Methanation Catalyst for Low CO Concentration

Hong-fang Ma, Cong-yi He, Hai-tao Zhang, Wei-yong Ying, Ding-ye Fang

***Abstract*—**A Ni-based catalyst supported by γ-Al_2O_3 was prepared by impregnation method, and the catalyst was used in a low CO and CO_2 concentration methanation system. The effect of temperature, pressure and space velocity on the methanation reaction was investigated in an experimental fixed-bed reactor. The methanation reaction was operated at the conditions of 190-240°C, 3000-24000ml•g^{-1}•h^{-1} and 1.5-3.5MPa. The results show that temperature and space velocity play important role on the reaction. With the increase of reaction temperature the CO and CO_2 conversion increase and the selectivity of CH_4 increase. And with the increase of the space velocity the conversion of CO and CO_2 and the selectivity of CH_4 decrease sharply.

***Keywords*—**Coke oven gas, methanation, catalyst, fixed-bed.

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I. Introduction

METHANATION reaction between carbon oxides and hydrogen over nickel catalysts to produce methane was firstly reported by Sabatier and Senderens in 1902[1]. Since then, it has been widely used in many processes, including purification of gas in ammonia synthesis and hydrogen production [2], [3]. The interest to the reaction as a promising route to produce synthetic natural gas (SNG) has remarkably grown during the last few years. Recently, a great deal of work has been directed towards SNG production by gasification of the coal or biomass to synthesis gas and subsequent methanation of the synthesis gas to SNG [4]-[6]. This route can improve the security of energy supply and reduce the emission of green house gas [7].

Extensive studies have been conducted on several metal based catalytic systems using Ni [8]-[11], Ru [12]-[14], Co [15] and Fe [16] on various oxide supports ($A1_2O_3$ [9], [17], SiO_2 [18], [19], ZrO_2 [20], [21] and TiO_2 [22]). Ni-based catalysts were most extensively studied because of its high activity and selectivity for methane formation as well as its low cost [23], [24].

Coke oven gas is the tail gas of coke industry product, and its major partsare H_2 and CH_4 which would make large pollution if it was vented in the air directly. In industry, the coke oven gas was burned as fuel, which would increase the amount of CO_2 in air and make big waste of nature resource. Coke oven gas methanation reaction can turn the CO and CO_2 into CH_4 which can be used as town gas for normal life, and it has a nice market and social effect.

A kind of catalyst for methanation from coke oven gas was prepared and tested in this paper. The BET and XRD were used for catalyst characterization, and the reaction performance of catalyst was investigated in lab, which can provide the basis for industrial use of this kind of catalyst.

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II. Experiment

A. Preparation of Catalyst

The Ni-based catalyst used in the experiment was prepared by the impregnation method using $Ni(NO_3)_2•6H_2O$ and γ-Al_2O_3. After impregnation at 60°C for 12h, the samples were dried at 120°C for 12h and calcined in static air at 550 for 6h. The surface structure was shown in Figs. 1 & 2.

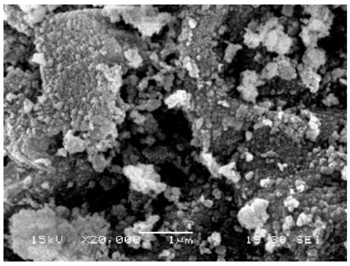

Fig. 1 SEM Diagram

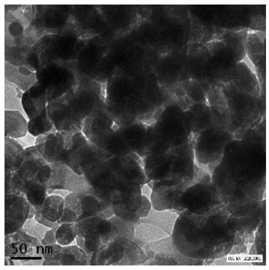

Fig. 2 TEM Diagram

Nitrogen adsorption-desorption isotherms were obtained with a Micrometrics ASAP 2020 device. Prior to N_2 adsorption, the samples were degassed at 200°C for 4h. Specific surface areas were measured by the multipoint Brunauer-Emmet-Teller (BET) method. Total pore volume and sizes were evaluated using the standare Barrett-Joyner-Halenda (BJH) treatment. The results of the treatment are shown as Table I, Fig. 3 and Fig. 4 separately. The BET treatment results are shown in Table I, the pore size distribution is shown as Fig. 3 and the adsorption & desorption curve is shown as Fig. 4.

Power X-ray diffraction (XRD) patterns were recorded on a

Rigaku D/Max 2550 using Cu Kα radiation at 40kV and 100mA. XRD patterns were recorded over a 2θ from 10°-80° and a step size of 0.02°. The results of XRD are shown as Fig. 5.

From Fig. 5, it could be known that in the prepared catalyst, the Ni is survived as NiO and $NiAl_2O_4$.

TABLE I
THE TEXTURE OF THE SUPPORTED CATALYST

	Surface Area M^3/G	Pore Volume cm^3/g	Pore Size nm
Al_2O_3	104.47	0.464	17.72
24Ni-Al_2O_3	78.77	0.313	15.89

24Ni-Al_2O_3 means the loading of Ni on Al_2O_3 is 24 wt. %.

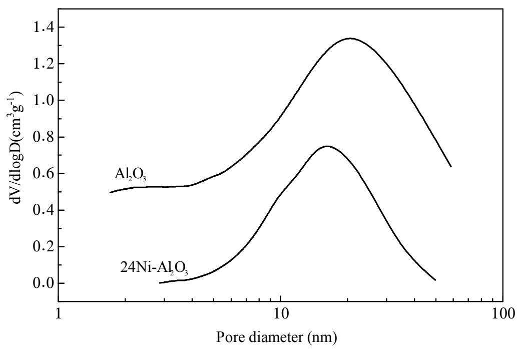

Fig. 3 The pore size distribution curve

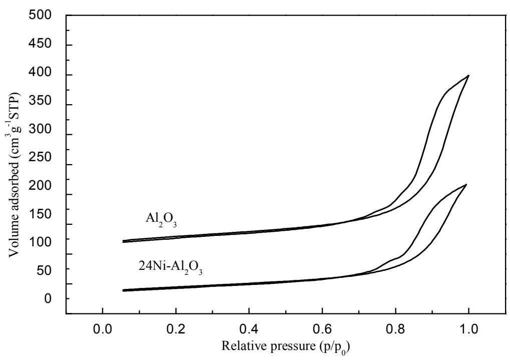

Fig. 4 The adsorption & desorption curve

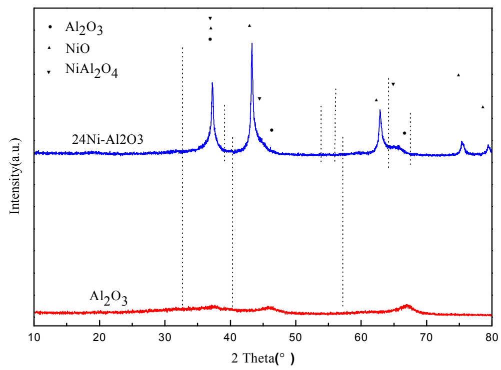

Fig. 5 The results of XRD

B. Performance Test

In order to investigate the performance of the catalyst, the experiment was carried out in a fix bed reactor in lab. The composition of the feed gas of the experiment was similar with the industrial feed gas which was: CO 3.28%, CO_2 3.53%, CH_4 38.76%, H_2 37.60%, and the rest was N_2. The H/C rate of the synthesis gas used in the experiment was 5.523.

Fig. 6 demonstrates the experimental fixed-bed reactor system used in the experiment. N_2 (1) was used to clean the system and protect the catalyst. H_2 (2) was used for the reduction of the Ni-based catalyst. The mass flowmeter (5) controls the space velocity during the reaction. The methanation is reacting in the fixed-bed reactor (7) and the product go through the condensor (8) and gas-liquid separator (9) to remove the water and the removed water is collected in the liquid collector(10). The counterbalance valve (11) is used to control the pressure in the system. The rate of the product flow is measured by the soap film flowmeter (12).

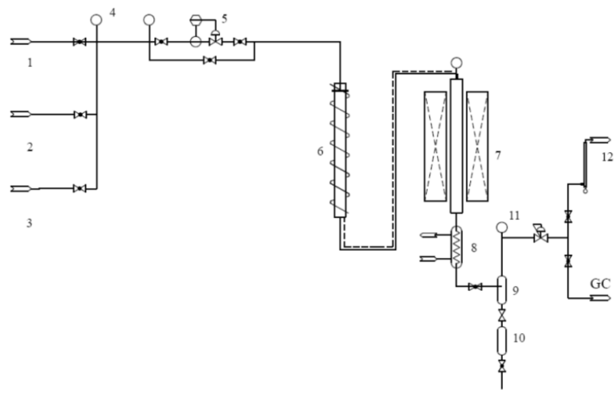

Fig. 6 The experimental flow sheet
1-N_2; 2-H_2; 3-Synthesis gas; 4- Pressure Gauge; 5- Mass flowmeter; 6-Cleaner; 7-Fixed-bed reactor; 8-Condensor; 9- Gas-liquid separator; 10-Liquid collector; 11- Counterbalance valve; 12- Soap film flowmeter

The experiment was carried out under the conditions as follow: temperature ranged from 190 to 240°C, space velocity ranged from 3000-24000ml•g^{-1}•h^{-1},and pressure ranged from 1.5-3.5MPa.

Because water is the only liquid product, only the gas product was analyzed in the GC (Agilent 7890A).

III. Effect of Operating Condition

A. Effect of Temperature

The effect of operating temperature was investigated when the temperature ranged from 190-240°C, and the pressure was 2.0MPa, the space velocity was 6000ml·g^{-1}·h^{-1}.The effect on the CO and CO_2 conversions and the CH_4 selectivity is shown in Figs. 7 and 8.

Fig. 7 shows that the conversions of CO and CO_2 increase sharply with the increase of temperature. CO conversion achieves 100% above 220°C, and the CO_2 didn't react under 210°C and the conversion of CO_2 achieves 100% at 240°C. This shows the Ni-based catalyst has a high activity at low temperature.

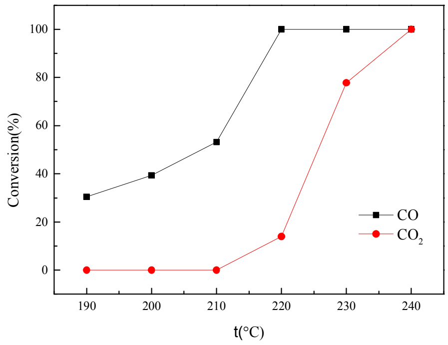

Fig. 7 Effect of temperature on conversion

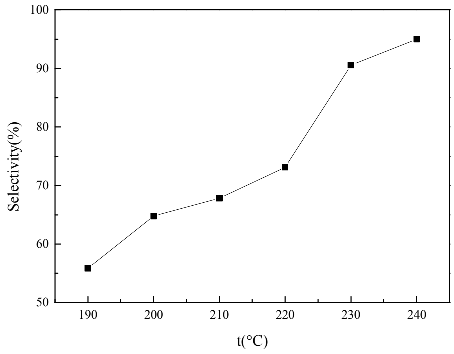

Fig. 8 Effect of temperature on the CH4 selectivity

Fig. 8 shows the effect of the temperature on the CH_4 selectivity. The CH_4 selectivity increase apparently with the increase of temperature. When operating temperature ranges from 190-240°C, the CH_4 selectivity could increase from 55-95%, so a higher temperature is conducive to the formation of CH_4.

Both Figs. 7 and 8 show that temperature plays an important role in the reaction.

B. Effect of Space Velocity

The effect of the space velocity was investigated when the space velocity ranged from 3000-24000ml•g^{-1}•h^{-1}, and the pressure was 2.0MPa, the temperature was 210°C.The effect on the CO and CO_2 conversions and the CH_4 selectivity is shown in Figs. 9 and 10.

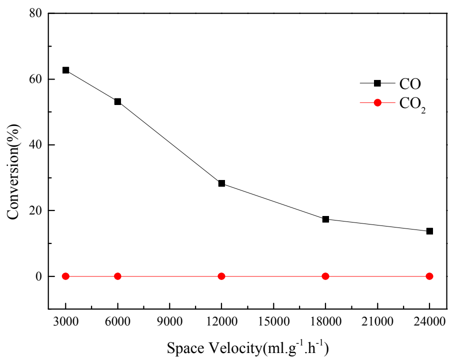

Fig. 9 Effect of space velocity on conversion

Fig. 9 shows that with the increase of space velocity, the conversion of CO decreased and because of the low temperature (210°C), the CO_2 didn't react.

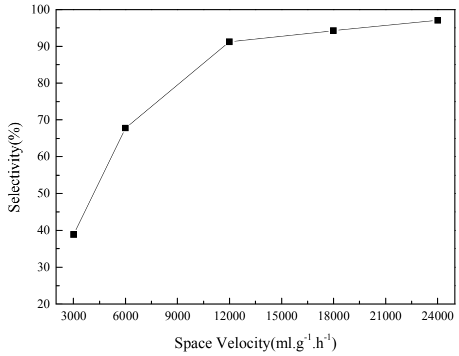

Fig. 10 Effect of space velocity on the CH4 selectivity

Fig. 10 shows that the CH_4 selectivity increases with the increase of space velocity, meaning higher space velocity is good for the formation of CH_4.

C. Effect of Pressure

The effect of the pressure was investigated as the operating temperature was 210°C and the space velocity was 6000ml•g^{-1}•h^{-1}. The effect on the CO and CO_2 conversions and the CH_4 selectivity is shown in Figs. 11 and 12.

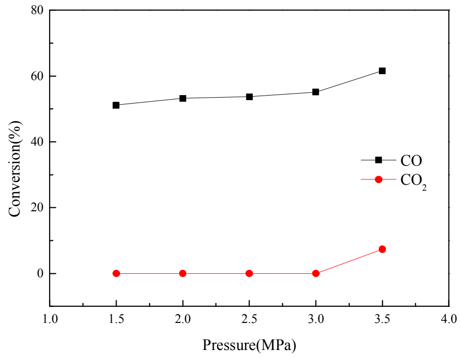

Fig. 11 Effect of pressure on the conversion

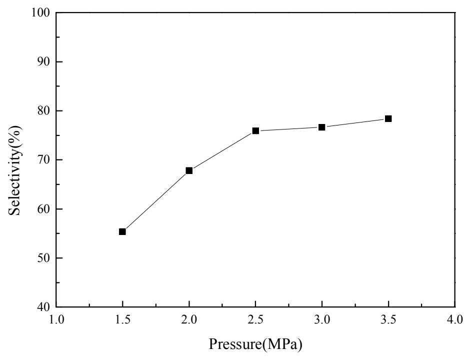

Fig. 12 Effect of pressure on the CH_4 selectivity

Fig. 11 shows that with the operating pressure increased, the CO conversion increases slightly and the CO_2 didn't react until the pressure increases to 3.5MPa, which means that the pressure affect the methanation slightly for the concentration of CO and CO_2 was low in the feed gas.

From Fig. 12, it could be known that the selectivity of CH_4 increases with the pressure increased. As we know that the methanation reaction is a volume reduction reaction, so higher pressure is more benefit for methanation than other reactions in the reactor.

IV. Conclusion

The catalyst of methanation from coke oven gas was prepared and it was characterized by BET and XRD. The results show that the catalyst has a good physical pore structure and in the catalyst, the active site of Ni is survived as NiO and $NiAl_2O_4$.

The experimental results show that the prepared catalyst has a high activity at low temperature (190-240°C). With the temperature increased the CO and CO_2 conversion and the CH_4 selectivity increased obviously which means that higher temperature is benefit for CO and CO_2methanation reaction.

Space velocity and pressure also affect the reaction a lot. The decrease of space velocity and the increase of pressure both lead to the increase of CO and CO_2 conversion, and a higher space velocity and pressure are good for the formation of CH_4.

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