Isotopic studies on the mechanism of partial oxidation of CH_4 to syngas over a Ni/Al_2O_3 catalyst

Chunyi Li [a,*], Changchun Yu [b] and Shikong Shen [b]

[a] *College of Chemistry and Chemical Engineering, University of Petroleum, Dongying 257061, Shandong Province, PR China*
E-mail: chyli@mail.hdpu.edu.cn
[b] *Catalytic Key Laboratory of CNPC, University of Petroleum, Changping, Beijing 102200, PR China*

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An isotopic transient technique and XPS were used to investigate the mechanism of partial oxidation of CH_4 to syngas over a Ni/Al_2O_3 catalyst at atmospheric pressure and 700 °C. The experimental results show that CH_4 can decompose easily and quickly to H_2 and Ni_xC over the reduced catalyst, and Ni_xC can react rapidly with NiO from Ni oxidized by O_2 to CO or CO_2 depending on the relative concentration of Ni_xC around NiO on the catalyst surface. Both H_2 and CO are primary products in partial oxidation of CH_4. Isotopic tracing experiments prove that most of CO_2 produced during partial oxidation of CH_4 is from the surface reaction between Ni_xC and NiO, and it is impossible to mainly originate from the further oxidation of CO or the disproportionation of CO. The disproportionation of CO may happen at the experimental conditions, limited by thermodynamic equilibrium, however, the conversion of CO is very low. The pulse experiments of CH_4/O_2 and CH_4/CO_2 with stoichiometric ratio show that the rate of partial oxidation of CH_4 is faster than that of CH_4 reforming with CO_2, this implies that partial oxidation of CH_4 is unlikely to proceed *via* a combustion reforming mechanism. All the results support the direct oxidation mechanism: H_2 is from CH_4 decomposition and CO is the product of the surface reaction between Ni_xC and NiO.

KEY WORDS: methane; partial oxidation; syngas; mechanism

1. Introduction

The tremendous abundance of natural gas, in which CH_4 is the principal component, is a valuable resource for mankind. It is mainly used for heating or power generation purposes. With the decrease of crude oil reserves, many chemical products or fuels will be produced with natural gas in the new century. To produce chemicals or fuels, indirect conversion of CH_4 *via* syngas should be considered firstly, for direct conversion of CH_4, *i.e.*, oxidative coupling of CH_4 has met some difficulty that cannot be overcome for a short while. Industrially, syngas is traditionally produced by steam reforming of natural gas. In recent years, partial oxidation of CH_4 has been largely studied because of its potential to reduce the cost of syngas [1].

Many supported metal catalysts, such as supported Rh, Pt, Pd, Ru, Re, Ir, Ni, Fe and Co, *etc*., have been studied for partial oxidation of CH_4 to syngas [2–25]. Supported noble Rh catalysts exhibit excellent performances [2], but their price is rather expensive. Supported Ni catalysts have similar performance with supported Rh, and the price of Ni is far lower. So the studies on supported Ni catalyst have attracted numerous researchers [3–12].

About the mechanism of partial oxidation of CH_4, it is generally assumed to proceed according to two distinct routes: the direct oxidation mechanism and the indirect oxidation (combustion reforming) mechanism. The direct oxidation mechanism means that H_2 originates directly from the decomposition of CH_4 and CO is from the reaction between surface oxygen and surface carbon species originating from CH_4 decomposition. In the direct oxidation mechanism, some authors [7,20,26] thought that the side product CO_2 is formed by the further oxidation of CO, and others [27,28] claimed that CO_2 is produced together with CO and is also the product of the reaction between surface oxygen and surface carbon species. In the indirect oxidation mechanism, about 25% CH_4 firstly combusts to H_2O and CO_2 with complete consumption of O_2, and then the remaining CH_4 reforms with H_2O and CO_2 to H_2 and CO [16,29,30]. Obviously, H_2 and CO are secondary products here.

Shen *et al.* [31] proposed that partial oxidation of CH_4 to syngas over a Ni/Al_2O_3 catalyst proceeds by the direct oxidation mechanism. Concretely, it is described as follows:

$$CH_4 + x\mathrm{Ni} \rightarrow 4\mathrm{H} + \mathrm{Ni}_x\mathrm{C}, \quad x = 1\text{–}3 \tag{1}$$

$$2\mathrm{H} \rightarrow H_2 \tag{2}$$

$$O_2 + 2\mathrm{Ni} \rightarrow 2\mathrm{NiO} \tag{3}$$

$$2\mathrm{H} + \mathrm{NiO} \rightarrow H_2O \tag{4}$$

$$\mathrm{Ni}_x\mathrm{C} + \mathrm{NiO} \rightarrow \mathrm{CO} + (x+1)\mathrm{Ni} \tag{5}$$

$$\mathrm{Ni}_x\mathrm{C} + 2\mathrm{NiO} \rightarrow CO_2 + (x+2)\mathrm{Ni} \tag{6}$$

In the paper, the isotopic transient technique and XPS were used to investigate partial oxidation of CH_4 to syngas over the Ni/Al_2O_3 catalyst, and further pieces of evidence of the above mechanism have been given.

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[*] To whom correspondence should be addressed.

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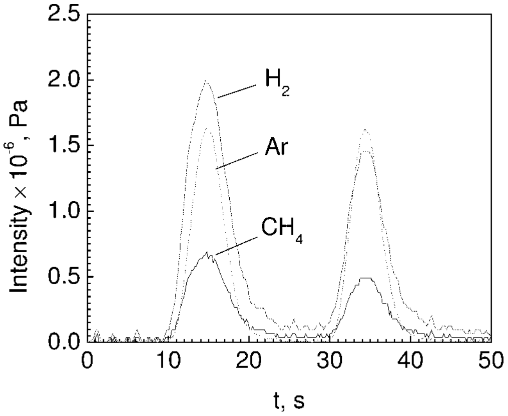

Figure 1. Pulses of 1/1 (mol) CH_4/Ar (0.39 ml for each pulse) in 30 ml/min He over the catalyst reduced by H_2 at 700 °C for 2.5 h.

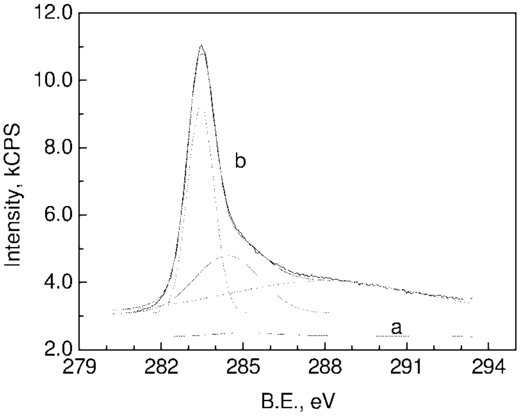

Figure 2. XPS C 1s spectra for the catalysts. (a) The reduced catalyst and (b) the carbon-deposited catalyst.

2. Experimental

The 8 mol% Ni/Al_2O_3 catalyst was prepared by co-precipitation and the preparing steps have been described in detail elsewhere [32]. 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 granule range is 0.3–0.45 mm.

The isotopic transient apparatus has been introduced in [31]. 30 mg catalyst was placed in the middle of the quartz reactor with inside diameter of 5.5 mm, and the other space of the reactor was filled with 0.45–0.9 mm quartz sand to shorten the residence time of the reactants and products to quicken the response speed of transient. The height of the catalyst bed was about 2 mm. An AI-FUZZY temperature controller combined with a K thermocouple controlled the reactor temperature. The products were detected by an on-line AMETEK quadrupole mass spectrometer with eight channels and the minimum dwell time 3 ms. All the experiments were carried out at atmospheric pressure and 700 °C. The total flow rate at the inlet of the reactor was 30 ml/min. Both ^{13}CO (91.7 mol%) and $^{18}O_2$ (92.9 mol%) were purchased from Merck Frosst Canada Company.

The X-ray photoelectron spectra of the carbon-deposited catalyst were recorded in a VG Scientific ESCALAB 210 electron spectrometer, equipped with a Mg K_α X-ray source and a hemispherical electron analyzer. The peak positions are relative to the binding energy of Al 2p at 74.6 eV.

3. Results

3.1. Decomposition of CH_4 over the reduced catalyst

The catalyst was reduced with pure H_2 for 2.5 h at 700 °C, then 1/1 (mol) CH_4/Ar pulses were conducted in pure He, where Ar as the tracer was used to indicate the decomposing rate of CH_4. In figure 1, H_2 from CH_4 decomposition appears simultaneously with inert tracer Ar after the pulses, which illuminates that the rate of CH_4 decomposition is fast; otherwise the response of H_2 must have some delay compared to that of Ar, for inert gas Ar does not adsorb on the surface of the catalyst, and its residence time may be seen as zero. The formation of H_2, however, is a complex process including CH_4 adsorbing, decomposing, and hydrogen combining to H_2 and its desorbing. If any one of these steps is slow, then H_2 cannot possibly respond with Ar at the same time.

The catalyst was firstly reduced under the same conditions, and then we switched the gas from H_2 to CH_4. After the switch, CH_4 decomposed immediately to produce H_2. When CH_4 finished decomposing and no H_2 was produced, we switched the atmosphere to pure Ar at once and cooled the reactor in an ice/water bath. Thus we prepared the carbon-deposited catalyst. The carbon-deposited catalyst and only reduced catalyst were then characterized by XPS. The results are shown in figure 2. Between 280 and 288 eV, the spectrum of the carbon-deposited catalyst has two carbon peaks compared to that of the reduced catalyst. The one corresponding to 283.5 eV can be ascribed to metal carbides Ni_xC ($x = 1$–3) [33,34], and we call the other corresponding to 284.5 eV transition carbon.

In TPO of the carbon-deposited catalyst, only CO, CO_2 and no H_2O were detected. This means that CH_4 can decompose thoroughly to hydrogen and carbon over the catalyst [35]. As for whether CH_4 decomposes step by step in the sequence $CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow C$ or not, no direct evidence was obtained in the experiments. Furthermore, metal carbides are easy to be oxidized and transition carbon is more difficult [35]. And metal carbides can convert to transition carbon at high temperature [35,36]. These results show that the carbides from CH_4 decomposition initially may be Ni_xC. Therefore, the decomposition of CH_4 over the Ni/Al_2O_3 catalyst can be described with reactions (1) and (2) in section 1.

3.2. Decomposition of CH_4 over the oxidized catalyst

In [32], the transient experiment from O_2/Ar to CH_4 shows that only small amounts of CO_2 and CO are detected and CH_4 does not decompose just after the switch. After 3–4 s inducing period during which nearly no product is produced and metal Ni sites, which are necessary for CH_4

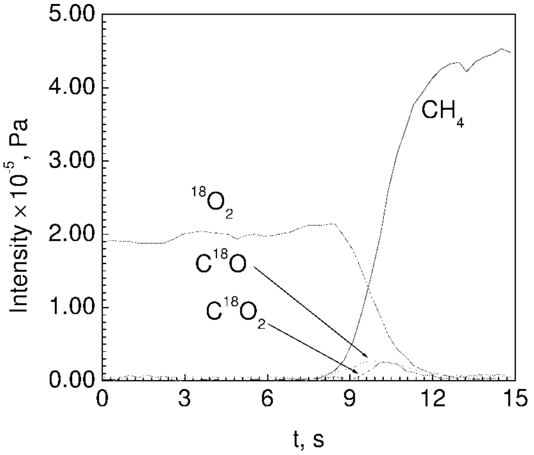

Figure 3. Transient switch from 1/2 (mol) $^{18}O_2$/Ar to CH_4 over the catalyst oxidized in 1/2 (mol) O_2/He at 700 °C for 1 h.

decomposing, are formed on the oxidized catalyst surface, CH_4 starts to decompose with the formation of H_2, and a great deal of CO and CO_2 are produced simultaneously. The CO and CO_2 produced just after the switch are due to the reaction between CH_4 and adsorbed oxygen for we have excluded the possibility of gas phase reaction between CH_4 and O_2 at the experimental conditions. The CO and CO_2 produced with CH_4 decomposing together are from the reaction between Ni_xC and NiO (reactions (5) and (6)). Here, isotopic experiments were conducted to prove these viewpoints further.

The catalyst was firstly oxidized in 1/2 (mol) O_2/He for 1 h and 1/2 (mol) $^{18}O_2$/Ar for 1 min in turn at 700 °C, then the switch from $^{18}O_2$/Ar to pure CH_4 was performed (figure 3). In the figure, only a little $C^{18}O$ and $C^{18}O_2$ appear and CH_4 does not decompose. The amount of adsorbed oxygen species on the catalyst surface is very small and CH_4 is far surplus, but there is $C^{18}O_2$ produced, which proves that CH_4 is easy to be oxidized by adsorbed oxygen and the oxidation is nonselective. No CO or CO_2 is detected here. This means adsorbed oxygen can exchange with gas phase $^{18}O_2$ rapidly.

Before switching to CH_4, if the catalyst bed was swept with pure He for several minutes, the result was completely different (figure 4). For the formation of metal Ni sites during the sweeping [32], CH_4 decomposes immediately after the switch, and H_2, CO and CO_2 are produced. The intensity of CO approaches that of CO_2 at the very beginning of the switch, for the amount of Ni_xC from CH_4 decomposition is relatively small compared to that of NiO on the catalyst surface. With the increase of the quantity of Ni_xC, the difference between the intensity of CO and that of CO_2 is enlarged. This proves that to produce CO or CO_2 is dependent on the relative concentration of Ni_xC around NiO on the catalyst surface. Obviously, the reaction between Ni_xC and NiO, different from that between CH_4 and adsorbed oxygen, is not only fast, but also more selective at the condition of deficient O_2. Furthermore, that no $C^{18}O$ or $C^{18}O_2$ is detected in figure 4 shows that the $^{18}O_2$ in gas phase cannot exchange with the oxygen in NiO rapidly.

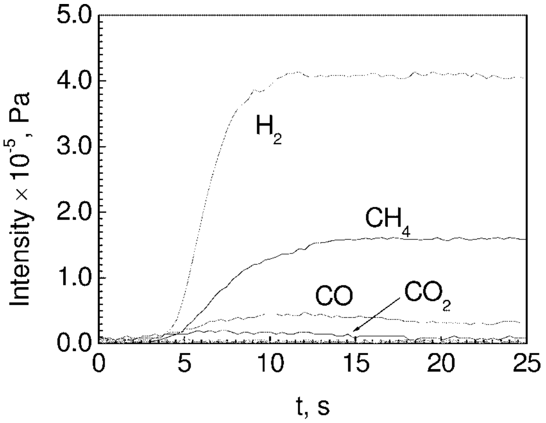

Figure 4. Transient switch from He to CH_4 after oxidation of the catalyst with 1/2 (mol) O_2/He for 1 h and 1/2 (mol) $^{18}O_2$/Ar for 1 min in turn.

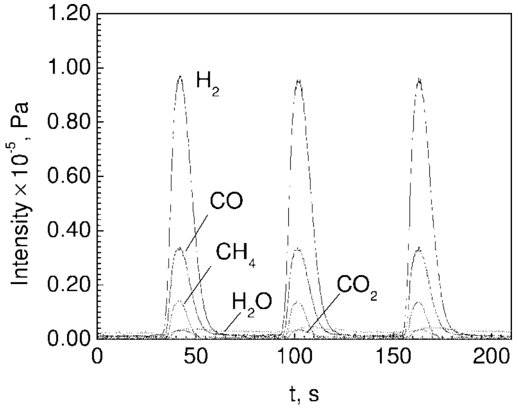

Figure 5. Pulse reaction of 2/1 (mol) CH_4/O_2 (5 ml) in 30 ml/min He over the catalyst reduced by H_2 for 2 h at 700 °C.

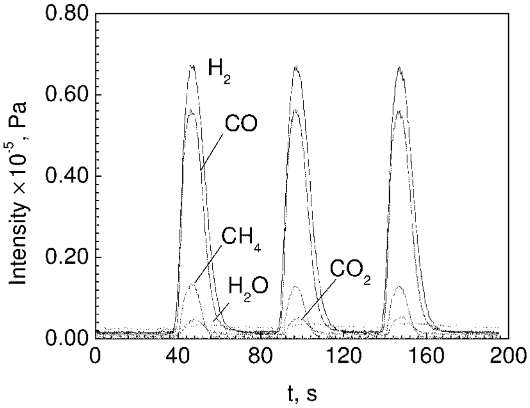

Figure 6. Pulse reaction of 1/1 (mol) CH_4/CO_2 (5 ml) in 30 ml/min He over the catalyst reduced by H_2 for 2 h at 700 °C.

3.3. Pulses of 2/1 (mol) CH_4/O_2 and 1/1 (mol) CH_4/CO_2

The pulses of 2/1 (mol) CH_4/O_2 and 1/1 (mol) CH_4/CO_2 were conducted in 30 ml/min pure He over the reduced catalyst at 700 °C to investigate the rates of partial oxidation and reforming. The pulse quantity was 5 ml and the results are shown in figures 5 and 6, respectively. In figure 5, H_2 and CO are the main products, and H_2O and CO_2 produced are only a little. In figure 6, H_2 and CO are also the main products.

Partial oxidation of CH_4 is a warm exothermic reaction, and CH_4 reforming with CO_2 is an endothermic reaction. Reaction rate, however, is sensitive to temperature. The reason to use the pulse reaction method is to avoid the influence of thermal effect. Because the amount of reactants pulsed is small and the contact time with the catalyst bed is very short – less than 10^{-2} s, for the height of the catalyst bed is only about 2 mm – the reaction heat released or adsorbed and its influence on the temperature of the catalyst bed can be neglected.

Both in partial oxidation of CH_4 and in CH_4 reforming with CO_2, H_2 originates from CH_4,

$$CH_4 + \tfrac{1}{2}O_2 \rightarrow 2H_2 + CO \tag{7}$$

$$CH_4 + CO_2 \rightarrow 2H_2 + 2CO \tag{8}$$

So, in figures 5 and 6, we use the ratio of the maximum peak intensities of the H_2 produced and the remaining CH_4 to represent the conversion of CH_4. In figure 5, it is about 6.3. In figure 6, however, it is only about 4.8. Therefore, although the reaction conditions are the same, the conversion of CH_4 in partial oxidation is remarkably higher than that in CH_4 reforming with CO_2. Furthermore, O_2 is consumed completely in partial oxidation, while CO_2 is not in CH_4 reforming. Obviously, the rate of partial oxidation of CH_4 is faster than that of CH_4 reforming with CO_2.

3.4. Transient responses from He to 10/5/1 (mol) $CH_4/O_2/Ar$

Over the reduced catalyst, the transient switch from pure He to 10/5/1 (mol) $CH_4/O_2/Ar$ with the same flow rate was performed at 700 °C and the responses were normalized with the formula

$$F = \frac{y - y_0}{y_\infty - y_0}, \tag{9}$$

where F is the normalized intensity and y_0, y and y_∞ are the intensity at the beginning, at any time and at the end of response, respectively. The normalized results are shown in figure 7. After the switch, the products H_2 and CO appear simultaneously with the inert tracer Ar, and their normalized responses are intertangled together. This indicates that the producing rates of H_2 and CO are very fast. If it is supposed that H_2 and CO are secondary products from the reforming reactions of the remaining CH_4 with CO_2 and H_2O, combustion products of CH_4 with O_2, it is impossible for H_2 and CO to response together with Ar, for reforming reactions, especially CH_4/H_2O reforming, are slower than partial oxidation of CH_4 [27,37].

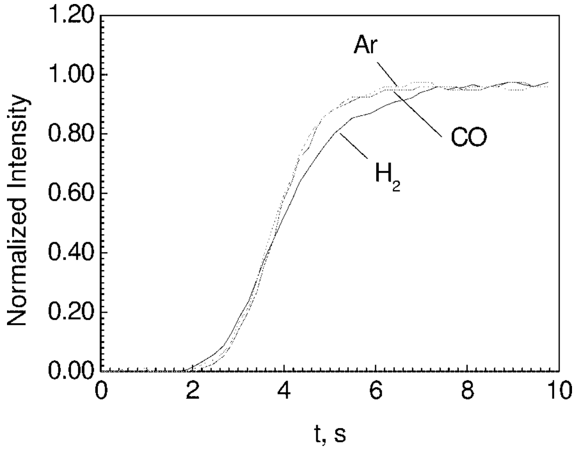

Figure 7. Normalized responses after the transient switch from 30 ml/min He to 10/5/1 (mol) $CH_4/O_2/Ar$ with the same flow rate over the catalyst reduced by H_2 for 2 h at 700 °C.

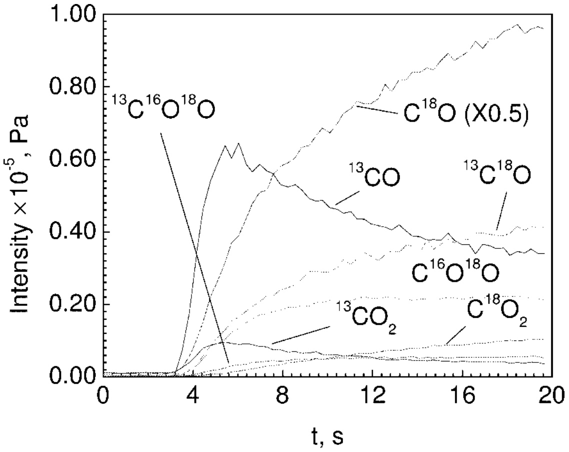

Figure 8. Transient responses from 2/1/1 (mol) $CH_4/O_2/He$ to 2/1/2/1/1 (mol) $CH_4/^{18}O_2/H_2/^{13}O/Ar$ at 700 °C.

3.5. Isotopic transient responses from 2/1/1 (mol) $CH_4/O_2/He$ to 2/1/2/1/1 (mol) $CH_4/^{18}O_2/H_2/^{13}O/Ar$ and from 2/1/1 (mol) $CH_4/O_2/He$ to $CH_4/^{18}O_2/Ar$

After $CH_4/O_2/He$ had reacted for 20 min over the catalyst pre-reduced at 700 °C in pure H_2, a transient switch to $CH_4/^{18}O_2/H_2/^{13}CO/Ar$ was conducted. The results are shown in figure 8. Adding of certain amounts of ^{13}CO to the reactants is to investigate the disproportionation of CO during partial oxidation of methane. The products after the switch include $C^{18}O$, $C^{16}O^{18}O$, CO, $C^{18}O_2$, $^{13}C^{18}O$, $^{13}CO_2$ and $^{13}C^{16}O^{18}O$. The selectivity to total carbon monoxide is 88%.

If CO_2 originates mainly from the disproportionation of CO during partial oxidation of methane, there should be more $^{13}CO_2$ after the switch. But in figure 8, the maximum content of $^{13}CO_2$ in total carbon oxides is only about 1.5%. So CO_2 must mainly originate from other reactions. There is about 12% $^{13}C^{18}O$ at 20 s in figure 8. This shows that the disproportionation of ^{13}CO happens and is very fast

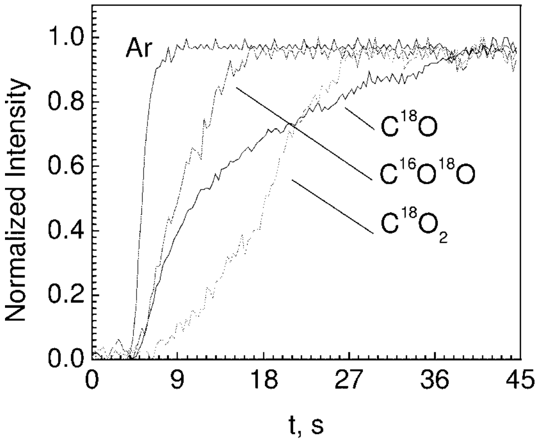

Figure 9. Transient responses of the switch from 2/1/1 (mol) $CH_4/O_2/He$ to $CH_4/^{18}O_2/Ar$ with the same ratio in steady state at 700 °C.

for $^{13}C^{18}O$ can only be formed from ^{13}CO by

$$2^{13}CO \rightleftharpoons {}^{13}C_{sur} + {}^{13}CO_2 \tag{10}$$

$$^{13}C_{sur} + {}^{18}O_{sur} \rightleftharpoons {}^{13}C^{18}O \tag{11}$$

However, disproportionation of CO is limited by thermodynamic equilibrium. As though the disproportionation of CO is not the main origin of CO_2, by the reaction, C in gas phase can exchange with surface C.

If CO_2 is mainly from the further oxidation of CO, there should be more $^{13}CO^{18}O$ after the switch. In fact, the maximum content of $^{13}CO^{18}O$ is only 1.2%. So further oxidation of CO is impossible to be the main origin of CO_2.

In figure 8, most carbon dioxide is $CO^{18}O$ at the beginning of the switch, and $C^{18}O_2$ substitutes $CO^{18}O$ little by little with time on stream. After the switch, O can only be from the catalyst surface, and further oxidation of CO is not easy to occur under the experimental conditions. So $CO^{18}O$ is from surface reaction among Ni_xC, NiO and $Ni^{18}O$. With the decrease of NiO and the increase of $Ni^{18}O$, the possibility to $CO^{18}O$ drops and the possibility to $C^{18}O_2$ rises gradually. So the intensity of $C^{18}O_2$ increases little by little and the intensity of $CO^{18}O$ firstly increases and then decreases after the switch. $CO^{18}O$ and $C^{18}O_2$ are the two most abundant carbon dioxides. Therefore, surface reaction between Ni_xC and NiO is the main origin of CO_2.

The steady-state isotopic transient experiment supports the above conclusions, too. At 700 °C after $CH_4/O_2/He$ had reacted for 20 min over the reduced catalyst, a steady-state transient switch was conducted from $CH_4/O_2/He$ to $CH_4/^{18}O_2/Ar$, where He and Ar were the tracers. The input responses of Ar, $C^{18}O$, $C^{18}O_2$ and $CO^{18}O$ were normalized with the formula (9). The results are shown in figure 9. Ar, $C^{18}O$ and $CO^{18}O$ begin to response nearly at the same time after the switch, however, the response of $C^{18}O_2$ has some delay compared to that of Ar, $C^{18}O$ and $CO^{18}O$. At the very beginning just after the switch, there is relatively more NiO and less $Ni^{18}O$ on the catalyst surface, so the possibility to produce $CO^{18}O$ is higher than that to produce $C^{18}O_2$. With the increase of surface ^{18}O, the possibility to produce $C^{18}O_2$ increases gradually, but the possibility to $CO^{18}O$ decreases. So the intensity of $CO^{18}O$ firstly increases then decreases, and the response of $C^{18}O_2$ has some delay compared to the inert tracer Ar.

The above results show that CO_2 mainly originates from the surface reaction between Ni_xC and NiO, not from the disproportionation of CO or the further oxidation of CO.

4. Discussion

There are still arguments about the mechanism of partial oxidation of CH_4 over supported metal catalysts. Some authors thought that the reaction proceeds by a direct oxidation mechanism, and others insisted that a combustion reforming mechanism is reasonable. Perhaps, the mechanism is different over different catalysts or under different reaction conditions. Based on the above experimental results, however, the possibility that the reaction proceeds by a direct oxidation mechanism is larger than that by a combustion reforming mechanism over the Ni/Al_2O_3 catalyst under the experimental conditions.

The decomposition of CH_4 is the precondition for the direct oxidation mechanism. If CH_4 cannot decompose quickly, the conversion of CH_4 and the selectivities to H_2 and CO must be affected. In figure 1, we can see clearly that CH_4 does decompose rapidly over the reduced catalyst. Combustion of CH_4 and O_2 is the precondition for the combustion reforming mechanism. It is the same that this step must proceed quickly, otherwise the conversion and selectivities will be limited. According to Dissanayake's point of view [29], the catalyst bed consists of three different regions from the top down. The first of these, contacting the initial CH_4/O_2 feed mixture, is $NiAl_2O_4$, which has only moderate activity for complete oxidation of CH_4 to H_2O and CO_2. The second region is NiO/Al_2O_3, over which complete oxidation of CH_4 to H_2O and CO_2 occurs. The third portion consists of reduced Ni/Al_2O_3, over which reforming reactions of the remaining CH_4 with H_2O and CO_2 to H_2 and CO happen. Surely, NiO/Al_2O_3 catalyst can catalyze the combustion reaction. When 2/1 (mol) CH_4/O_2 gas flow passes through the oxidized catalyst under the experimental conditions, the conversions of CH_4 and O_2 are all very low [32]. Obviously, the subsequent reforming reactions of the remaining CH_4 with CO_2 and H_2O cannot proceed with high CH_4 conversion, even though there is reduced Ni/Al_2O_3 below the oxidized. However, when the catalyst is reduced, the reaction can proceed with about 90% CH_4 conversion, complete consumption of O_2, and more than 90% syngas selectivity. The Ni/Al_2O_3 catalyst must be reduced for CH_4 cannot decompose over NiO. If the catalyst is oxidized, partial oxidation of CH_4 will not be able to proceed normally at 700 °C [32].

If partial oxidation of CH_4 goes by combustion reforming mechanism and the first step of combustion can proceed thoroughly, the second step, the remaining CH_4 reforming with H_2O and CO_2 from the first step must proceed simultaneously. Otherwise, the selectivity to H_2 or CO will be lowered for H_2O or CO_2 cannot convert to H_2 or CO effectively. That is to say, the rates for CH_4 reforming with H_2O and CO_2 should be fast, at least, they should not be slower than the overall rate of partial oxidation. Tang *et al.* [27] pulsed 2/1 (mol) CH_4/O_2 and 1/1 (mol) CH_4/CO_2 at 650 °C, the conversion of CH_4 in the former pulse is more than 60%, and that in the latter is only 26.2%. Our results in section 3.3 are consistent to that. So the rate of partial oxidation is faster than that of CH_4 reforming with CO_2 at 700 °C. Furthermore, if combustion reforming is the real mechanism of partial oxidation, adding steam in the reactant will promote the second step, consequently, the conversion of CH_4 and the selectivity to H_2 will be improved. However, Zhang [38] found that the conversion and selectivity do not change when adding steam into the reactor during partial oxidation of CH_4. Vermeiren *et al.* [37] also proved that partial oxidation of CH_4 is 13 times faster than the reforming reaction of CH_4 with H_2O. These all indicate that partial oxidation of CH_4 to syngas is impossible to proceed by the combustion reforming mechanism with very short contacting time.

Moreover, partial oxidation of CH_4 to syngas is a fast and exothermic reaction, so the temperature of the catalyst bed is unlikely to be uniform. In our experiments, about 90% CH_4 conversion can be achieved although the height of the catalyst bed is only 2 mm. That is to say, even though the catalyst bed is higher, maybe most of the reaction takes place only within the very thin bed nearby the inlet of the catalyst bed. The heat released causes the temperature of the part of the catalyst bed increase, thus, the temperature gradient is formed along the axis of the reactor. If combustion reforming is the real mechanism, and the higher temperature within the inlet region is caused by the combustion of CH_4 with total O_2, the strong endothermic reforming reactions of the remaining CH_4 with H_2O and CO_2 will be impossible to proceed rapidly over the below catalyst bed as the temperature is low.

During partial oxidation of CH_4, there is a little carbon species on the catalyst surface that can participate in the reaction under the experimental conditions, which is favorable for keeping the catalyst reduced. From the point of view of the reaction between Ni_xC and NiO, some active carbon species existing on the catalyst surface may mean reaction (5) is the rate-limiting step of partial oxidation of CH_4 to syngas. For Ni_xC can convert slowly to graphite, which is inert and affects the activity of the catalyst under the experimental conditions, *via* transition carbon at high temperature [35], reducing the activity of the catalyst for CH_4 decomposition appropriately and promoting the reaction between Ni_xC and NiO by adjusting the composition of the catalyst may be favorable for improving the performance of anti-carbon deposition.

5. Conclusions

At atmospheric pressure and 700 °C, CH_4 decomposes easily and quickly to H_2 and Ni_xC over the reduced catalyst, and Ni_xC can react rapidly with NiO from Ni oxidized by O_2 to CO or CO_2 depending on the relative concentration of Ni_xC around NiO on the catalyst surface. Both H_2 and CO are primary products in partial oxidation of CH_4. CO_2 is also mainly from the surface reaction between Ni_xC and NiO, not from the combustion of CH_4 with O_2, and the contribution of the disproportionation of CO or the further oxidation of CO to CO_2 can nearly be neglected. The rate of partial oxidation of CH_4 is faster than that of the reforming of CH_4 with CO_2 under the same conditions. All of these support the direct oxidation mechanism described as reactions (1)–(6). Reaction (5) may be the rate-limiting step for partial oxidation of CH_4 to syngas.

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