

Effects of Temperature and Time of CH₄ Decomposition on the Carbon Deposition over Ni/Al₂O₃ Catalyst^{*}

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Abstract The effects of temperature and time on the nature of carbon deposition over Ni/Al₂O₃ catalyst were investigated using an on – line quadruple mass spectrometer method. The experimental results suggested that the initial carbon species , viz. Ni_xC , produced by CH₄ decomposition over reduced Ni/Al₂O₃ , trends to diffuse into the bulk at lower temperature (600/700°C) and to transform into more inactive carbon species at higher temperature (700/800°C) and longer duration. The catalyst deactivates quickly for CH₄ decomposition at higher temperature due to the blocking of active sites by immobile carbon species.

Key words Methane decomposition , Ni/Al₂O₃ catalyst , Carbon species , Diffuse , Transformation

1 Introduction

Under the reaction conditions of partial oxidation of methane (POM) , carbon deposits on the surface of Ni – based catalyst and deactivates the catalyst. It is believed that carbon deposition in POM reaction is mainly caused by the decomposition of CH₄ and Boudouard reaction of CO. Claridge *et al.* found that under the temperature typical for POM reaction (777°C)^[1] , the amount of carbon caused by CH₄ decomposition is almost 20 times that by Boudouard reaction.

In our previous work , the effects of preparation method of catalysts on the nature of carbon species , the relationship between them and the performance of POM reaction were discussed^[2]. In the present work the effects of temperature and time on the nature of carbon deposition were investigated.

2 Experimental

All the catalytic reactions were performed in a micro fixed – bed quartz reactor. 60mg 7% Ni/Al₂O₃ prepared by co – precipitation was used after pre – reduction in H₂ for 1h under ambient pressure at 700°C . The total gas flow rate was 30mL/min. An on – line quadruple mass spectrometer was used to analyze the efflux from the reactor. The experimental method and apparatus were described in detail elsewhere^[3].

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3 Results and discussion

In the first set of experiments, decomposition of CH₄ is carried out over Ni/Al₂O₃ at 600, 700 and 800 °C, respectively, and the responses of H₂ are shown in Fig. 1. CH₄ is decomposed with the generation of H₂ immediately after its contact with reduced Ni/Al₂O₃ catalyst. The formation of H₂ stops within about 200s at 700 and 800 °C, while it lasts about 1000s at 600 °C (Fig. 1 a). The amounts of H₂ formed at 600 and 700 °C are 4.6 and 1.8 times that at 800 °C, which means that the lower the reaction temperature is, the larger the amount of CH₄ can be decomposed. The increased slope of H₂ in Fig. 1b suggested that CH₄ decomposition rate increases with the raise of temperature.

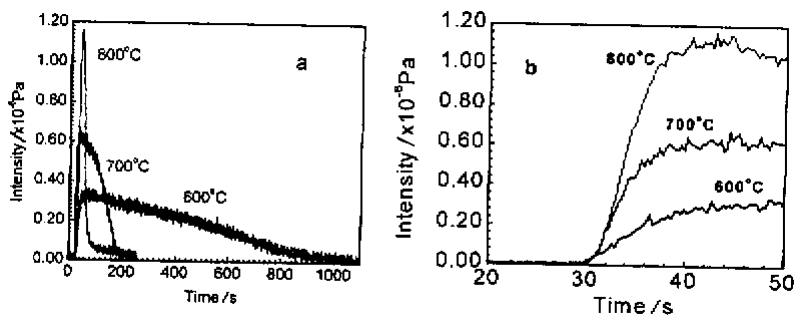


Fig. 1 H₂ responses from CH₄ decomposition at different temperatures
a. Whole process, b. the enlarged initial parts (from 20 to 50s).

The surface metallic Ni centers are active sites for the dissociation of CH₄ to H₂ and Ni_XC (X = 1 ~ 3), and Ni_XC does not catalyze the dissociation of CH₄^[4]. It is believed that hydrocarbons dissociate to produce highly reactive monoatomic carbon (C_α), which is easily oxidized to carbon monoxide. However, if an excess of C_α is formed or its oxidation reaction is slow, then there is a tendency for C_α to transfer to some much less reactive carbon species (bulk carbon or carbon whisker). This process may consist of, firstly, carbon species formation on the front surface of metal, and then dissolution and diffusion in metal, and finally deposition on the rear surface of metal^[6,7]. Poirier *et al.*^[5] reported a fast deactivation of catalyst due to the blocking of active sites on 10% Ni/Al₂O₃ at 900 °C.

From the viewpoint of thermodynamic equilibrium, the increase of temperature is conducive to the diffusion of bulk carbon to the surface and then keep on it, which decreases the surface potential energy. However, the surface carbon tends to diffuse into the bulk at lower temperature, that is, the mobility of carbon enhances when the temperature drops. It can be seen from Fig. 1 that, the higher the temperature of CH₄ decomposition, the faster the deactivation of Ni/Al₂O₃ catalyst. The reason may be that a large amount of Ni_XC is formed and can not diffuse into the bulk at such a high temperature, 800 °C, due to its inferior mobility. As a result, the surface active sites covered by carbon species can not be restored and fast deactivation is unavoidable. While at low temperature the initial surface carbon species has high mobility and can diffuse or dissolve into the bulk of catalyst, which releases the surface metallic Ni sites and allows the dissociation of CH₄ to continue.

Temperature – programmed oxidation were undertaken after CH₄ decomposition over Ni/Al₂O₃ at 600 , 700 and 800°C , respectively(Fig. 2). CO₂ is the only oxidation product on Ni/Al₂O₃ catalyst. The maximum temperatures of CO₂ peaks and relative amounts of carbon after fitting the CO₂ curve using Origin5.0 software are listed in table 1.

As shown in Fig.2 and table 1 , the oxidation of accumulated carbon on Ni/Al₂O₃ catalyst produced only two CO₂ peaks centered at about 550 and 670°C ,

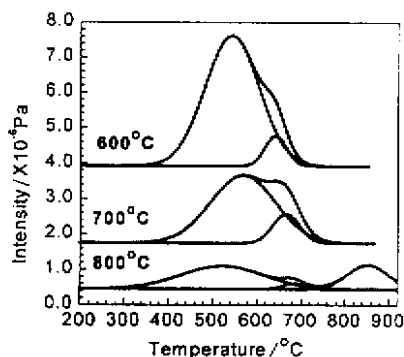


Fig. 2 TPO of carbon species formed by CH₄ decomposition at different temperatures

Table 1 Temperatures of CO₂ peaks and relative amounts of carbon

CH ₄ decompo – sition temp./°C	Temperature of CO ₂ peak/°C			Amount of carbon /10 ⁻⁵ mol			Relative amount of accumulated carbon
	1	2	3	1	2	3	
600	556	660	/	17.7	1.3	/	3.6
700	572	668	/	7.2	1.6	/	1.7
800	522	682	847	3.5	0.2	1.6	1.0

respectively , when CH₄ is decomposed at 600 and 700°C . Since these two peaks are close to each other and possess similar oxidation performance , we consider that they are associated with Ni_XC. When CH₄ is decomposed at 800°C , in addition to those two peaks , another CO₂ peak is observed at 847°C and the amount of carbon species which can be oxidized at lower temperature(Ni_XC) decreases remarkably. This result indicated that a part of Ni_XC has transferred to a kind of inert carbon species , the oxidation of which requires higher temperature. Since carbon species have low mobility and tend to aggregate at high temperature , it is reasonable to suggest that the peaks appeared over 800°C are associated with oxidation of the inert carbon species.

In the second series of experiments , TPO experiments were conducted after the decomposition of CH₄ over reduced Ni/Al₂O₃ at 700°C for 6min , 2h and 6h , respectively.

It was seen from Fig.3 that all TPO profiles have two low – temperature CO₂ peaks centered at about 550 and 670°C , respectively. In addition , only in the sample reacted for 6 h , carbon species , which needs an oxidation temperature higher than 800°C , are formed. The TPO results also revealed that the amounts of carbon have no significant difference even though the time on stream changes from 6min to 6h. The reason may be that the surface active sites are almost completely blocked after 6min CH₄ decomposition at 700°C (Fig.1) , and the relatively low mobility of carbon species prevents the further decomposition of CH₄ . The carbon species on the surface eventually aggregate when kept at this relatively high temperature for a long time. These results illustrated that the transformation of carbon to the less reactive species is facilitated by the longer duration of CH₄ decomposition.

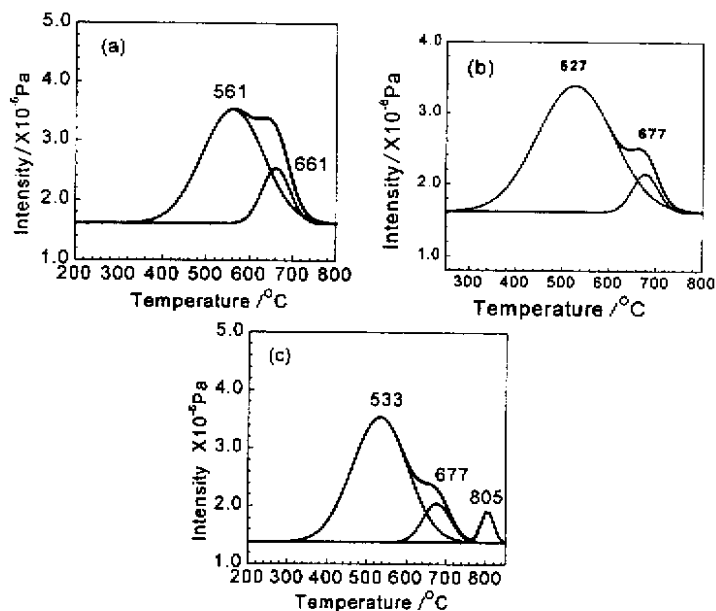


Fig. 3 TPO profiles of carbon species formed after CH₄decomposition for (a)6min ,(b)2 h ,(c)6 h at 700°C

Table 2 TPO results of different CH₄decomposition time

CH ₄ decompo - sition time	Temperature of CO ₂ peak/°C			Amount of carbon/10 ⁻⁵ mol			Relative amount of accumulated carbon
	1	2	3	1	2	3	
6min	550	660	/	7.2	1.6	/	1.0
2h	527	677	/	8.2	1.2	/	1.1
6h	534	680	805	9.3	1.2	0.9	1.3

4 Conclusion

The temperature of carbon production and the duration of its formation, i.e., the length of time for which the surface was kept at a given temperature, have strong effects on nature of the carbon species formed on the surface of Ni based catalyst. The experimental results suggested that the initial carbon species, viz. Ni_xC, produced by CH₄ decomposition over reduced Ni/Al₂O₃, can aggregate and transform into more inactive carbon species. Higher temperature and longer duration are favorable for this transformation. Carbon species possesses high mobility at lower temperature. The catalyst deactivates quickly at higher temperature due to the blocking of active sites by immobile carbon species.

Reference

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Ni/Al₂O₃催化剂上甲烷的分解温度和时间对积炭的影响*

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摘要: 用在线质谱法研究了 Ni/Al₂O₃ 催化剂上甲烷分解温度和时间对积炭的影响。实验结果表明: 在 600–800℃ 内甲烷在还原的 Ni/Al₂O₃ 催化剂上可分解为表面碳物种(即 Ni_xC)和氢气, 这种表面碳物种在较低的温度下可扩散进入体相, 在高温下可逐步转化为低活性的碳物种。在 800℃ 下由于表面碳物种不能扩散进入体相, 金属镍中心迅速被表面碳物种覆盖, 导致甲烷分解反应失活。

关键词: 甲烷分解; Ni/Al₂O₃ 催化剂; 碳物种; 扩散; 转化

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