



# Effect of reaction variables on CO methanation process over NiO–La<sub>2</sub>O<sub>3</sub>–MgO/Al<sub>2</sub>O<sub>3</sub> catalyst for coal to synthetic natural gas

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**Abstract** Reaction variables for methanation process were investigated using self-independently developed NiO–La<sub>2</sub>O<sub>3</sub>–MgO/Al<sub>2</sub>O<sub>3</sub> catalyst in a big lab scale reactor. The effects of reaction parameters, such as temperature, pressure, H<sub>2</sub>/CO flow ratio and space velocity on the activity of methanation catalyst were studied. 100 % CO conversion and 95 % of selectivity of methane can be achieved at 400 °C and 3 MPa with the feed ratio of H<sub>2</sub>/CO as 3.25:1 and space velocity of 12,000 h<sup>-1</sup>. The optimization reaction parameters were suggested on the basis of this work for the further development and commercialization of methanation catalyst.

**Keywords** Methanation · Carbon monoxide · Synthetic natural gas · Catalyst

## Introduction

Methanation is one of the key techniques for the coal to synthetic natural gas [1]. This technology requires catalyst with high activity and high stability due to the strong exothermicity of the methanation reaction. Currently, commercial methanation technology is being supplied by Lurgi (LURGI), Johnson Matthey (DAVY) and Topsoe (TOPSØE). All of these processes are equipped with a fixed-bed reactor [2–4]. Ni-based catalyst is often the most practical choice for methanation because of its relatively high activity and low price. NiO/Al<sub>2</sub>O<sub>3</sub> catalysts have been

intensively explored for the methanation of carbon monoxide [5].

A satisfactory methanation catalyst should be excellent, coking-resistant, and possess high thermal stability at high temperature and pressure [6–8]. The target of this work is to develop a nickel-based catalyst. It is found that the addition of lanthanum increased the catalyst stability [9]. MgO was found to be an effective promoter to improve resistance to carbon deposition and to minimize Ni particles' sintering [10–12]. In this paper, we would like to study the effect of the reaction conditions on the NiO–La<sub>2</sub>O<sub>3</sub>–MgO/Al<sub>2</sub>O<sub>3</sub> catalyst to investigate the effects of reaction variables on the methanation. Moreover, the operation parameters would be optimized for the further development and commercialization of methanation catalyst.

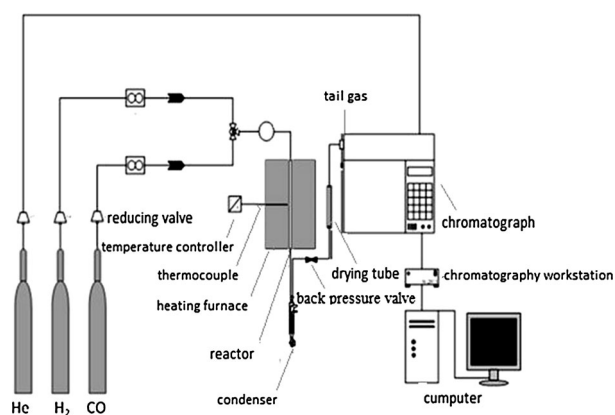
## Experimental method

### Experimental device

All the experiments were carried out with a high-temperature, high-pressure fixed-bed reactor system. The flow chart of the experimental apparatus is shown in Fig. 1. The system is composed of three parts, which are gas mixer system, reactor system and analysis system. The feed gas is decompressed by the pressure-reducing valves of different gas cylinders. The flow rate of feed gas is controlled by a mass flowmeter. After mixing, proportional synthesis gas is introduced into the high-pressure reactor. The tail gas from the reactor is cooled with 10 °C cold water trap to convert it into gas and liquid phases. Then the outlet gas filtered by dryer is connected to an Agilent GC 7890B instrument for online measurement. The liquid product collected from the

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**Fig. 1** Flow chart of the experimental apparatus

liquid collector was weighed and analyzed afterward. During the reaction, the content of all components was analyzed by GC 7890B, such as CO, CO<sub>2</sub>, H<sub>2</sub>, CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub> and C<sub>3</sub>H<sub>8</sub> by TCD and FID detectors with proper column separation. Carbon monoxide conversion ( $C_{CO}$ ), methane space–time yield ( $STY_{CH_4}$ ) and selectivity to methane ( $S_m$ ) were determined by following formulas:

$$C_{CO} = \frac{V_{CO,in} - V_{CO,out}}{V_{CO,in}} \times 100 \%$$

$$C_{H_2} = \frac{V_{H_2,in} - V_{H_2,out}}{V_{H_2,in}} \times 100 \%$$

$$STY_{CH_4} = \frac{V_{CH_4,out} \times 16 \times 60}{m_{cat} \times 22,400} \text{ (g} \cdot \text{kg}_{cat}^{-1} \cdot \text{h}^{-1}\text{)}$$

$$S_{mCH_4} = \frac{V_{CH_4,out}}{V_{CO,in} - V_{CO,out}}$$

$m_{cat}$ : Mass of the catalyst (g);  $V_{i,in}$  (ml/min) and  $V_{i,out}$  (ml/min) are the inlet and outlet volumetric flow rate of species  $i$  ( $i = \text{CO}, \text{CH}_4$ ), respectively.

### Catalyst preparation

The NiO–La<sub>2</sub>O<sub>3</sub>–MgO/Al<sub>2</sub>O<sub>3</sub> catalyst precursor was prepared using coprecipitation method at constant pH. Aqueous solutions of the metal nitrates and the precipitating agent (NaOH/Na<sub>2</sub>CO<sub>3</sub>) were simultaneously dripped into beaker. The pH during precipitation in the stirred beaker was maintained at a constant value 8. After finishing the addition of the precipitation agent, the resultant slurry was aged at 80 °C for 12 h under constant stirring, followed by filtration, washing and drying overnight at 120 °C. The catalyst precursor was calcined in a muffle burner at 450 °C for 4 h. Graphite and cement were added in the catalyst precursor for granulation and tableting, steam and curing treatment. The resultant catalyst products have NiO content of 40 wt %, MgO content of 15 wt % and La<sub>2</sub>O<sub>3</sub>

content of 5 wt %. It has relatively more meso-pores with average pore size of 9.5 nm. It was ground and meshed to 425–850 μm particles for experiments.

### Catalyst evaluation

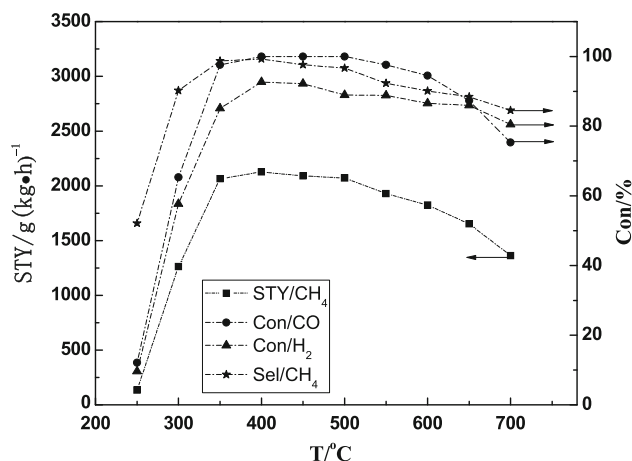
The catalyst sample was loaded into a pressurized fixed-bed reactor. Firstly, a gas stream consisting of H<sub>2</sub>:N<sub>2</sub> with ratio of 1:4 was used for NiO reduction for 4 h at temperature of 550 °C. Then, the reactor was cooled to 200 °C at the end of the reduction. The pressure of the system was slowly increased with nitrogen gas. The feed gas was switched into the reactor gradually to the required pressure. The activity of methanation catalyst was tested for reaction temperature of 250–700 °C, the reaction pressure of 1–4 MPa, the flow ratio of the H<sub>2</sub>/CO as 2:1–4:1 and the space velocity of 6000–48,000 h<sup>-1</sup>.

## Result and discussion

### Reaction temperature

Holding the reactor pressure at 1 MPa, a space velocity of 12,000 h<sup>-1</sup> and H<sub>2</sub>/CO of flow rate of 3, the effect of temperature on methanation reaction was investigated from 250 to 700 °C. The experiment results are shown in Fig. 2.

With increase of temperature, carbon monoxide and hydrogen conversion rate, selectivity and space–time yield of methane were firstly increased and then decreased gradually. When the reactor temperature reached 400 °C, the CO conversion and the H<sub>2</sub> conversion reached the highest value. This is due to the methanation reaction being an exothermic reaction; lower temperature favors the CO



**Fig. 2** CO and H<sub>2</sub> conversion, CH<sub>4</sub> selectivity, and CH<sub>4</sub> space–time yield at different temperatures at 1 MPa, H<sub>2</sub>/CO = 3,  $S_v = 12,000 \text{ h}^{-1}$

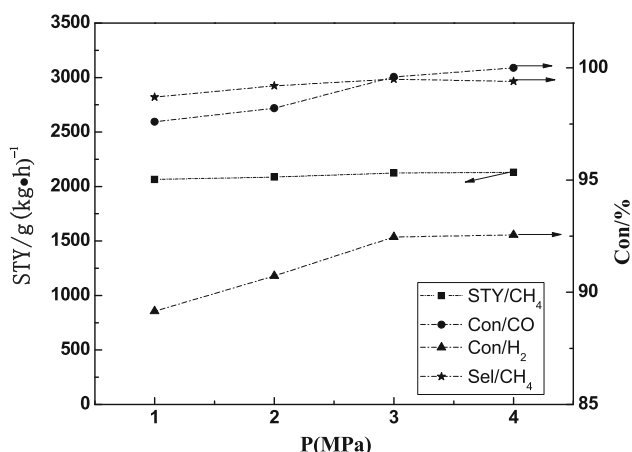
conversion [13]. When the reaction temperature increased, the equilibrium constant of the reaction rate decreased, leading to a lower CO conversion. Moreover, the methanation reaction is a reversible reaction. Methanation reaction equilibrium moves in the reverse direction at higher temperature. All this would inhibit the conversion of CO at high temperature [14].

For methanation reaction, the basic requirements for the catalyst are that it must maintain the activity at the temperatures during the normal operation, meanwhile, it should be able to start up the reaction at the possible lowest temperature so as to keep the inlet temperature as low as possible. This would relieve the thermal effects of the entire reactor bed [15]. Under our experimental conditions, the optimal temperature range is between 350 and 450 °C; methanation reached the desired CO conversion between 350 and 450 °C temperature range, which is consistent with the thermodynamic prediction of methanation by previous researchers [16, 17].

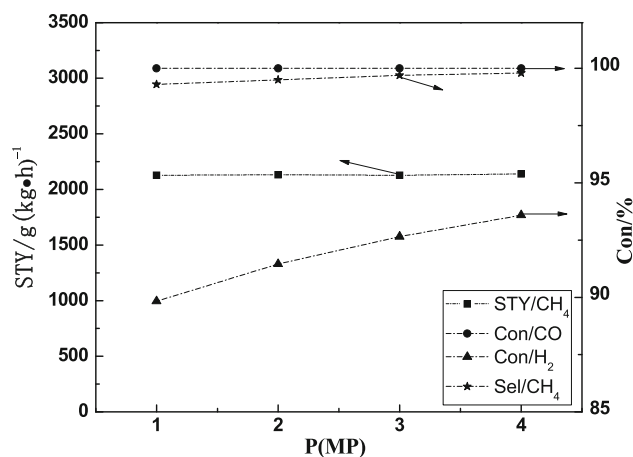
### Reaction pressure

Maintaining a temperature of 350–450 °C, a space velocity of 12,000 h<sup>-1</sup>, H<sub>2</sub>/CO ratio of flow rate of 3, the effect of pressure on methane synthesis reaction was studied from 1 to 4 MPa. The experiment results are shown in Figs. 3, 4 and 5.

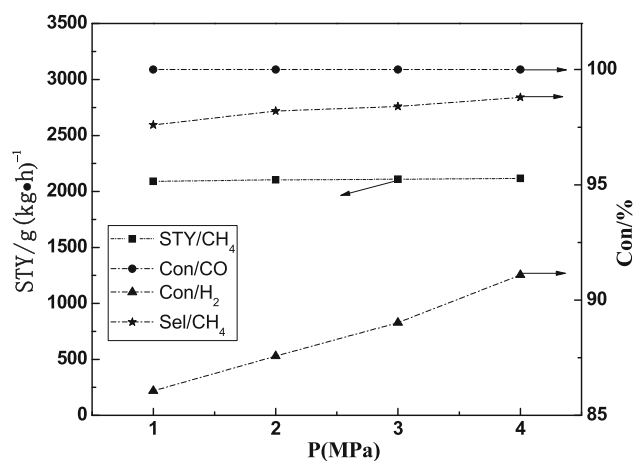
Figures 3, 4 and 5 present the change of carbon monoxide and hydrogen conversion, methane selectivity and STY at different temperatures and different pressures. When the temperature was 350 °C, the conversion rate of carbon monoxide, hydrogen and methane increased gradually with the increase of pressure, while the selectivity of methane increased and then tended to be stable. The space-time yield of methane was gradually increased with the increase of pressure as well. The carbon monoxide



**Fig. 3** CO and H<sub>2</sub> conversion, CH<sub>4</sub> selectivity, and CH<sub>4</sub> space-time yield at different pressures at 350 °C, H<sub>2</sub>/CO = 3, S<sub>V</sub> = 12,000 h<sup>-1</sup>



**Fig. 4** CO and H<sub>2</sub> conversion, CH<sub>4</sub> selectivity, and CH<sub>4</sub> space-time yield at different pressures at 400 °C, H<sub>2</sub>/CO = 3, S<sub>V</sub> = 12,000 h<sup>-1</sup>



**Fig. 5** CO and H<sub>2</sub> conversion, CH<sub>4</sub> selectivity, and CH<sub>4</sub> space-time yield at different pressures at 450 °C, H<sub>2</sub>/CO = 3, S<sub>V</sub> = 12,000 h<sup>-1</sup>

conversion rate remained at 100 % as the pressure increased, when the temperature was 400–450 °C. However, the space-time yield of methane remained constant when the temperature was 400–450 °C. According to the kinetics of the reaction, the number of moles of carbon monoxide methanation reaction is reduced; increasing of pressure is in favor of the reaction equilibrium because the reaction constant is shifted to the gas volume decreasing direction [18, 19]. The experimental data showed that the conversion of carbon monoxide can be improved at a relatively low temperature with the increase of pressure. However, the increase of pressure has little effect on the conversion of carbon monoxide when temperature is higher than 350 °C. It indicated the high pressure was not necessary for methanation reaction pressure at high temperature. When the pressure increases to a certain degree, the catalyst activity is not affected. The optimal pressure must be determined when considering the load of industrial

production and the thermodynamic effects of methanation reaction in the normal production process.

### H<sub>2</sub>/CO ratio of the syngas

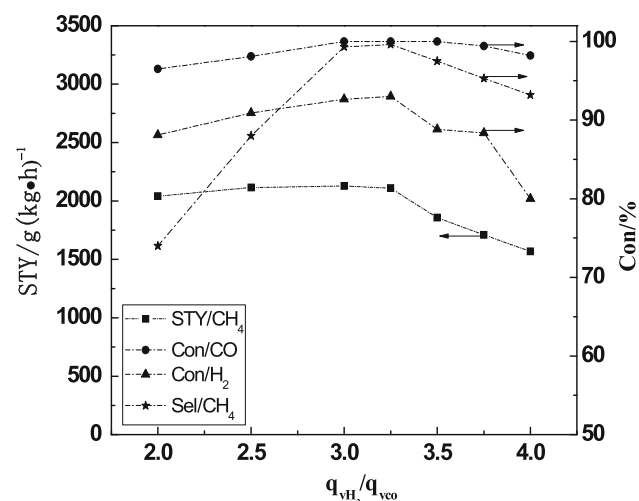
Maintaining a temperature of 400 °C, 1 MPa pressure, the effect of H<sub>2</sub>/CO ratio on methane synthesis reaction was studied at flow rate of 2:1, 2.5:1, 3:1, 3.25:1, 3.5:1, 3.75:1 and 4:1. The experiment results are shown in Fig. 6.

Figure 6 shows that the trends of methane selectivity and the space–time yield of carbon monoxide and hydrogen change with the H<sub>2</sub>/CO ratio. However, the carbon monoxide conversion rate tended to be stable at the H<sub>2</sub>/CO ratio of more than 3. The best theoretical molar ratio of the methane reaction is H<sub>2</sub>/CO flow ratio of 3:1, when the mass transfer process is not considered [20]. However, in order to avoid carbon deposition on the surface of nickel catalyst, the practical reaction condition of H<sub>2</sub>/CO ratio is usually higher than the stoichiometric ratio [21, 22]. The conversion rate of carbon monoxide and the space–time yield of methane were highest when the H<sub>2</sub>/CO ratio of the raw gas was 3.25:1, which was suggested as most suitable for the process of methane conversion.

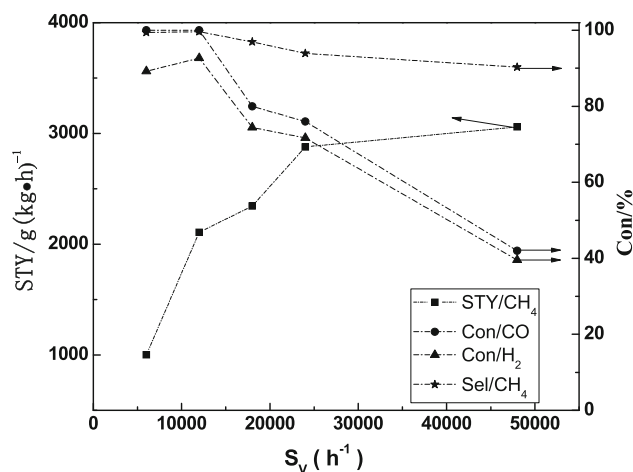
### Space velocity

Maintaining a temperature of 400 °C, 1 MPa pressure, H<sub>2</sub>/CO ratio of flow rate of 3.25:1, the effect of space velocity on methane synthesis reaction was studied at 6000, 12,000, 18,000, 24,000 and 48,000 h<sup>-1</sup> conditions. The experiment results are shown in Fig. 7.

Figure 7 shows that the conversion of carbon monoxide and hydrogen, selectivity and the space–time yield of methane are increased with the increase of space velocity.



**Fig. 6** CO and H<sub>2</sub> conversion, CH<sub>4</sub> selectivity, and CH<sub>4</sub> space–time yield at different H<sub>2</sub>/CO ratios at 400 °C, 1 MPa, S<sub>v</sub> = 12,000 h<sup>-1</sup>



**Fig. 7** CO and H<sub>2</sub> conversion, CH<sub>4</sub> selectivity, and CH<sub>4</sub> space–time yield at different space velocities at 400 °C, 1 MPa and H<sub>2</sub>/CO = 3.25

The methanation reaction activity was gradually decreased when the velocity is higher than 12,000 h<sup>-1</sup>. Then, the space–time yield of methane downward trend is more significant. This is because the contact time between the feed gas and the catalyst surface becomes shorter at high space velocity. The effective collision between reactants and feed gas is reduced, and the conversion efficiency of the methanation reaction is reduced. Production at low space velocity is beneficial to improve single pass conversion of carbon monoxide in the actual production process, but productivity of the reactor will be very low. Single pass conversion rate was lower in high space velocity operating conditions. In order to improve the utilization efficiency of the feed gas, the feed gas needs many cycles, which will increase the operation cost. Thus, a proper space velocity needs to be selected to ensure that the catalyst activity is optimal in the actual production. Our experimental results suggest that the space velocity of 12,000 h<sup>-1</sup> gives a balance of operation and productivity.

### Conclusion

In this study, the effects of the reaction variables such as temperature, pressure, H<sub>2</sub>/CO ratio of the feed and space velocity on the activity of methanation catalyst for CO methanation have been investigated. According to the experimental results, the high pressure was not necessary for methanation reaction pressure at high temperature. The optimal pressure needs to be determined when considering the load of industrial production and the thermodynamic effects of methanation reaction in the normal production process. From our experimental, the optimal temperature range is between 350 and 500 °C, the optimal H<sub>2</sub>/CO ratio

of the raw gas is 3.25:1 and the optimal space velocity is  $12,000 \text{ h}^{-1}$ . These parameters were suggested as most suitable for the process of syngas to methane conversion.

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