Effect of K⁺ on the performance of Ni/Al₂O₃ high temperature methanation catalyst

Dong Peng 1, Bing Wei 1, Zhengu Zhang 1, Shaodan Zhao 1, Rong Li 1, Longlong Xu 1 and Wenhua Zhang 2, *

1 Tianhua Chemical Branch, Xi’an Sunward Aeromat Co., Ltd., Xi’an, China
2 Nanchang Institute of Technology, Nanchang, China

*Corresponding author e-mail: zhangwenhua_610@163.com

Abstract. The effects of potassium ions on the properties of co-precipitation Ni/Al₂O₃ high temperature methanation catalysts were investigated. The catalysts were characterized by low temperature nitrogen adsorption (BET), X-ray diffraction (XRD), and hydrogen programmed reduction (H₂-TPR). Activity tests showed that the activity of the catalyst decreased with increasing of potassium ions, but the anti-carbon capacity of the catalyst increased first and then decreased. The activity deactivation is due to the decrease of specific surface area measured by BET. On this basis, the effect of kaliophilite on the performance of Ni/Al₂O₃ methanation catalyst was investigated. The results showed that the addition of kaliophilite had little effect on the specific surface area and activity of the catalyst, but could significantly improve the anti-carbon capacity of the catalyst.

1. Introduction

Due to the relative shortage of natural gas resources in China, the demand for natural gas in China will increase from 170 billion m³ to 200 billion m³ from 2015 to 2020, and the gap of natural gas will increase from 65 billion m³ to about 100 billion m³[1]. Thus, producing natural gas from relatively abundant and cheap coal resources has developed rapidly in recent years in China [2, 3]. But the required high temperature methanation catalyst still needs to be imported. Therefore, it is an urgent task to develop high effect methanation catalysts for large-scale industrial application in China [4].

Literature investigation revealed that Ru [5], Ni [6], Co [7] and Fe [8] are effective methanation catalysts. Among them, Ni-based catalysts are relatively inexpensive, having high CO methanation activity and high CH₄ selectivity. The Al₂O₃ carrier not only has high strength and large specific surface, but also has moderate acidity and alkalinity on the surface, moderate interaction with active components, and is an excellent high-temperature methanation catalyst carrier. Therefore, the most commonly used high temperature methanation catalyst is Ni/ Al₂O₃. Methanation reaction is a strong exothermic reaction, the temperature in the methanation reactor can reach up to 700°C [9]. Carbon deposition is easy to occur at high temperature, resulting in deactivation of the catalyst [10-12]. Therefore, improvement of the anti-carbon deposition of Ni/Al₂O₃ catalyst is important for industrial application.

In this study, a K-Ni/Al₂O₃ catalyst was prepared (NiO content: 50%, K₂O content: 0~3%) to investigate the effect of potassium ions on the performance of the Ni/Al₂O₃ methanation catalyst, and
further investigate effect of potassium mineral kaliophilite on the performance of Ni/Al$_2$O$_3$ methanation catalyst.

2. Experiment

2.1. Catalyst preparation
Kaliophilite was prepared as a self-made sample according to literature [13]. The reagents used in this paper are all analytical pure and purchased from Tianjin Tianli chemical reagent co., LTD.

Preparation of K$^+$ containing catalyst sample: Prepare 0.3 mol/L potassium carbonate solution, start stirring, heat up to 80 °C. Dissolve needed amount of aluminum nitrate and nickel nitrate (total cationic concentration is 0.8 mol/L) in water and slowly add it to the sodium carbonate solution. After that, the mixture was stirred for 30 min, filtered and dried at 120 °C, and then impregnated with an aqueous solution containing potassium carbonate. The obtained sample was then dried at 120 °C and calcined at 450 °C for 2 h. The samples were named by the content of K$_2$O. For example, if the K$_2$O content is 0.1%, the catalyst is denoted as CP-K-0.1.

Preparation of kaliophilite containing catalyst sample: Prepare 0.3 mol/L potassium carbonate solution, start stirring, heat to 80 °C. Dissolve needed amount of aluminum nitrate and nickel nitrate (total cationic concentration is 0.8 mol/L) in water and slowly add it to the sodium carbonate solution. Add kaliophilite after the addition, continue to stir 30 mins, filtered and washed, dried at 450 °C for 2 h at 120 °C. This sample is named as CP-KX.

2.2. Catalyst characterizations
The specific surface area, pore size and pore volume of the samples were examined by N$_2$ adsorption at 77 K and carried out on a JW-BK122W (Beijing Jingweigaobo, China) equipment. The pore volume and the pore size were calculated using the Barrett-Joyner-Halenda (BJH) formula. X-ray powder diffraction (XRD) was performed on D8 X-ray diffractometer equipment with Cu Kα radiation, λ = 1.54060 Å. The redox property of the catalysts was studied by hydrogen temperature programmed reduction (TPR) on a TP-5080 adsorption instrument (TianJinXianQuan Co., China, gas composition: H$_2$ (3 mL/min) and N$_2$ (27 mL/min), heating rate: 10 °C/min).

2.3. Catalytic testing
Active test for methanation reaction was conducted at 200 - 600 °C in a fixed-bed reactor at atmospheric pressure. A quartz tube with inner diameter of 3 mm was used as the reactor. Before the catalytic performance evaluation, the sample was reduced at 550 °C for 2 h under a gas flow containing 10% H$_2$ and 90% N$_2$. After that the following testing conditions were applied: 50 mg catalyst; feed gas (5.0 L/h) contains 60 mol% H$_2$, 20 mol% CO and 20 mol% N$_2$. The product passed through a cold trap to condense water. The gas composition of effluent dry gas was analyzed by gas chromatography (SP-7890, Shandong Lunanruihong, China)

3. Results and discussion

3.1. Catalyst characterization results

3.1.1. N$_2$ adsorption. The specific surface, pore size and pore volume results of the prepared samples are shown in Table 1. It can be seen from the table that CP-K-0 possessed largest specific surface, and the value gradually decreased with increase of potassium content. When the potassium content reaches 3.0%, the specific surface area reduced to 80 m$^2$/g, while the corresponding pore size gradually increases from 4.2 nm to 10.5 nm. The CP-KX sample has almost the same data compared with CP-K-0, indicating that the addition of kaliophilite has no effect on the stucture of Ni/Al$_2$O$_3$ methanation catalysts.
Table 1. BET test results of the potassium-containing catalyst samples prepared

| Catalyst | Specific surface (m²/g) | Pore size (nm) | Pore volume (cm³/g) |
|----------|-------------------------|----------------|---------------------|
| CP-K-0   | 180                     | 4.2            | 0.33                |
| CP-K-0.3 | 171                     | 4.3            | 0.31                |
| CP-K-0.6 | 156                     | 5.2            | 0.30                |
| CP-K-1   | 144                     | 6.7            | 0.31                |
| CP-K-2   | 102                     | 9.6            | 0.30                |
| CP-K-3   | 80                      | 10.5           | 0.29                |
| CP-KX    | 177                     | 4.2            | 0.32                |

Figure 1. XRD patterns of the prepared catalysts.

3.1.2. XRD. It can be seen from the Fig. 1 that only the diffraction peak of NiO appears in the catalysts, indicating that most of the catalyst is amorphous, and the catalyst dispersion is high. With the increase of potassium content, the intensity of the peaks of NiO gradually increases, indicating that the addition of potassium ions will lead to the growth of NiO grains. As a result, the specific surface area of the catalysts decreased, which is consistent with N₂ adsorption.

3.1.3. TPR. As can be seen from Fig. 2, the prepared samples have two reduction peaks at 200 - 400 °C and 450-800 °C, which correspond to the reduction of free NiO particles and NiO having strong interaction with carrier, respectively [14]. With the increase of potassium ion content, the peak at low temperature increases, indicating that the free NiO content in the catalyst increased. With the increase of potassium content, the initial reduction temperature (IF) of the peak at high temperature increased firstly and then decreased. The IF of CP-KX and CP-K-0 samples was about 450 °C, of CP-K-1 was 490 °C and of CP-KX-3 was 450 °C. The results showed that K⁺ can adjust the interaction force between NiO and the carrier, thus changing the carbon deposition resistance of the catalyst.
3.2. Experimental results of methanation activity

It can be seen from Fig. 3 that K⁺ has a large influence on the activity of the catalyst, the activity of the catalyst at low temperature remarkably decreased, especially when K₂O content exceeds 1%. But at above 350°C, all prepared samples had a high CO conversion rate, close to 100%. With a further increase in temperature, CO conversion decreased due to thermodynamic equilibrium limitations. The addition of kaliophilite did not decrease the activity.

A long-term life test was carried out at 600°C. The investigation of the anti-carbon deposition ability of the catalyst is mainly determined by the following methods: The following two indicators are mainly used for comparison: one is the bed resistance of the reactor during the reaction process; the other is the carbon deposition amount of the catalyst after the reaction. The measurement method of carbon deposition is: the reducing catalyst is oxidized by air at 200 °C after reaction, and then the mass of the reaction tube is measured, the carbon deposition amount is the difference between the mass and the initial mass. The bed resistance is shown in Fig. 4 and the amount of carbon deposition is shown in Fig. 5.

![Figure 2. TPR profiles of the prepared catalysts.](image1)

![Figure 3. Results of methanation activity of the prepared catalysts.](image2)
It can be seen from Fig. 4 that the bed resistance rises rapidly for CP-K-0. After 100 h, the bed resistance reaches 90 kPa, and the carbon deposition amount is 120 mg. The anti-carbon deposition ability of the catalysts increased obviously with K\(^+\) added in when K\(_2\)O content is less than 0.6%. After the continuous operation for 100 h, the bed resistance of CP-K-0.6 only increased 3 kPa and the carbon deposition amount is 20 mg. However, with further increasing of K\(^+\), the anti-carbon deposition ability of the catalysts decreased. The bed resistance of CP-K-2 reached up to 90 kPa after 50 h running and CP-K-3 for 30 h running. Combined with the TPR result, it can be inferred that the weak anti-carbon deposition ability of CP-K-2 and CP-K-3 samples is due to the formation of free NiO, which are strong carbon deposit centers after reduction. CP-KX sample has excellent anti-carbon deposition as good as CP-K-0.6. The reason is that kaliophilite can release K\(^+\) at high temperatures. Compared with impregnated potassium carbonate, the method of adding kaliophilite have many advantages, such as the simple process and the low cost. It is also the fact that K\(^+\) is not easily lost during use, and the anti-carbon deposition ability can be maintained for a long time by adding kaliophilite to Ni/Al\(_2\)O\(_3\) methanation catalysts.

![Figure 4. Bed pressure drop during the long-term life test of the prepared catalyst sample.](image-url)

![Figure 5. The carbon content of the prepared catalyst sample during heat resistance (CP-K-2 and CP-K-3 samples stop reacting after the bed resistance reaches 90 KPa).](image-url)
4. Conclusion
In this paper, potassium carbonate was used as the potassium source to investigate the effect of potassium ion on the performance of co-precipitated Ni/Al$_2$O$_3$ high temperature methanation catalyst. The methanation tests showed that K$^+$ had significant impact on the performance of the catalyst. N$_2$ adsorption tests indicated that the specific surface area of the catalyst gradually decreased with the increase of K$^+$. XRD results revealed that K$^+$ can cause the growth of NiO particles. TPR tests indicates K$^+$ can increase the content of free NiO and can adjust the interaction force between NiO and the carrier. Catalytic performance showed that the activity of the catalyst at low temperature decreased with the increase of K$^+$. The reason is that the size of reduced Ni microcrystalline, which is the active center in the methanation reaction, was increased by the addition of K$^+$. The anti-carbon deposition ability of the catalysts increased firstly and then decreased with the addition of K$^+$. The addition of kaliophilite has little effect on the surface area and activity of the catalyst, but it can significantly improve the anti-carbon deposition ability of the catalyst. The reason was that kaliophilite can slowly release potassium ions at high temperature. This study shows that the Ni/Al$_2$O$_3$ high-temperature methanation catalyst promoted by kaliophilite has excellent activity and anti-carbon deposition ability, which makes it has good prospect of industrial application.

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