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Effect of supports on the carbon deposition of nickel catalysts for methane reforming with CO_2

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Abstract

Five nickel catalysts on different supports were studied for methane reforming with CO_2. Although all catalysts almost reached equilibrium conversion, the content of carbon deposition differed widely from each other. The effect of supports on carbon deposition of nickel catalysts was investigated. The acid–base property of catalysts characterized by TPD and XPS was correlated with the content of carbon deposition. With the increase in base strength of catalysts the content of carbon deposition decreased.

1. Introduction

Methane reforming with steam is used extensively in industry to form synthesis gas rich in hydrogen suitable for processes such as the synthesis of ammonia or methanol. In Fischer–Tropsch reaction, however, excess H_2 suppresses chain growth and decreases the selectivity to higher hydrocarbons. CO_2 reforming produces higher CO/H_2 ratios. In addition, CO_2 reforming is more endothermic than steam reforming and accordingly can be used in storing solar energy or in transferring nuclear energy to remote areas. Nickel catalysts have a high catalytic activity for methane reforming with CO_2, but the reforming process is easily interrupted due to carbon deposition and shattering of catalysts [1]. Therefore, it is important to manage the inhibition of carbon

Table 1
Properties of catalyst and product distribution and content of carbon deposition

Catalyst[a]	Composition of support (Wt%)[b]	Surface area (m^2/g)	Product distribution (mol%)[c]				Carbon deposition (Wt%)
			CH_4	CO_2	CO	H_2	
Ni-1	S	2. 8	2. 5	5. 0	48. 8	43. 7	4. 9
Ni-2	95S+3C+2M	1. 8	2. 8	5. 7	48. 9	42. 6	3. 4
Ni-3	A	2. 9	2. 6	4. 9	48. 7	43. 8	0. 3
Ni-4	95A+5M	2. 1	2. 2	4. 2	49. 4	44. 2	1. 6
Ni-5	95A+5C	3. 0	2. 5	4. 5	49. 7	43. 3	1. 5
Equillibrium Product Distribution			2. 5	4. 5	49. 7	43. 3	

[a] Content of NiO=7-8 Wt%, content of RE_2O_3=0. 2-0. 3 Wt%

[b] S=SiO_2, C=CaO, M=MgO, A=α-Al_2O_3

[c] Product distribution of dry gas

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deposition on nickel catalysts. The objective of this study is to investigate the effect of support on carbon deposition.

2. Experimental

Catalysts were prepared by the impregnation method. The properties of the catalysts are given in Table 1. The testing of the catalysts was carried out in a fixed bed reactor at atmosphere. Catalysts were reduced in H_2 at 750°C for 1 h before adding the feed gas. All catalysts were investigated under the same operating conditions as follows: T (outlet of catalyst) = 750°C, $CO_2/CH_4 = 1.2$, SV = 6600 h^{-1}, volume of catalyst = 4 ml, particle size of catalyst = 1–2 mm, time of reaction = 4 h. Under these operating conditions, it is certain that carbon deposition on the catalysts occurs according to thermodynamic calculations [1].

3. Results and discussion

The results of catalytic activity and content of carbon deposition shown in Table 1 indicate that the CH_4 conversion on all nickel catalysts almost reaches equilibrium conversion, but the content of carbon deposition differs widely from each other. In addition, it must be pointed out that the content of NiO and Re_2O_3 for all catalysts was strictly controlled in the range in which the content of the active component had no obvious effect on the content of carbon deposition [2]. Therefore, carbon deposition mainly depends on supports.

It is evident that the content of carbon deposition of catalyst based on SiO_2(Ni-1) is higher than that of catalyst based on α-Al_2O_3(Ni-3). Addition of MgO and CaO to the SiO_2(Ni-2) decreases carbon deposition, whereas addition of MgO and CaO to an α-Al_2O_3 based catalyst (Ni-4, Ni-5) appears to increase carbon deposition.

The TPD curves of CO_2 for catalysts are presented in Fig. 1. One can easily find that all catalysts have a high peak near 180°C corresponding to weak base centers. The distributions of base sites on the Ni-2, Ni-4 and Ni-5 catalysts which contain MgO and CaO become broad, and there appear shoulder peaks at higher temperatures which correspond to strong base centers. The comparison of carbon deposition with the basicity of catalysts shows that apart from Ni-3, strong base centers are favorable for depressing carbon deposition. Compared with Ni-1, the stronger the basicity for Ni-2, the less is the carbon deposition. For Ni-4 and Ni-5, the same trend between basicity and carbon deposition is shown. The results reveal that the increase in base strength on the surfaces of catalysts can inhibit carbon deposition.

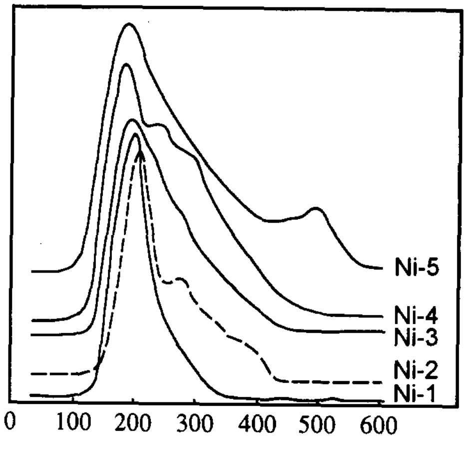

Fig. 1. TPD curves of CO_2.

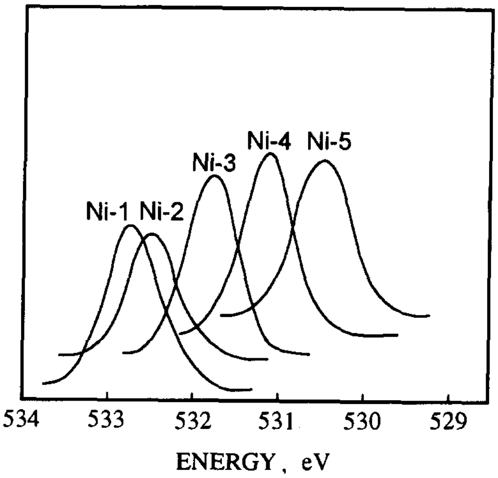

Fig. 2. O_{1s} binding energy spectra.

Table 2
Content of carbon deposition and rate of shattering

Catalyst	Ni-1	Ni-2	Ni-3	Ni-4	Ni-5
Carbon deposition (Wt%)	4.9	3.4	0.3	1.6	1.5
Rate of shattering (RS)[a]	0	0.6	7.8	56.3	35.6

[a] $RS\ (Wt\%)=\frac{\text{the weight of catalyst (particle size} <1\text{mm) after reaction}}{\text{the weight of catalyst (particle size}=1\text{-}2\text{mm) before reaction}}$

Fig. 2 shows the XPS peaks of the O_{1S} species on the surfaces of catalysts. It can be observed that the binding energy of O_{1S} decreases from Ni-1 to Ni-5, which indicates an increase in base strength on the surfaces of catalysts from Ni-1 to Ni-5 [3]. This order of basicity is in accord with that of TPD of CO_2.

The carbon formation reactions for CO_2 reforming of methane are as follows:

$$CH_4 \rightleftharpoons C+2H_2 \qquad (1)$$

$$2CO \rightleftharpoons C+CO_2 \qquad (2)$$

$$CO+H_2 \rightleftharpoons C+H_2O \qquad (3)$$

According to thermodynamical calculations, the carbon formation on catalysts is mainly caused by reactions (1) and (2). When the base strength on the surfaces of the catalysts increases, CO_2 is more easily adsorbed on the surfaces of the catalysts, which will relatively increase the concentration of CO_2 on the surfaces of the catalysts. Accordingly the equilibrium of reaction (2) will move towards the left, which will inhibit and partially remove carbon deposition on the surfaces of the catalysts.

It should be noted that the content of carbon deposition on Ni-4 and Ni-5 catalysts is more than that on Ni-3 catalyst, although the basicity on the surfaces of Ni-4 and Ni-5 is higher than that on the surfaces of Ni-3. Higher content of carbon deposition on Ni-4 and Ni-5 may be attributed to their serious shattering (Table 2). Since the process for methane reforming with CO_2 is greatly restricted by internal and external diffusion at high temperature, more micropores are exposed to an atmosphere of feed gas due to shattering of the catalyst, and molecules react easily with each other in micropores, which is accompanied by carbon deposition in micropores. This may prevent CO_2 from entering micropores. Finally, the role of removing carbon deposition of CO_2 is weakened. There maybe two factors to cause the shattering of catalyst. Firstly, $NiAl_2O_4$ is formed, accompanied with a large increase in volume which will damage the structure of crystals [1]. On the other hand, CO and CO_2 react with MgO and CaO at high temperature and under higher partial pressure of CO_2 and CO [4]. As a result, the bond structure will be destroyed.

4. Conclusion

Nickel catalysts supported on both SiO_2 and α-Al_2O_3 produced near-equilibrium conversions with high selectivity to CO for methane reforming with CO_2.

The use of SiO_2 as a support gave a high content of carbon deposition, and the addition of MgO and CaO resulted in less carbon deposition. The increase in base strength on the surfaces of catalyst appears important for depressing the formation of carbon. Catalyst supported on α-Al_2O_3 showed little carbon deposition, whereas the presence of MgO and CaO increased the formation of carbon, which might be attributed to serious shattering of the catalysts.

5. References

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