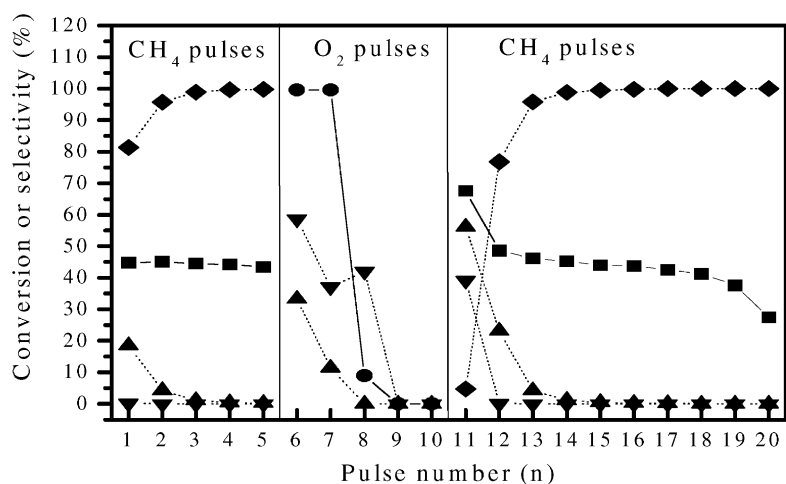

Fig. 3. Sequential pulse reactions of CH_4, O_2 and CH_4 over Ni/θ-Al_2O_3 (P) catalyst at 923 K (square: CH_4 conversion, circle: O_2 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity, diamond: Cs selectivity).

catalyst during previous CH_4 pulses to the total oxygen species present both on the catalyst and reaction system (C/O) plays also an important role in determining the selectivities of CO and CO_2. The higher the C/O ratio is, the lower the CO_2 selectivity will be when other operating conditions are kept the same. As the pulse volume of O_2 and carbon species over the catalyst are fixed, the CO_2 selectivity is enhanced with the ordinal O_2 pulses 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 resulting in the increase of CO_2 selectivity. So, both reaction temperature and C/O ratio are responsible for the product selectivities. For the first CH_4 pulse after O_2 pulses, 56.2% CO selectivity and 39.2% CO_2 selectivity at 923 K were obtained whereas 53.9% CO selectivity and 22.7% CO_2 selectivity were measured at 1023 K. This also supports our explanation on the co-effect of temperature and C/O ratio on the product selectivities.

3.1.3. Ni/θ-Al$_2$O$_3$ (R)

Figs. 4 and 5 show the reaction results of sequential pulses of CH_4, O_2, and CH_4 over Ni/θ-Al$_2$O$_3$ (R) catalyst at 1023 and 923 K, respectively. It is clear that the catalyst deactivated after three pulses of CH_4 at 1023 K confirming that the metallic nickel is responsi-

ble for CH_4 decomposition to surface Cs. As a consequence, it is clearly demonstrated that the Ni/θ-Al$_2$O$_3$ (R) deactivated much easier than Ni/θ-Al$_2$O$_3$ (P) for the decomposition of CH_4 at 1023 K by comparing the results shown in Figs. 2 and 4. Furthermore, less CO (11.34%) and CO_2 (0.05%) were produced in comparison with those over Ni/θ-Al$_2$O$_3$ (F) and Ni/θ-Al$_2$O$_3$ (P). Combining the above results, it is clear that the decrease of CH_4 conversion over these catalysts 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. Since the catalyst was well reduced before CH_4 pulses, the oxygen species to form CO and CO_2 must be from the support and were very scarce as shown by the low selectivities of gaseous carbon-containing products.

The amount of carbon deposited on the catalyst for the five pulses of CH_4 and the amount of carbon removed from the catalyst for the five pulses of O_2 were calculated assuming 100% carbon balance. The results are shown in Table 1. Irrespective of the state of the catalyst, the amount of carbon deposited after five pulses of CH_4 was higher at 1023 K than that at 923 K. At the same time, the amount of carbon deposited on Ni/θ-Al$_2$O$_3$ (R) was higher than that on Ni/θ-Al$_2$O$_3$ (P) at 923 K due to the existence of higher amount of reactive oxygen species over Ni/θ-Al$_2$O$_3$ (P).
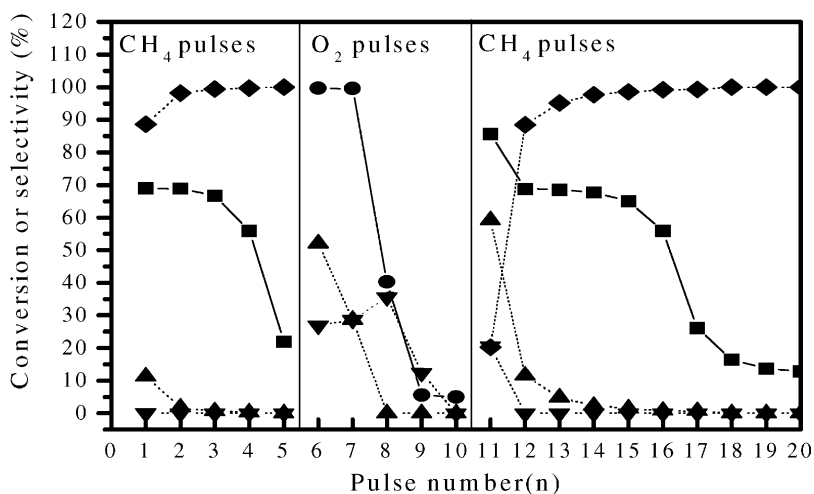

Fig. 4. Sequential pulse reactions of CH_4, O_2 and CH_4 over Ni/θ-Al$_2$O$_3$ (R) catalyst at 1023 K (square: CH_4 conversion, circle: O_2 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity, diamond: Cs selectivity).
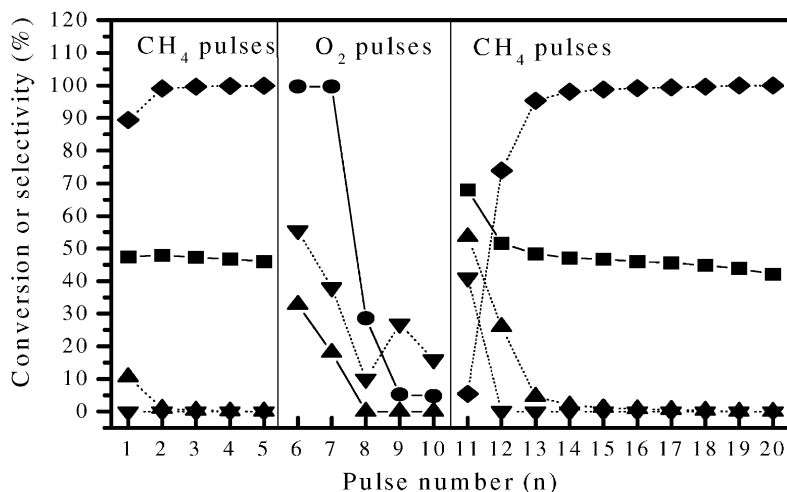
Fig. 5. Sequential pulse reactions of CH_4, O_2 and CH_4 over Ni/θ-Al$_2$O$_3$ (R) catalyst at 923 K (square: CH_4 conversion, circle: O_2 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity, diamond: Cs selectivity).

Moreover, the majority of carbon ($\sim$85%) deposited on the catalyst during CH_4 pulses could be removed by several pulses of O_2.

3.2. Schemes for CH_4 activation

From the above results, it can be seen that the oxygen species present on the catalyst play a very important role in the production of CO, CO_2 and Cs during the CH_4 decomposition. By comparing the CH_4 conversion for the first pulse of CH_4 after O_2 pulses over Ni/θ-Al$_2$O$_3$ (P) and Ni/θ-Al$_2$O$_3$ (R) with that over Ni/θ-Al$_2$O$_3$ (F), it can be concluded that the reoxidized catalyst is more active for the decomposition of CH_4 than Ni/θ-Al$_2$O$_3$ (F). At the same time, the selectivity of CO_2 over the reoxidized catalyst was higher than that over Ni/θ-Al$_2$O$_3$ (F) for the first CH_4 pulse. This is possibly caused by the oxygen species, which are physically adsorbed or weakly chemisorbed on the surface of the reoxidized catalyst.
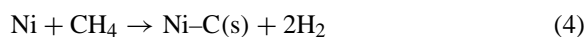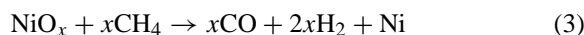
As mentioned above, the only source of oxygen is from the catalyst because there is no gas-phase oxygen existing in the system during CH_4 pulses. So, the state of oxygen species on the catalyst must be responsible for determining the selectivities of CO and CO_2. TPR results [23] indicate that three kinds of nickel species exist over Ni/θ-Al$_2$O$_3$ (F), i.e. relatively free NiO species (small peak with peak maximum at 753 K), the complex NiO$_x$ species strongly interacting with θ-Al$_2$O$_3$ (large peak with peak maximum at 913 K) and highly dispersed NiAl$_2$O$_4$ species (small peak with peak maximum at 1073 K). By integrating the peak areas of the three species mentioned above, it is estimated that the percentages of the oxygen species assigned to relatively free NiO, NiO$_x$, and NiAl$_2$O$_4$ are 5.0, 90.1 and 4.9%, respectively. As the relatively free NiO has higher oxidizing ability, this kind of oxygen species is responsible for the production of CO_2. Moreover, the successive oxidation of CO (s) to CO_2, which depends on the C/O ratio and the reaction

Table 1

The results of sequential pulse reaction of CH_4 and O_2 over supported Ni catalysts

Catalysts	Temperature (K)	C deposition (mmol)	C removed (mmol)	C removed (%)
Ni/θ-Al$_2$O$_3$ (F)	1023	0.1107	–	–
Ni/θ-Al$_2$O$_3$ (P)	923	0.0942	0.0839	89.07
Ni/θ-Al$_2$O$_3$ (R)	923	0.1026	0.0891	86.84
	1023	0.1218	0.1033	84.81

temperature, also contributes to the production of CO_2. At the same time, the complex NiO_x species, which are not so easily reduced, are reasonably supposed to be responsible for the partial oxidation of CH_4 to CO and H_2 as shown in reaction (3). It has been well established that the existence of strong-metal-support interactions (SMSI) influences the surface electronic properties of metal particles. In the present case, the bond strength of Ni–O of NiO_x species over the catalyst is favorable to the formation of CO when it interacts with CH_4 due to the SMSI-like interactions between NiO and θ-Al_2O_3 support. Lu et al. [21] reported that the CH_4 conversion was very low when CH_4 was pulsed over a fresh 9 wt.% Ni/γ-Al_2O_3 catalyst at 973 K. Moreover, only highly dispersed $NiAl_2O_4$ peak at $\sim$1073 K appeared in the TPR spectra of the fresh catalyst. When the present results are taken into account, it is reasonable to ascribe the low CH_4 conversion over Ni/γ-Al_2O_3 to the low activity of $NiAl_2O_4$. Thus, it is rational to propose that the $NiAl_2O_4$ species is very difficult to react with CH_4 at the present conditions. This explanation is very well matched with the above pulse results and the following schemes for CH_4 activation were proposed.

$$4NiO + CH_4 \rightarrow CO_2 + 2H_2O + 4Ni \qquad (2)$$

$$NiO_x + xCH_4 \rightarrow xCO + 2xH_2 + Ni \qquad (3)$$

$$Ni + CH_4 \rightarrow Ni\text{–}C(s) + 2H_2 \qquad (4)$$

when CH_4 was pulsed over Ni/θ-Al_2O_3 (F) for the first time, NiO_x was the most abundant surface species. In this case reaction (3) is the main reaction. Once NiO_x is reduced to Ni, then reaction (4) is the most prevalent reaction.

3.3. CH_4/O_2 pulses

To study POM mechanism, mixed gas of CH_4/O_2 with a stoichiometric ratio of 2 was pulsed over Ni/θ-Al_2O_3 (F), Ni/θ-Al_2O_3 (P), Ni/θ-Al_2O_3 (R) catalysts. The results over Ni/θ-Al_2O_3 (F) are given in Fig. 6. The CH_4 conversion was about 50% during the initial five pulses, which was much lower than that for CH_4 pulses as shown in Fig. 1. Moreover, there was no hydrogen detected until the fifth pulse of CH_4/O_2. This is quite different from the results of pure CH_4 pulses, which reveals that the reaction of CH_4 with lattice oxygen of NiO is more facile than its reaction with gaseous oxygen. Moreover, the selectivity of CO_2 was much higher than that of CO. As the lattice oxygen of NiO_x (large TPR peak with peak maximum at 913 K) is favorable to the production of CO, it is reasonable to conclude that the main pathway for the production of CO_2 must be successive oxidation of CO (s), which is formed from the interaction of CH_4 with NiO_x.

Furthermore, the pulsed oxygen was almost completely consumed with a CO_2 selectivity of about 90%
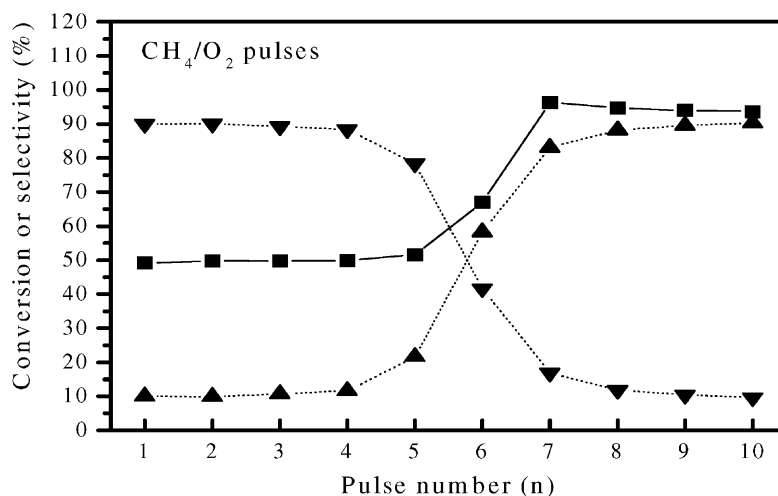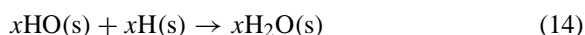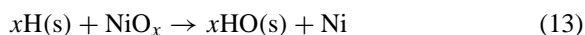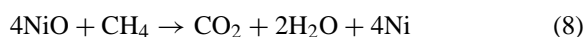

Fig. 6. Pulse reaction of $CH_4/O_2(2/1)$ over Ni/θ-Al_2O_3 (F) catalyst at 1023 K (square: CH_4 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity).

for the first four pulses. According to the oxygen balance, the CH_4 conversion should be about 25% based on the oxygen present in the feed. This suggests that a certain part of the oxygen must be provided from the catalyst, e.g. the lattice oxygen of NiO, during the initial four pulses. So, it can be concluded that metallic nickel was generated and the amount of metallic nickel increased with the ordinal pulse number until its steady state. This is comparable with the results over the supported Rh catalysts [24].

3.3.1. POM mechanism over Ni/θ-Al₂O₃ (F)

Combining the above results and the mechanism of the CH_4 activation, it is reasonable to suggest the following mechanism for POM over Ni/θ-Al₂O₃ (F). CH_4 is oxidized substantially by the lattice oxygen of NiO_x species over the catalyst to form CO (s) and H (s), while the NiO_x is reduced to metallic nickel, which is partially replenished by the gas-phase oxygen based on the fact that metallic nickel is accumulated with the ordinal pulse of CH_4/O_2. In the present case, the C/O ratio is low, which is favorable to the successive oxidation of CO (s) to CO_2 rather than the desorption of CO (s) to CO (g). So, the majority CO (s) is oxidized to CO_2 (s), which leads to higher selectivity of CO_2 in the products. The alternative source for the production of CO_2 is from the complete oxidation of CH_4 by the relatively free NiO over the catalyst according to reaction (2) while the metallic Ni from the reduction of relatively free NiO can be reoxidized by O_2. With increasing pulse of CH_4/O_2 (at present case, five pulses of CH_4/O_2), the accumulated metallic nickel is sufficient to dissociate CH_4 to surface carbon and H so that the C/O ratio is increased, causing the desorption of CO (s) to CO(g). In this case, CO (s) would rather desorb to produce gaseous CO than oxidize to CO_2 (s). At the same time, H (s) may react with oxygen species to form H_2O since there was no hydrogen detected in the products for the initial four pulses. The above mechanism can be expressed as follows.

$$xCH_4 + NiO_x \rightarrow xCO(s) + 4xH(s) + Ni \qquad (5)$$

$$xCO(s) + NiO_x \rightarrow xCO_2(s) + Ni \qquad (6)$$

$$2CO(s) + O_2 \rightarrow 2CO_2(s) \qquad (7)$$

$$4NiO + CH_4 \rightarrow CO_2 + 2H_2O + 4Ni \qquad (8)$$

$$CO(s) \rightarrow CO(g) \qquad (9)$$

$$CO_2(s) \rightarrow CO_2(g) \qquad (10)$$

$$2Ni + xO_2 \rightarrow 2NiO_x \qquad (11)$$

$$2Ni + O_2 \rightarrow 2NiO \qquad (12)$$

$$xH(s) + NiO_x \rightarrow xHO(s) + Ni \qquad (13)$$

$$xHO(s) + xH(s) \rightarrow xH_2O(s) \qquad (14)$$
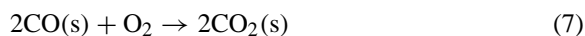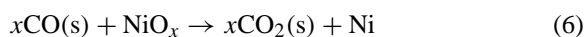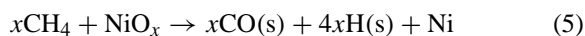
3.3.2. POM mechanism over Ni/θ-Al₂O₃ (P) and Ni/θ-Al₂O₃ (R)

In contrast to the fresh catalyst, the CH_4 conversion and CO selectivity were very high and stable during all the pulses of CH_4/O_2 over Ni/θ-Al₂O₃ (F) after five pulses of CH_4, which can be seen in Fig. 1. In the previous part, it has been demonstrated that metallic nickel is produced and substantial amount of carbonaceous materials is deposited after several pulses of CH_4 over the fresh catalyst. From the above results, we can conclude that the existence of metallic nickel on the catalyst is a prerequisite for POM. Furthermore, the carbonaceous materials deposited on the catalyst during CH_4 pulses are not poisons during the following pulses of CH_4/O_2, which can be confirmed from the high activity of the catalyst for POM during the following CH_4/O_2 pulses. It is believed that hydrocarbons dissociate to produce highly reactive monatomic carbon (C_α) which can be easily gasified through the reaction with surface oxygen species to form CO. However, if there is an excess of C_α formed or the gasification reaction with surface oxygen is slow, polymerization to C_β, which is less reactive than C_α, is favored. As a result, C_β may accumulate on the surface [25]. According to the above viewpoint and the high POM activity of the catalyst for the following CH_4/O_2 pulses, it is rational to suggest that the highly reactive monatomic carbon (C_α) may dominate on the catalyst after five pulses of CH_4.

Fig. 7 shows the pulse results of CH_4/O_2 over Ni/θ-Al₂O₃ (P) at 1023 K. It is clear that CH_4 conversion and CO selectivity were at a steady state even for the first pulse. This suggests that POM is the main reaction over the partially reduced catalyst when CH_4/O_2 was pulsed. So, here it is again confirmed that metallic nickel forms the active sites for POM.

To study the surface state of the catalyst after CH_4/O_2 pulses, CH_4 was pulsed after 15 pulses of CH_4/O_2. The selectivity of CO (15.7%) was lower
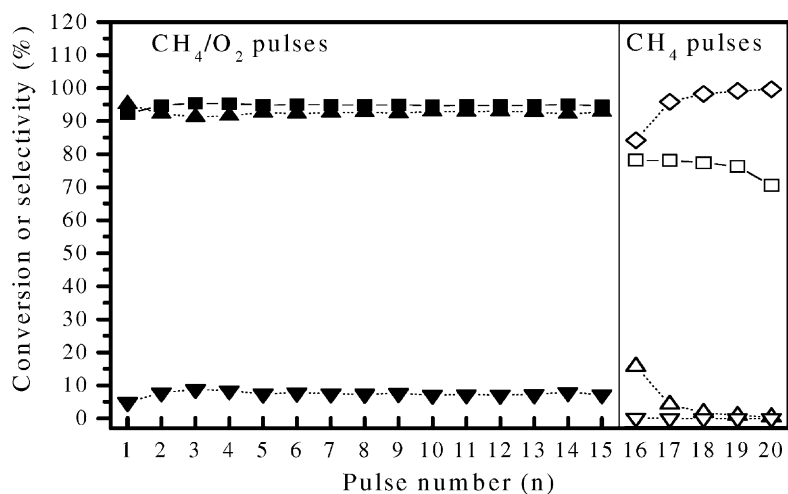
Fig. 7. Pulse reaction of $CH_4/O_2(2/1)$ and CH_4 over Ni/θ-Al$_2$O$_3$ (P) catalyst at 1023 K (solid symbols: CH_4/O_2 pulses, open symbols: CH_4 pulses; square: CH_4 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity, diamond: Cs selectivity).

than that over Ni/θ-Al$_2$O$_3$ (P) (29.1%, Fig. 2), which indicates that a certain part of the lattice oxygen was consumed during the pulses of CH_4/O_2. Here, it can be tentatively suggested that NiO$_x$ species are the active phase for POM. At the same time, the CH_4 conversion (78.1%) was higher than that over Ni/θ-Al$_2$O$_3$ (P) (69.7%, Fig. 2), which suggests that the activity for CH_4 dissociation is enhanced after CH_4/O_2 pulses.

By comparison, the results of CH_4/O_2 pulses over Ni/θ-Al$_2$O$_3$ (R) catalyst are shown in Fig. 8. The CH_4 conversion for the initial three pulses of CH_4/O_2 was slightly lower than that for the steady state. This indicates that the presence of oxygen species with appropriate bond strength of Ni–O is beneficial to POM. For the CH_4 pulses after CH_4/O_2 pulse, it is worthy to note that the CO selectivity for the first CH_4 pulse

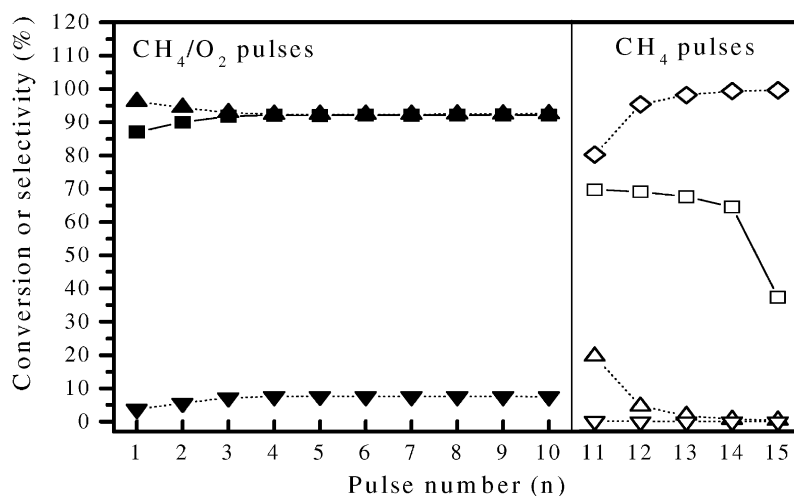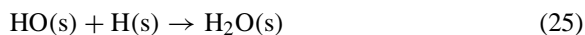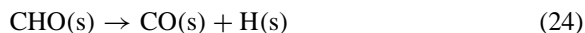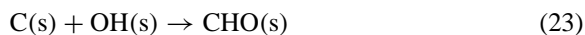Fig. 8. Pulse reaction of $CH_4/O_2(2/1)$ over Ni/θ-Al$_2$O$_3$ (R) catalyst at 1023 K (solid symbols: CH_4/O_2 pulses, open symbols: for CH_4 pulses; square: CH_4 conversion, up triangle: CO selectivity, down triangle: CO_2 selectivity, diamond: Cs selectivity).

was almost twice higher than that over Ni/θ-Al$_2$O$_3$ (R) (Fig. 4). Since the catalyst has already been well reduced before CH$_4$/O$_2$ pulses, the higher CO selectivity indicates that there was still additional oxygen species remaining on the catalyst besides the mobile oxygen from the support after 10 pulses of CH$_4$/O$_2$. Here, it is clear that NiO$_x$ species form the active phase for POM.

Comparing the results shown in Figs. 1 and 6–8, one can conclude that CH$_4$ conversion and the selectivities of CO and CO$_2$ can reach almost the same steady state irrespective of the initial state of the catalyst during CH$_4$/O$_2$ pulses at 1023 K. Moreover, POM was the overwhelming reaction occurring at the steady state. This implies that the same surface state can be reached during pulses of CH$_4$/O$_2$ although the initial states of the catalyst are different. As a matter of fact, the Ni/θ-Al$_2$O$_3$ (P) catalyst with the coexistence of NiO$_x$ and metallic nickel showed higher activity toward POM than both Ni/θ-Al$_2$O$_3$ (F) and Ni/θ-Al$_2$O$_3$ (R). Thus, it is reasonable to propose that NiO$_x$ is also an active species for POM. From the above results and discussion, one can conclude that both the phases of metallic nickel and NiO$_x$ with appropriate bond strength of Ni–O are responsible for POM. As the reaction of CH$_4$ with the lattice oxygen of NiO$_x$ is more facile than its reaction with gaseous oxygen, as demonstrated above, it is rational to suggest that the mechanism of POM mainly follows the surface reactions of the dissociated CH$_4$ and the lattice oxygen. Because of the existence of a small part of relatively free NiO over the fresh catalyst, alternatively, a part of CO$_2$ may be from the complete oxidation of CH$_4$ by the relatively free NiO over the catalyst. This can be expressed as follows:

$$CH_4 + Ni \rightarrow C(s) + 4H(s) \tag{15}$$

$$2Ni + xO_2 \rightarrow 2NiO_x \tag{16}$$

$$2Ni + O_2 \rightarrow 2NiO \tag{17}$$

$$xC(s) + NiO_x \rightarrow xCO(s) + Ni \tag{18}$$

$$xCO(s) + NiO_x \rightarrow xCO_2(s) + Ni \tag{19}$$

$$2CO(s) + O_2 \rightarrow 2CO_2(s) \tag{20}$$

$$4NiO + CH_4 \rightarrow CO_2 + 2H_2O + 4Ni \tag{21}$$

$$xH(s) + NiO_x \rightarrow xHO(s) + Ni \tag{22}$$

$$C(s) + OH(s) \rightarrow CHO(s) \tag{23}$$

$$CHO(s) \rightarrow CO(s) + H(s) \tag{24}$$

$$HO(s) + H(s) \rightarrow H_2O(s) \tag{25}$$

$$CO(s) \rightarrow CO(g) \tag{26}$$

$$CO_2(s) \rightarrow CO_2(g) \tag{27}$$

$$2H(s) \rightarrow H_2(g) \tag{28}$$

$$H_2O(s) \rightarrow H_2O(g) \tag{29}$$
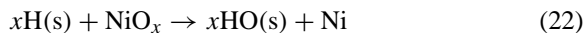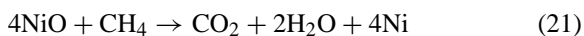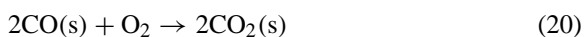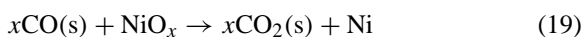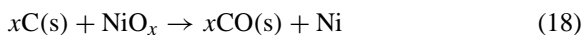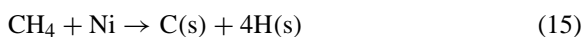
Accompanying the dissociation of CH$_4$ over the metallic nickel, some part of the nickel is oxidized to NiO$_x$ and relatively free NiO by the gas-phase oxygen. In the following step, surface carbon from CH$_4$ dissociation reacts with NiO$_x$ to form CO (s) and give metallic nickel. In this case, the metallic nickel is recycled by dissociation of CH$_4$ and ended up by the reduction of NiO$_x$, which can be replenished by gaseous oxygen. The CO (s) may desorb from the surface of the catalyst or react successively with oxygen species to form CO$_2$ according to the temperature and C/O ratio in the system. A small part of CO$_2$ may also be from the interaction of CH$_4$ with relatively free NiO through reaction (21), which can be reoxidized by O$_2$ through reaction (17).

4. Conclusion

Based on the above results and discussion, conclusions can be drawn as follows:

1. Irrespective of the reduction degree of the Ni/θ-Al$_2$O$_3$, the catalyst exhibits a high activity for CH$_4$ dissociation.
2. CH$_4$ can be partially oxidized to CO and H$_2$ by the lattice oxygen of NiO$_x$ present on the Ni/θ-Al$_2$O$_3$ (F); the selectivity is enhanced by the existence of the SMSI-like interaction between NiO and θ-Al$_2$O$_3$ support.
3. The metallic nickel is the active sites for CH$_4$ dissociation to surface carbon species, and its existence is a prerequisite for POM.
4. Both the reaction temperature and C/O ratio are critical to determining the selectivities of CO and

CO_2. The higher the reaction temperature and the C/O ratio are, the higher the CO selectivity.

5. Not only the metallic nickel but also NiO_x species with suitable bond strength of Ni–O plays an important role in POM. The carbon species deposited on the catalyst for CH_4 dissociation react with NiO_x to form adsorbed CO (s) with the reduction of NiO_x to metallic nickel, which is replenished by the gaseous oxygen. The CO (s) either desorbs to form gaseous CO or reacts further to form CO_2 depending on the reaction temperature and the C/O ratio. This composes the main scheme for POM.

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