A study on the ignition process for the catalytic partial oxidation of methane to synthesis gas by MS-TPSR technique

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The ignition processes for the catalytic partial oxidation of methane (POM) to synthesis gas over oxidic nickel catalyst (NiO/Al_2O_3), reduced nickel catalyst (Ni^0/Al_2O_3), and Pt-promoted oxidic nickel catalyst ($Pt–NiO/Al_2O_3$) were studied by the temperature-programmed surface reaction (TPSR) technique. The complete oxidation of methane usually took place on the NiO catalyst during the CH_4/O_2 reaction, even with a pre-reduced nickel catalyst, and Ni^0 is inevitably first oxidized to NiO if the temperature is below the ignition temperature. It is above a certain temperature that Ni^0 is formed again, which leads to the start of the POM. The POM can be initiated at a much lower temperature on a Pt–NiO catalyst because of Pt promotion of the reduction of NiO. The POM in a fluidized bed can be easily initiated due to the addition of Pt.

KEY WORDS: ignition process; catalytic partial oxidation of methane; fluidized bed

1. Introduction

In recent years, the catalytic partial oxidation of methane to synthesis gas (POM) has been extensively investigated for natural gas utilization. The POM process has great promise as a replacement of the current highly endothermic steam reforming process. The catalytic partial oxidation of methane is mildly exothermic and can produce syngas of a molar ratio of H_2/CO of 2/1 which can be directly used as feedstock for methanol synthesis or Fischer–Tropsch synthesis. Moreover, the POM process can greatly enhance the production of syngas since it can be operated at very high space velocity.

Many previous studies on POM have been done over Ni-based catalysts in fixed beds [1–3]. In spite of its mild exothermicity, a hot spot can still be observed in fixed beds because of the high reaction rate of POM, which leads to the loss and aggregation of active Ni species [4,5]. Furthermore, the deactivation of the Ni-based catalyst by carbon deposition is often a problem in fixed beds [6,7].

The fluidized bed is a suitable device to handle this process. The “hot-spot” problem can be solved and the amount of carbon formation can be effectively limited in fluidized beds. Schmidt [8] reported that CH_4 conversion greater than 90% and selectivities higher than 95% could be obtained over Rh and Ni catalysts in a fluidized bed. Furthermore, no carbon deposit was found on the used catalyst. Santos et al. [9] obtained an almost flat temperature profile with conversion and selectivities close to equilibrium values. However, few people have investigated the ignition process of the POM, either in fluidized beds or in fixed beds. Schmidt [8] only mentioned that it was difficult to light off a stoichiometric mixture of CH_4 in air in a fluidized bed even at 700 °C. In order to overcome this problem, the catalyst was first lighted off in stoichiometric mixtures of C_3H_8 in air or NH_3 in air before CH_4 was introduced and C_3H_8 or NH_3 stream was then simultaneously switched off. Mleczko [10] reported that only at $T > 800\,^\circ C$ could the POM initiate over NiO/MgO and CoO/MgO catalysts. We found that the addition of Pt can greatly reduce the ignition temperature for POM in a fluidized bed. In this paper, our aim is to investigate the ignition process of POM over NiO, Ni^0 and Pt–NiO catalysts by MS-TPSR.

2. Experimental

2.1. Catalyst preparation

The alumina spheres support had an average particle size of ∼80 μm with a surface area of 70 m^2/g, and the packing density was 1.11 g/cm^3. The 8 wt% Ni/γ-Al_2O_3 catalyst was prepared by impregnating γ-Al_2O_3 support with a nickel nitrate solution of known concentration for 24 h, which was then dried and calcined in air at 600 °C for 4 h. 0.1 wt% Pt/γ-Al_2O_3 and 0.1 wt% $Pt–NiO/\gamma$-Al_2O_3 catalysts were prepared by impregnating γ-Al_2O_3 and 8 wt% Ni/γ-Al_2O_3 catalyst in a H_2PtCl_6 solution of known concentration for 24 h, which was then dried and calcined in air at 600 °C for 4 h. The reduced nickel catalyst was reduced *in situ* in H_2 at 700 °C for 0.5 h.

2.2. TPSR experiments

TPSR experiments were carried out using CH_4/He or $CH_4/O_2/He$ diluted gas under steady flow conditions. The temperature was increased at a rate of 10 °C/min. The effluents from the reactor were analyzed by an on-line mass

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spectrometer (Balzers GSD-300 Quadrupole MS). The data collecting and processing were performed by a personal computer. The mass spectrometer was operated in a multichannel mode to analyze CH_4, O_2, CO, H_2, CO_2, and H_2O simultaneously.

2.3. H_2-TPR

H_2-TPR experiments were performed with 5% vol/vol H_2/Ar mixed gas with a flow rate of 25 ml/min. The TCD signal was detected by an on-line GC 920. The amounts of the catalysts used were 20 mg and the temperature was increased at 10 °C/min.

2.4. Apparatus

A 22 mm i.d. and 350 mm length quartz reactor equipped with a sintered quartz distributor was used as a fluidized bed. A quartz thermowell (o.d. 3 mm) was used for monitoring the bed temperature. At the top of the reactor, a 50 mm i.d. and 20 cm height expansion section was used to disengage the catalyst. Reaction temperature varied between 600 and 800 °C. The fluidization height of 5 g catalyst was 5 cm under a feed rate of 600 ml/min at 800 °C. The product gases were analyzed by on-line gas chromatography.

3. Results and discussion

3.1. TPSR over NiO and Ni^0 catalysts

3.1.1. CH_4-TPSR over NiO

Figure 1 shows the response of CH_4-TPSR over the NiO catalyst. It can be seen that CH_4 began to be consumed at 510 °C, and simultaneously, small amounts of CO_2, CO, and H_2O were detected, then a large amount of H_2 was produced. These results revealed that NiO was first reduced to Ni^0 by CH_4, then CH_4 dissociation took place over Ni^0 sites to generate H_2, and simultaneously, surface C species were deposited over the Ni^0 active sites following the dissociation of CH_4. Subsequently, active atomic hydrogen and H_2 also reduce NiO followed by H_2O production. CH_4 conversion and H_2 generation reached a maximum at 570 °C, and then declined gradually because of the occupancy of active Ni^0 sites by surface C species.

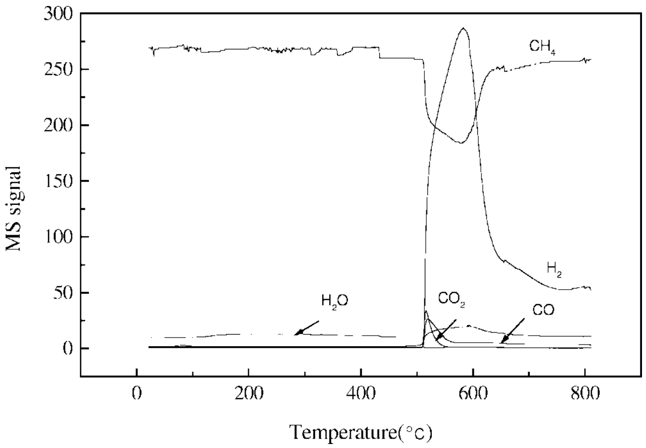

Figure 1. CH_4-TPSR spectra for NiO catalyst.

The interaction of CH_4 with NiO can be represented by the following steps:

$$CH_4 + NiO \rightarrow CO_2 + CO + H_2O + Ni^0 \quad (T \geqslant 510\,°C)$$
$$CH_4 + Ni^0 \rightarrow Ni \cdots C + H$$
$$2H \rightarrow H_2$$
$$2H + NiO \rightarrow Ni^0 + H_2O$$
$$H_2 + NiO \rightarrow Ni^0 + H_2O$$

3.1.2. CH_4/O_2-TPSR over NiO and Ni^0 catalysts

Figure 2 shows the responses of CH_4/O_2-TPSR over the NiO catalyst. One can see that CH_4 and O_2 began to be consumed at 450 °C, and then CO_2 and H_2O were detected. With increase in temperature, CH_4 and O_2 conversion increased as well as the amount of H_2O and CO_2, but no H_2 was detected, which indicated that only the complete oxidation of CH_4 took place over the NiO catalyst. At 770 °C, O_2 achieved complete conversion, and CH_4 conversion was 25%, which is in agreement with the complete oxidation reaction of CH_4 under a CH_4/O_2 ratio of 1/2, and subsequently, a small amount of H_2 was detected. By comparing with the results in figure 1, it can be seen that only at $T > 770$ °C could NiO be reduced to Ni^0 by CH_4 during the CH_4/O_2 reaction. Dissanayake [11] also found that the POM could initiate on oxidized nickel catalyst at 750 °C, and Ni was mainly in the form of the oxidic Ni before the POM initiated. Also, Ni was mainly in the form of reduced Ni after POM took place.

The response of CH_4/O_2-TPSR over the Ni^0 catalyst is shown in figure 3. One can see that O_2 began to be consumed at ca. 300 °C, and subsequently CH_4 conversion began. CO_2 and H_2O responses were then detected. It can be inferred that Ni^0 was oxidized to NiO, and subsequently, the deep oxidation of CH_4 took place over NiO. Jin also found a transformation of Ni valence during the CH_4/O_2 reaction on

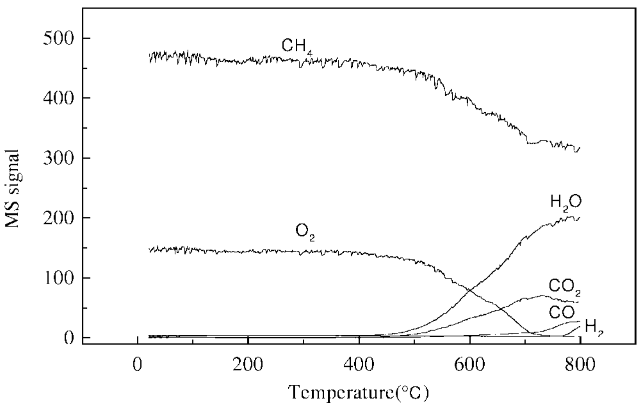

Figure 2. CH_4/O_2-TPSR spectra for NiO catalyst.

$Ni/\alpha\text{-}Al_2O_3$ [12]. Only at $T > 760\,^\circ C$ was a small amount of H_2 detected. The results indicated that Ni^0 was first oxidized to NiO at lower temperature during the CH_4/O_2 reaction, and therefore, the starting behavior for POM on the Ni^0 catalyst was actually almost identical to that on NiO.

The reaction of CH_4 with O_2 over the Ni^0 catalyst can be represented by the following steps:

$$\begin{aligned}
&Ni^0 + O_2 \rightarrow NiO\\
&CH_4 + O_2 \rightarrow CO_2 + H_2O \quad \text{(over NiO)}\\
&CH_4 + NiO \rightarrow CO_2 + CO + H_2O + Ni^0\\
&CH_4 + Ni^0 \rightarrow Ni \cdots C + H\\
&2H \rightarrow H_2\\
&O_2 + Ni^0 \rightarrow Ni \cdots O\\
&Ni \cdots C + Ni \cdots O \rightarrow Ni^0 + CO
\end{aligned}$$

3.2. TPSR over the Pt–NiO catalyst

3.2.1. CH_4-TPSR

Figure 4 shows the responses of CH_4-TPSR over the Pt–NiO catalyst. It can be seen that CH_4 began to be consumed at 400 °C, and simultaneously small amounts of CO_2, CO, and H_2O were produced followed by the production of H_2. The production of H_2 in CH_4-TPSR on the Pt–NiO catalyst was in two fractions. Besides the H_2 production peak between 500 and 600 °C which was also present on the NiO catalyst, a new H_2 production peak was observed between 400 and 500 °C. Correlated with the H_2-TPR results in figure 5, one can see that only at $T > 500\,^\circ C$ could NiO be reduced by H_2 on the NiO catalyst. As to the Pt–NiO catalyst, besides the H_2 consumption peak at $T > 500\,^\circ C$, an additional H_2 consumption peak appeared at ~450 °C (the H_2 consumption peak at 300 °C is attributed to the reduction of oxidic Pt), which is in agreement with the H_2 production peak in CH_4-TPSR on the Pt–NiO catalyst. The results showed that the addition of Pt was beneficial for the reduction of oxidic Ni.

3.2.2. CH_4/O_2-TPSR

Figure 6 shows the responses of CH_4/O_2-TPSR over a Pt–NiO catalyst. It can be seen that a transient process was observed at 526 °C, then CH_4 and O_2 conversion steeply increased, and simultaneously, large amounts of H_2 and CO were produced, which indicated that POM initiated on the Pt–NiO catalyst.

Choudhary [13] reported that the addition of Pt into $NiAl_2O_4$ could reduce the starting temperature for POM. They supposed that the active H atoms from the dissocia-

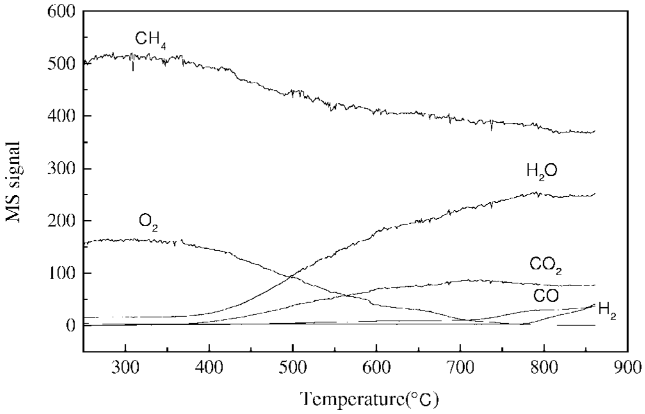

Figure 3. CH_4/O_2-TPSR spectra for Ni^0 catalyst.

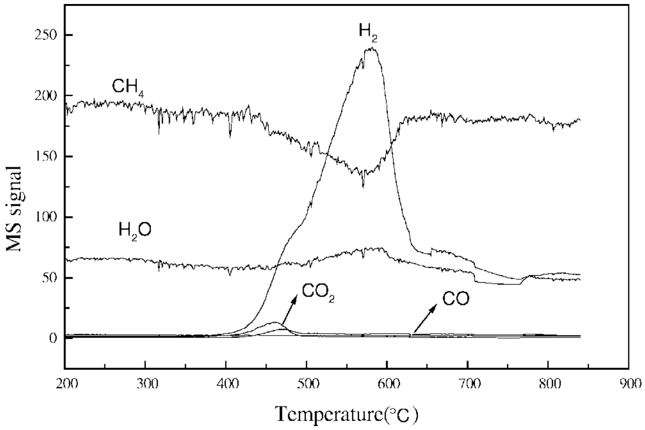

Figure 4. CH_4-TPSR spectra for Pt–NiO catalyst.

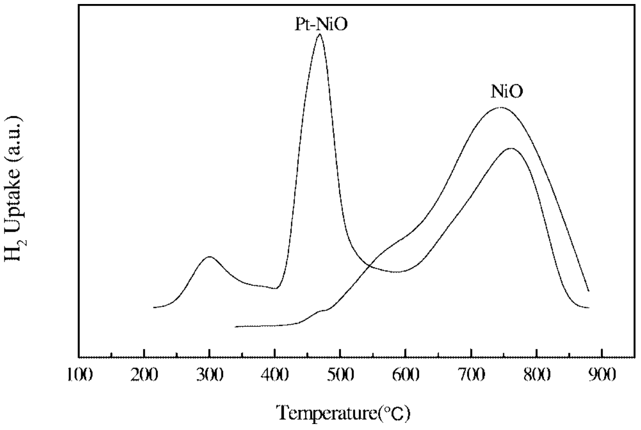

Figure 5. H_2-TPR spectra for NiO and Pt–NiO catalysts.

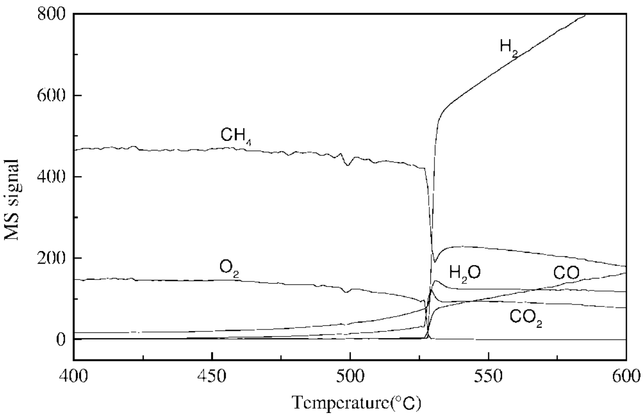

Figure 6. CH_4/O_2-TPSR spectra for Pt–NiO catalyst.

Table 1
Comparison of the starting temperature and catalytic performance for POM.

Catalyst	Starting temp. (°C)	T react. (°C)	CH_4 conv. (%)	CO sel. (%)	H_2 sel. (%)
Ni^{0} [a]	700	600	62.1	64.6	85.1
		700	77.4	83.0	92.0
		800	92.3	93.4	97.5
Pt–NiO	500	600	62.0	65.1	86.9
		700	78.8	84.5	94.6
		800	91.8	94.3	98.4
Pt	500	700	27.9	13.3	17.1

[a] Ni^0: NiO was reduced in H_2 at 700 °C for 0.5 h, then $CH_4 + O_2$ was switched into the reacting system at 700 °C.

tion of CH_4 on Pt^0 spilled over from Pt^0 to $NiAl_2O_4$, and reduced the $NiAl_2O_4$ to Ni^0 there. Oxidic Pt was first reduced by CH_4 during the CH_4/O_2 reaction, and once Pt^0 was present, the activation of CH_4 began on Pt^0. Then the active H atoms from the dissociation of CH_4 spilled over from Pt^0 to NiO and reduced NiO to Ni^0 there. Therefore the addition of Pt was helpful to the reduction of NiO. Once Ni^0 appeared, CH_4 and O_2 could be activated on Ni^0, and the active Ni···O and Ni···C intermediates reacted to produce CO, which indicated that POM initiated.

The reaction of CH_4 with O_2 over Pt–NiO catalyst can be expressed as

$$
\begin{aligned}
&CH_4 + PtO \rightarrow Pt^0 + CO_2 + H_2O\\
&CH_4 + Pt^0 \rightarrow Pt \cdots C + 4H\\
&2H + NiO \rightarrow Ni^0 + H_2O\\
&CH_4 + Ni^0 \rightarrow Ni \cdots C + 4H\\
&2H \rightarrow H_2,\ O_2 + Ni^0 \rightarrow Ni \cdots O\\
&Ni \cdots C + Ni \cdots O \rightarrow Ni^0 + CO
\end{aligned}
$$

3.3. *Comparison on the ignition process of Pt–NiO and NiO catalysts in a fluidized bed*

The experiments were carried out at a flow rate of 600 ml/min with CH_4/O_2 of 2.0. On the NiO catalyst, when the furnace temperature increased to 550 °C, the bed temperature sharply increased from ∼550 to ∼672 °C. CH_4 and O_2 conversion were ∼24 and 85.5%, respectively, and large amounts of CO_2 and H_2O were simultaneously produced which indicated that the consumption of CH_4 mainly results in the complete oxidation of CH_4. Only at >800 °C could a little H_2 be detected, so it was more difficult for POM to rapidly light off in a fluidized bed.

According to the above results from CH_4/O_2-TPSR on the Ni^0 catalyst, because the oxidation of Ni^0 to NiO by O_2 was much more rapid than the reduction of NiO to Ni^0 by CH_4 at lower temperatures, Ni^0 was first oxidized to NiO during the CH_4/O_2 reaction. However, after the NiO catalyst was pre-reduced in H_2 at 700 °C, and subsequently the CH_4 and O_2 mixture was directly switched into the reacting system at 700 °C, POM instantly initiated. This is because the O_2 oxidation was comparable with the CH_4 reduction at a higher temperature, CH_4 and O_2 were simultaneously activated on Ni^0 sites, which avoids the transformation of Ni^0 to NiO during CH_4/O_2 reaction.

As for the Pt–NiO catalyst, when the furnace temperature increased to ∼500 °C, the bed temperature sharply increased to 600 °C, 100 and >60% of O_2 and CH_4 conversions were achieved, and simultaneously, a large amount of CO and H_2 was generated, and POM started. The results in table 1 show that a bed temperature rise as high as 180 °C was observed at 500 °C over Pt catalyst, and only 27.9% of CH_4 conversion was obtained accompanying the complete conversion of O_2, and the detected products were mainly CO_2 and H_2O, which indicated that the complete oxidation of CH_4 took place over the Pt catalyst. However, after POM initiated on the Pt–NiO catalyst, the CH_4 conversion and product selectivity obtained were almost similar to that over the Ni^0 catalyst at various temperatures, which indicated that the addition of Pt could facilitate the reduction of NiO, and only Ni^0 sites were the main active sites for POM on the Pt–NiO catalyst.

4. Conclusion

The ignition processes for the catalytic partial oxidation of methane (POM) to synthesis gas over NiO, Ni^0, and Pt–NiO catalysts were studied by the temperature-programmed surface reaction (TPSR) technique. NiO and Ni^0 catalysts had almost the same ignition temperature for POM during the CH_4/O_2 reaction. However, POM could rapidly take place over the Pt–NiO catalyst at much lower temperatures. POM in a fluidized bed can be easily initiated by the addition of Pt, and almost identical catalytic performance was obtained on the Pt–NiO and Ni^0 catalysts. The addition of Pt facilitated the reduction of NiO. Ni^0 sites are the main active sites for POM on the Pt–NiO catalyst.

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