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Role of the surface state of Ni/Al_2O_3 in partial oxidation of CH_4

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The effect of gas phase O_2 and reversibly adsorbed oxygen on the decomposition of CH_4 and the surface state of a Ni/Al_2O_3 catalyst during partial oxidation of CH_4 were studied using the transient response technique at atmospheric pressure and 700 °C. The results show that, when the catalyst surface is completely oxidized under experimental conditions, only a small amount of CO and H_2 can be produced from non-selective oxidation of CH_4 by reversibly adsorbed oxygen which is more active in oxidizing CH_4 completely than NiO via the Rideal–Eley mechanism and both the conversions of CH_4 and O_2 and the selectivities to CO and H_2 are very low. Therefore, keeping the catalyst surface in the reduced state is the precondition of high conversion of CH_4 and high selectivities to CO and H_2. The surface state of the catalyst decides the reaction mechanism and plays a very important role in the conversions and selectivities of partial oxidation of CH_4. During partial oxidation of CH_4, no oxygen species but a small amount of carbon exists on the catalyst surface, which is favorable for maintaining the catalyst in the reduced state and the selectivity of CO. The results also indicate that direct oxidation is the main route for partial oxidation of CH_4, and the indirect oxidation mechanism is not able to gain dominance in the reaction under the experimental conditions.

Keywords: methane, partial oxidation, syngas, Ni/Al_2O_3, gas phase O_2, adsorbed oxygen species, surface state

1. Introduction

The study on the conversion of natural gas containing mostly CH_4 to value-added products, such as easily transportable fuels, via direct or indirect methods is driven by the tremendous abundance of natural gas [1]. Direct conversion of CH_4, for example oxidative coupling of CH_4, has met some difficulty. Indirect conversion of CH_4 via syngas is promising, so economical production of syngas from CH_4 has been a hotspot of research.

Partial oxidation of CH_4 to syngas has the following advantages over the conventional steam reforming process: (i) the syngas with low H_2/CO ratio ($\sim$2) is suitable for methanol and Fischer–Tropsch synthesis; (ii) partial oxidation of CH_4 is a slightly exothermic reaction and is much more energy-efficient than steam reorming of CH_4 which is highly endothermic; (iii) a smaller reactor can be used to achieve high CH_4 conversion and selectivities to CO and H_2 with short contact time ($\leqslant 10^{-2}$ s); and (iv) partial oxidation of CH_4 is mechanically simpler than the steam reforming process, since it is completed within a single train, and does not need any external heaters [2–4]. Consequently, partial oxidation of CH_4 to syngas has attracted even more attention of researchers in recent years.

The reaction mechanism of partial oxidation of CH_4 has evoked controversies. Some authors [5–8] pointed out that the partial oxidation of CH_4 to syngas proceeds via an indirect oxidation mechanism, namely: complete combustion of CH_4 to CO_2 and H_2O and a subsequent reforming reaction of the residual CH_4 with CO_2 and H_2O to CO and H_2. However, other authors [9–11] claimed that CO and H_2 are produced directly while CO_2 is formed by further oxidation of CO. Besides, parallel formation of CO and CO_2 has also been suggested over transition metals supported on metal oxide [12]. Tang et al. [2] investigated the reaction mechanism over Pt/Al_2O_3 using the deuterium isotope effect with the pulse MS method and their experimental results supported the parallel mechanism. Our work [13,14] on partial oxidation of CH_4 to syngas over Ni/Al_2O_3 supports the direct oxidation mechanism. CH_4 decomposes on active metallic Ni sites to H_2 and Ni_xC, and then Ni_xC reacts with NiO formed by oxidation of metallic Ni by O_2 to CO or CO_2 depending on the concentration of NiO around Ni_xC.

It should be mentioned that partial oxidation of CH_4 to syngas is a complicated process [2]. Different pre-treating conditions or different surface states of the catalyst may affect its reactivity and selectivity, and even may change the reaction mechanism. In this paper, the transient response technique has been used to investigate the effects of gas phase O_2, reversibly adsorbed oxygen species, NiO on the Ni/Al_2O_3 catalyst surface, and the surface state of the catalyst in partial oxidation of CH_4. Some new evidences for the direct oxidation mechanism are given, and the reasons of high selectivity to CO are also discussed.

2. Experimental

The 8% (mol, Ni/(Ni + Al)) Ni/Al_2O_3 catalyst was prepared by co-precipitation with a 1 mol/l mixture solution of

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$Ni(NO_3)_2$ and $Al(NO_3)_3$ using a 1 mol/l NH_4OH solution as the precipitant. The pH of the solution was maintained at 7.5 during precipitation. The precipitate was aged for 6 h, filtered, washed with distilled water, dried at 100 °C for 10 h, then calcined in air at 400 °C for 10 h, crushed and sieved to 0.3–0.45 mm. The BET surface area and the dispersion of Ni on Al_2O_3 measured by ASAP2010 are 280 m^2/g and about 5%, respectively.

The experimental apparatus has been depicted elsewhere [13]. All experiments were carried out in a fixed-bed quartz microreactor 5.5 mm in diameter at atmospheric pressure and 700 °C, and the total flow rate was 30 ml/min. 30 mg Ni/Al_2O_3 catalyst was placed in the middle part of the reactor and the other space was filled with 0.45–0.9 mm quartz. The furnace was controlled by an AI-FUZZY temperature controller with linear heating rate between room temperature and 850 °C. Heating rates between 1 and 30 °C/min are possible. The temperature was measured by a K-type thermocouple.

Transient switch was operated with a four-way valve and pulse experiments were performed using a six-way sampling valve with a 0.39 ml quantifying tube. The effluents of the reactor were monitored by a quadrupole mass spectrometer (AMTEK QuadLink 1000) with the minimum dwell time of 3 ms.

XRD characterization of catalyst samples was conducted with BDX3200 X-ray powder diffractometer made by Qingniao Company of Beijing University.

3. Results

3.1. Alternative pulses of O_2 and CO with different time intervals and transient experiments from 1/1 O_2/He to Ar

After three O_2 pulses with 10 s intervals over the Ni/Al_2O_3 catalyst pre-reduced at 700 °C for 1 h, a CO pulse was carried out with different time intervals between the third O_2 pulse and the CO pulse. The results are shown in figure 1 (only the third O_2 pulse was drawn). With the increase of the time interval between the O_2 and CO pulses, the quantity of CO_2 formed by the oxidation of CO pulsed after the O_2 pulse decreases.

In 30 mg catalyst, there are about 46 μmol Ni atoms and 2.3 μmol on the catalyst surface. For each O_2 pulse, there are about 32 μmol oxygen atoms. Ni is very easy to be oxidized under the experimental conditions. Therefore, after three O_2 pulses, nearly all the Ni atoms on the catalyst surface are oxidized to NiO. We have proved that CO is more difficult to be oxidized by NiO at 700 °C [15], so there must be other oxygen species on the catalyst surface with higher oxidative activity. We consider they are adsorbed oxygen species. To get more direct evidence, we did the transient experiments from 30 ml/min 1/1 O_2/He to the same flow rate pure Ar with and without catalyst in the reactor, respectively. The results are shown in figure 2.

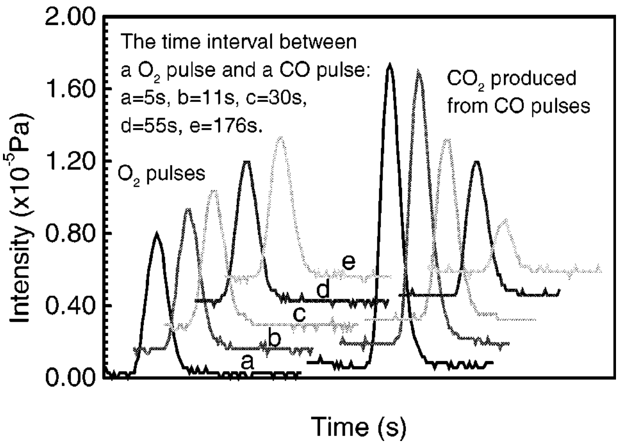

Figure 1. Alternative pulses of O_2 and CO with different time intervals.

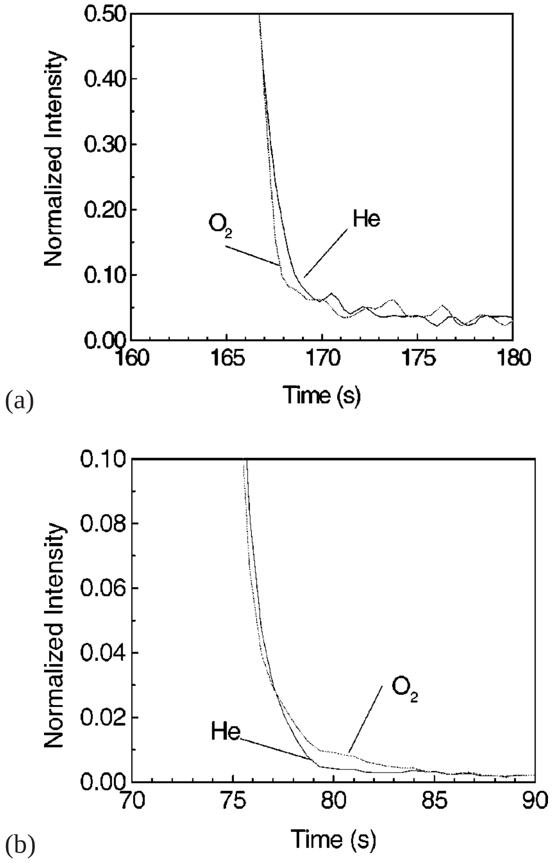

Figure 2. Responses of the transient from 30 ml/min 1/1 O_2/He to 30 ml/min pure Ar at 700 °C. (a) Without catalyst in the reactor, (b) with 30 mg Ni/Al_2O_3 in the reactor.

If O_2 can be adsorbed on the catalyst at 700 °C, as compared to the case without catalyst but with only quartz sand in the reactor, the O_2 transient decreasing response would delay somewhat. In fact, with He tracer as the reference, the O_2 transient decreasing response with catalyst in the reactor (figure 2(b)) has a little trailing as compared with that without catalyst (figure 2(a)). This illustrates that there must be a small quantity of reversibly adsorbed oxygen species that are in equilibrium with gas phase O_2. When the ambience

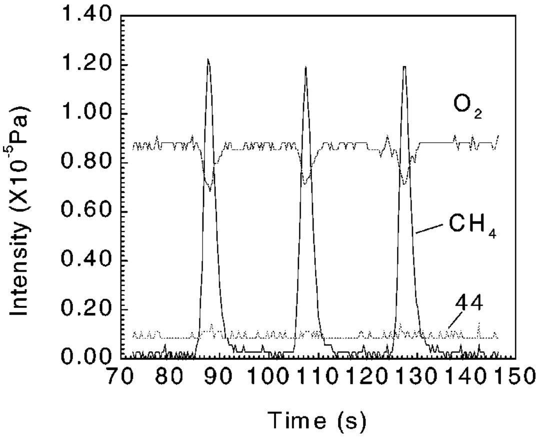

Figure 3. CH_4 pulses in 30 ml/min O_2 at 700 °C without catalyst in the reactor.

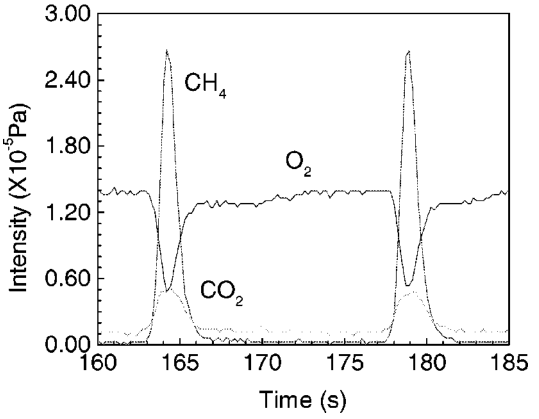

Figure 4. CH_4 pulses in O_2 atmosphere at 700 °C over the Ni/Al_2O_3 catalyst.

is changed to O_2-free Ar gas, they desorb quickly and a slight trailing is left in the responses of O_2.

3.2. CH_4 pulses in O_2 gas flow

Reversibly adsorbed oxygen is much more active than NiO in oxidizing CO at atmospheric pressure and 700 °C [15]. Whether or not it is also active to oxidize CH_4 is our concern. Before investigation, we must know whether the gas phase reaction of CH_4 and O_2 may occur under the experimental conditions.

Without catalyst in the reactor, CH_4 pulses were conducted in 30 ml/min O_2 gas flow at atmospheric pressure and 700 °C, and no significant CO_2 was detected (figure 3), which means that a gas phase oxidation reaction between CH_4 and O_2 does not occur under these conditions.

The above experiments were repeated with 30 mg Ni/Al_2O_3 catalyst in the reactor, and corresponding to each CH_4 pulse CO_2 appeared obviously, but no CO and H_2 were detected (figure 4). These results demonstrate the occurrence of a catalytic oxidation reaction. However, we cannot confirm that the CO_2 is from the reaction between CH_4 and adsorbed oxygen, for it is also possible that CH_4 reacts with NiO to form CO_2.

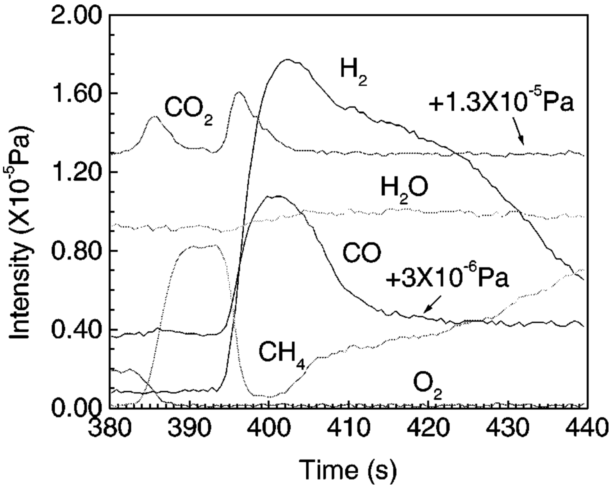

Figure 5. Responses of transient from 1/2 O_2/He to 2/1 CH_4/Ar over the catalyst oxidized for 1 h.

3.3. Transient experiments from 1/2(mol) O_2/Ar to 2/1(mol) CH_4/He

The catalyst was first oxidized in 30 ml/min 1/2 O_2/Ar gas flow for 1 h at 700 °C, then a transient switch to the same flow rate 2/1 CH_4/He was performed (figure 5). We can only detect a small amount of CO_2 just after the switch, and 3–4 s hereafter (389–393 s in figure 5) nearly no product is detected, then CH_4 starts to decompose. Accompanying the formation of H_2, a great deal of CO and CO_2 are produced. This indicates that there are oxygen species on the catalyst surface before the CH_4 decomposition. According to the residence time of the reversibly adsorbed oxygen and the quantity of CO and CO_2 produced here, we can infer that the catalyst is still in the oxidative form, that is, most of Ni on the catalyst surface is in the form of NiO before CH_4 decomposition. Since nearly no product is formed between the first CO_2 peak and CH_4 decomposition (389–393 s in figure 5), the conclusions that CH_4 cannot be oxidized by NiO and that the first CO_2 peak is the product from CH_4 oxidized by reversibly adsorbed oxygen can be made.

3.4. Transient experiments from 2/1(mol) CH_4/O_2 to 2/1(mol) CH_4/He and from 2/1(mol) CH_4/O_2 to pure He

The transient decreasing responses of CO and CO_2 from 2/1 CH_4/O_2 to 2/1 CH_4/He and from 2/1 CH_4/O_2 to pure He after the reaction of 2/1 CH_4/O_2 proceeding for 5 min at 700 °C over the catalyst pre-reduced for 1 h are shown in figure 6. The decreasing trends of CO and CO_2 in both cases are nearly the same, which indicates that there is no surplus oxygen on the catalyst surface. Otherwise CO and/or CO_2 will be produced continuously after the switch from 2/1 CH_4/O_2 to 2/1 CH_4/He and the decreasing responses will have some delay as compared to that from 2/1 CH_4/O_2 to pure He. So the catalyst surface is maintained in the reduced state during partial oxidation of CH_4, as has also been proved by XRD characterization for the catalyst sample over which partial oxidation of CH_4 proceeded for

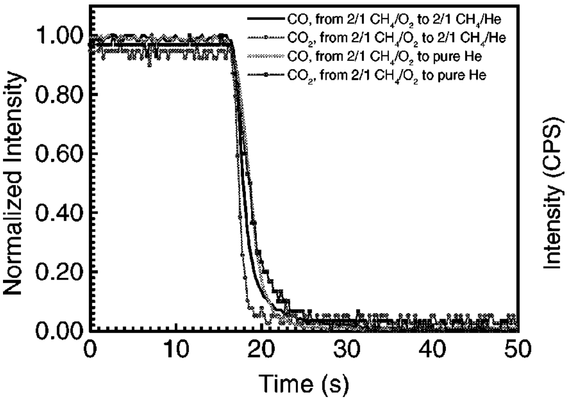

Figure 6. Decreasing responses of CO and CO_2 transient from 2/1 CH_4/O_2 to 2/1 CH_4/He and from 2/1 CH_4/O_2 to pure He with total flow rate 30 ml/min over the Ni/Al_2O_3 catalyst pre-reduced for 1 h and after partial oxidation of CH_4 proceeding for 5 min at atmospheric pressure and 700 °C.

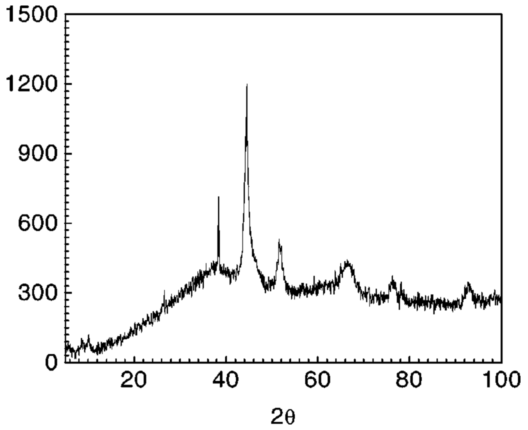

Figure 7. XRD characterization for the Ni/Al_2O_3 catalyst over which partial oxidation of CH_4 has proceeded for 5 h at 700 °C.

5 h (figure 7). In the figure, three Ni peaks ($2\theta = 44.6°$, 51.3° and 76.3°) were detected, and there were no NiO peaks. The result is consistent with those of the transient experiments.

3.5. Transient experiments from 2/1(mol) CH_4/O_2 to 2/1(mol) He/O_2

The transient switch from 2/1 CH_4/O_2 to He/O_2 was performed after CH_4/O_2 had reacted for 5 min over the catalyst pre-reduced at 700 °C. The results are shown in figure 8. After the switch, the intensity of CO_2 first increased, and then decreased slowly to the base line, which denotes the formation of CO_2. However, whether CO_2 comes from the oxidation of surface carbon species is not clear. To confirm this, we must exclude the possibility of the formation of CO_2 in the reaction between CH_4 and oxygen. Thus, the following experiments were performed: after the reaction of CH_4/O_2 over the catalyst pre-reduced at 700 °C proceeding for 5 min, the ambience was first switched to pure He to sweep the catalyst bed for 2 min, and then switched to 2/1 He/O_2. The results are shown in figure 9, in which significant CO_2 production can be seen. Consequently, there must be a certain amount of carbon species on the catalyst surface.

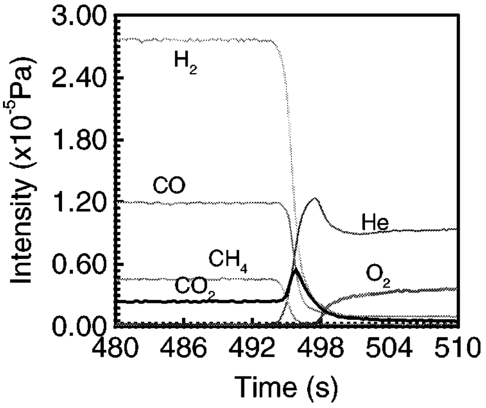

Figure 8. Transient responses from 2/1 CH_4/O_2 to 2/1 He/O_2 after partial oxidation of CH_4 for 5 min.

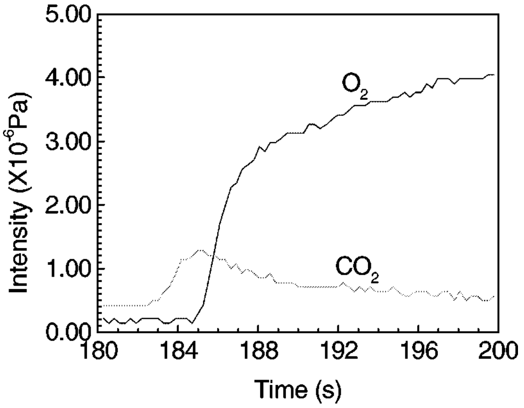

Figure 9. Reaction of 2/1 He/O_2 with the catalyst flushed by pure He for 2 min after partial oxidation of CH_4 for 5 min.

3.6. Temperature-programmed reaction of 2/1(mol) CH_4/O_2 over the reduced catalyst

Temperature-programmed reaction of 2/1 CH_4/O_2 at the rate of 26 °C/min was conducted after the Ni/Al_2O_3 catalyst had been reduced for 1 h at 700 °C. The results are shown in figure 10.

CO_2 and H_2O are produced originally at about 430 and at 600 °C CO and H_2 appear. The intensities of these products increase with the increase of temperature and remain nearly unchanged when the temperature is maintained at 700 °C. Here, the conversions of CH_4 and O_2 are 7.92 and about 10%, and the selectivities to H_2 and CO are 76.6 and 41.0%, respectively.

When the O_2 mass flow controller is closed, the intensity of CH_4 increases quickly, but all the intensities of H_2, O_2, CO and CO_2 decrease. About 40 s later, CH_4 starts to decompose, and H_2 and CO are produced at the same time. The results are similar to that in figure 5 and indicate that the surface of the catalyst is in the oxidative state during the temperature-programmed reaction. When the O_2 mass flow

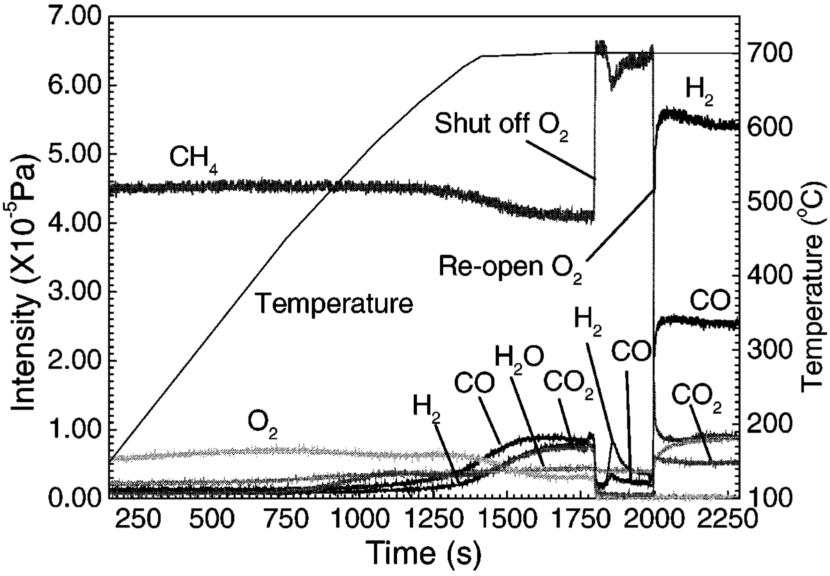

Figure 10. Temperature-programmed reaction of partial oxidation of methane conducted over a pre-reduced Ni/Al_2O_3 catalyst with the rate of 26 °C/min. O_2 was shut off for a few minutes when the temperature reached 700 °C and then retrieved.

controller is turned on again, the conversion of CH_4 and the selectivities to H_2 and CO are improved significantly, which are 81.3, 87.7 and 82.4%, respectively, and O_2 is consumed completely.

4. Discussion

4.1. The effect of different oxygen species on CH_4 adsorption and decomposition

Our previous work [13,14] has shown that Ni on the catalyst surface exists in the form of NiO after being oxidized for 1 h and there is a small amount of reversibly adsorbed oxygen on the catalyst. Reversibly adsorbed oxygen is more active than NiO in oxidizing CO [15]. In figures 4 and 5, it is evident that CH_4 is easy to be oxidized by adsorbed oxygen but difficult by NiO.

It can be seen from figure 4 that corresponds to each CH_4 pulse, only CO_2 is produced. In figure 5, after switching to CH_4, nevertheless, only CO_2 appears immediately. And there is a certain time during which nearly no product is formed before CH_4 starts to decompose. All these illustrate CH_4 cannot decompose over NiO. Active metallic Ni sites are needed for CH_4 decomposition [13,14].

Chen et al. [16] suggested that a certain amount of NiO in NiO crystal can dissociate without gas phase O_2 at 700 °C, so the atomic ratio of Ni/O is higher than the stoichiometric ratio. It is known that a single metal atom has no catalytic activity and a defective surface is more active [17]. Furthermore, when the environment changes, restructuring will occur on the surface of some metal crystals, such as Ir, Pt, Au, and semiconductors Si, Ge, GaAs, InSb, etc., and extends from the outer layer to several atom layers inside [18]. In our opinion, before CH_4 begins to decompose after the switch, zero-valence Ni atoms are formed on the oxidized catalyst surface, and these metallic Ni may be rearranged. When such metallic Ni site needed for CH_4 decomposition is formed, CH_4 starts to decompose on these sites.

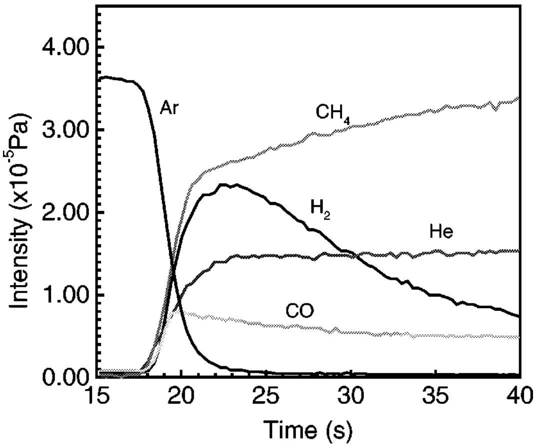

Figure 11. Responses of transient from pure Ar to 2/1 CH_4/He over the catalyst oxidized in 30 ml/min 1/2 O_2/Ar gas flow for 1 h and then swept with pure Ar for 3 min.

We define the time from the switch to the decomposition of CH_4 the induction period, during which CH_4 is first oxidized fully to CO_2 and H_2O by reversibly adsorbed oxygen on the catalyst and then metallic Ni atoms are formed and rearranged to form active metallic Ni sites for CH_4 decomposition.

To validate the above viewpoints, the catalyst was first swept with pure Ar for 3 min after being oxidized in 30 ml/min 1/2 O_2/Ar gas flow for 1 h at 700 °C, then a transient switch was performed from Ar to 2/1 CH_4/He. The results are shown in figure 11. After the switch, CH_4 almost decomposes immediately and no induction period appears. In fact, here the induction period has already finished during the sweep with pure Ar (figure 11).

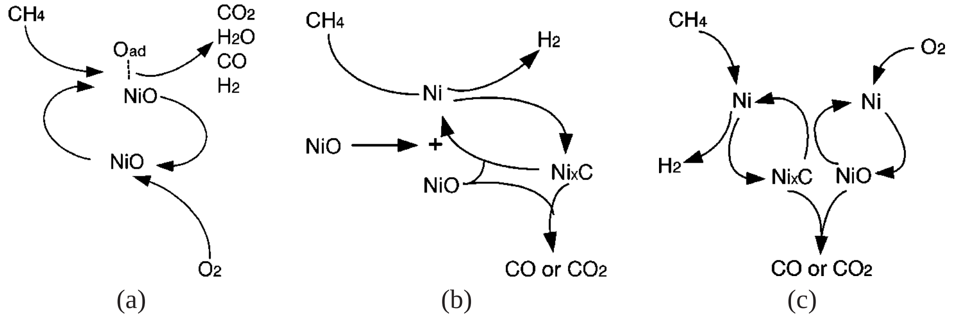

Figure 12. Schematic reaction mechanisms corresponding to figure 10: (a) before shutting off O_2, (b) after shutting off O_2 and (c) for re-opened O_2.

In figure 5, the first CO_2 peak is the result of the reaction between reversibly adsorbed oxygen and CH_4 via the Rideal–Eley mechanism, and the second one is the result of surface reaction of NiO and Ni_xC formed by CH_4 decomposition. The nature of these reactions is different. NiO cannot oxidize CH_4 directly, and it has difficulty in oxidizing CO, therefore, the high selectivity of CO during partial oxidation of CH_4 is closely related to these factors.

4.2. The surface state of Ni/Al_2O_3 catalyst during partial oxidation of CH_4

According to figure 6, once NiO is produced on the catalyst surface during partial oxidation of CH_4, it reacts immediately with Ni_xC from CH_4 decomposition to form a large amount of CO and a small amount of CO_2. Moreover, a part of NiO can also react with hydrogen from CH_4 decomposition to form H_2O. The catalyst surface maintains its reduced state. This is the precondition for partial oxidation of CH_4. If the catalyst surface has been oxidized before partial oxidation of CH_4 begins, the reaction mechanism will change. This will be discussed below.

On the catalyst surface, there is a small amount of carbon species (figures 8 and 9), which is favorable for keeping the catalyst from being oxidized, and for improving the selectivity to CO because the existence of carbon species can restrain the production of CO_2 to some extent.

4.3. The effect of surface state on the reaction mechanism

Slagtern et al. [19] found that the conversion of CH_4 and the selectivities to CO and H_2 over a Ni-based catalyst at increasing temperature are lower than that at decreasing temperature before the complete consumption of O_2 at temperature below 800 °C. These phenomena are similar to our results of temperature-programmed reaction shown in figure 10. The results predict that different surface states correspond to different reaction mechanisms.

Our previous work [13,14] has shown that partial oxidation of CH_4 over a Ni/Al_2O_3 catalyst proceeds via a direct oxidation mechanism, and CH_4 decomposes first on the active metallic Ni sites to H_2 and Ni_xC. However, in figure 8, after closing the O_2 mass flow controller, the intensity of H_2 decreases together with that of O_2, CO and CO_2, which implies that the H_2 produced is not from CH_4 decomposition over the active metallic Ni sites. Therefore, during the temperature-programmed reaction, the reaction is not via a direct oxidation mechanism.

According to the experimental results of temperature-programmed reaction, different mechanisms corresponding to different stages in figure 10 are suggested (figure 12).

During the temperature-programmed reaction, there is competitive adsorption between CH_4 and O_2 on metallic Ni sites, and O_2 adsorption is stronger than that of CH_4. Therefore, metallic Ni sites have been oxidized before the temperature is raised high enough for CH_4 decomposition. CH_4 cannot decompose on oxidized Ni sites, and NiO cannot oxidize CH_4. But CH_4 can be oxidized by reversibly adsorbed oxygen, which exists on the oxidized surface in the presence of O_2 in the system, via the Rideal–Eley mechanism at a certain temperature, and oxidized Ni catalyst is active for full oxidation of CH_4 [5,20]. The consumed reversibly adsorbed oxygen can be supplemented continuously by gas phase O_2, which keeps the catalyst from being reduced (figure 12(a)). The oxidation of CH_4 by adsorbed oxygen is non-selective, and the products may be H_2O and CO_2 or H_2O, CO_2, H_2 and CO depending on the temperature. High temperature is favorable for producing H_2 and CO, which is in agreement with the results published by Slagtern et al. [19].

The reaction between CH_4 and adsorbed oxygen is not a fast one, which can be inferred by the consumption of CH_4 and O_2 (figure 10), otherwise, the conversions of CH_4 and O_2 will not be so low during the temperature-programmed reaction. With the increase of the temperature, the O_2 adsorbing rate increases and is still faster than that of the reaction between CH_4 and adsorbed oxygen, for CO_2 and H_2O are always the main products, and O_2 has not been used up. When the relative amount of adsorbed oxygen is not sufficient, CO and H_2 are produced.

After closing the O_2 mass flow controller, the catalyst surface disengaged from O_2 ambient undergoes an induction period and active metallic Ni sites are formed (figure 12(b)), so CH_4 starts to decompose to H_2 and Ni_xC, and Ni_xC reacts further with NiO to CO or CO_2.

When the O_2 mass flow controller is re-opened, the catalyst is reduced due to the reaction between Ni_xC and NiO to CO or CO_2. CH_4 competes with O_2 to adsorb on active metallic Ni sites and decomposes immediately to H_2 and Ni_xC (figure 12(c)). Ni_xC can react quickly with NiO from

Ni oxidized by O_2 to CO or CO_2 [13,14]. So the catalyst can maintain its reduced state. Furthermore, partial oxidation of CH_4 proceeds via a direct oxidation route with the full consumption of O_2, therefore, the reaction rate, CH_4 conversion, and the selectivities to H_2 and CO can be improved significantly.

Thus, if the catalyst surface has been fully oxidized before letting the 2/1 CH_4/O_2 flow into the reaction system, CH_4 can only undergo a non-selective oxidative reaction with adsorbed oxygen via the Rideal–Eley mechanism, which causes the rather low conversion of CH_4 and the selectivities to CO and H_2. Only when the catalyst surface maintains its reduced state can CH_4 react with O_2 efficiently via a direct oxidation mechanism. Therefore, the surface state of the catalyst plays a crucial role in the conversion and selectivity of the reaction [20].

5. Conclusions

At atmospheric pressure and 700 °C, if the catalyst surface is in its oxidative state, gas phase O_2 will not be able to be used up and a certain amount of reversibly adsorbed oxygen will exist on the catalyst surface. Non-selective oxidation between CH_4 and reversibly adsorbed oxygen with high oxidation activity occurs easily via the Rideal–Eley mechanism, and both the conversion of reactants and the selectivities to H_2 and CO are very low. Thereby, during partial oxidation of CH_4, the catalyst must be maintained in the reduced state. Thus, CH_4 can react with O_2 via a direct oxidation mechanism with high conversion and selectivity. O_2 being consumed fully, a small amount of carbon species on the catalyst surface during the reaction and CO disproportionation limited by thermodynamic equilibrium under such conditions [15] are the main reasons why the selectivity to CO is very high.

The results also indicate that direct oxidation is the main route for partial oxidation of CH_4, and the indirect oxidation mechanism or combustion–reforming mechanism cannot gain dominance in the reaction under the experimental conditions.

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