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CHARACTERISTICS OF METHANE REFORMING WITH HIGH TEMPERATURE DOLOMITE

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ABSTRACT

In industrial production, a large amount of high temperature waste of dolomite is generated, and it can act as heat source and produce carbon dioxide. Methane reforming is one of typical chemical energy storage reaction to obtain syngas, and it can use heat source and carbon dioxide from high temperature dolomite. In this paper, catalytic activity and methane conversion of methane reforming with high temperature dolomite were studied, and the influence of temperature and inlet reactant flow rate was further analyzed. When bed temperature rose from 950°C to 1150°C, methane conversion can increase to as high as 52%, while it decreased with reactant flow rate increasing. According to Arrhenius empirical formula, the activation energy of methane reforming with high temperature dolomite is obtained as 99.1 kJ·mol^{-1}.

Keywords: waste heat, methane reforming with carbon dioxide, chemical energy storage

1. INTRODUCTION

High temperature dolomite as slag is very rich in industrial production as steelmaking [1-2], and it has large waste heat and excellent quality. Dolomite as one kind porous stone is calcined at 900°C to 1100°C to obtain a mixture of CaO and MgO. During the decomposition process, a large amount of carbon dioxide is released, and the decomposition of per ton of dolomite produces 232.4 m^3 of CO2.

Many researchers investigated thermochemical storage using high temperature slag. Liu et al [3] used copper slag as catalyst and heat source for methane reforming with carbon dioxide. The catalytic reforming activity was investigated and the kinetic equation of copper slag waste heat catalyzing methane reforming with carbon dioxide was established. The experimental results showed that the copper slag had high catalytic activity in high temperature range. Purwanto et al. [4] studied the effect of temperature on hydrogen production in methane reforming with carbon dioxide reaction by using hot slag particles as catalyst at temperatures ranging from 973 K to 1273 K. The results showed that slag was not only a heat medium, but also was a good catalyst for promoting decomposition. Barati et al. [5] proposed a waste heat recovery method for absorbing sensible heat of blast furnace slag by methane-steam reforming reaction.

The dolomite can be used to enhance methane steam reforming reaction. Johnsen et al. [6] designed an adsorption strengthening experiment using atmospheric pressure bubbling fluidized bed reactor. The research showed that dolomite was the CO_2 acceptor at 600°C and 1.013×10^{5}Pa, and equilibrium H_2 concentration was 98% under dry conditions. Arstad et al [7] used calcined dolomite as raw material and did adsorption-enhanced steam methane reforming experiment using a chamber-scale circulating fluidized bed reactor. The excellent adsorbent with carbon dioxide separation efficiency of about 65% was found. Based on fluidization in the bed reactor, Carlo et al. [8] numerically simulated the hydrogen production reaction of adsorption enhanced steam methane reforming (SE-SMR) was d. The results showed that the volume ratio of dolomite/catalyst had an effect on the adsorption strengthening reaction.

Available literature seldom investigated methane reforming with carbon dioxide using high temperature dolomite as heat source and carbon source. In this paper, catalytic activity and methane conversion of methane reforming with high temperature dolomite were studied. The effects of temperature and reactant flow rate on the reforming reaction were further analyzed, and the kinetic equation of the reaction was calculated due to Arrhenius empirical formula.

2. EXPERIMENTAL SYSTEM

As shown in Fig. 1, methane reforming experimental system is composed of a gas storage tank, a mass flow meter, an electric heating furnace, a tubular reactor, a condenser, a data collecting instrument, a gas chromatograph and a gas pipeline. The temperature of heating furnace was controlled in real time by a temperature control system, and the instantaneous heating power of the resistance furnace was recorded. The gas collection was performed at a desired temperature point, and sample gas was collected and analyzed.

In the experiment, the dolomite-filled tubular reactor was placed in an electric heating furnace. The tubular reactor is made of quartz of 800 mm in length with an outer diameter of 30 mm and an inner diameter of 26 mm. Between 300-500 mm from the inlet of the reactor, dolomite acted as heat source and catalyst. The dolomite used in the experiment was milky white irregular crystal particles, and the internal porous structure was sieved to a diameter of 2-3 mm. The porosity of bed was 0.42, and the thermocouple was placed at the center of the catalytic bed.

The main and side reactions of methane reforming with carbon dioxide are as follows:

$$CH_4+CO_2 \leftrightarrow 2CO+2H_2,\ \ \Delta H=247\mathrm{kJ/mol} \tag{1}$$

$$CO_2+H_2 \leftrightarrow CO+H_2O,\ \ \Delta H=41\mathrm{kJ/mol} \tag{2}$$

The stepwise thermal decomposition of dolomite is as follows:

$$CaMg(CO_3)_2 = CaCO_3+MgO+CO_2,\ \ \Delta H=209.68\mathrm{kJ/mol} \tag{3}$$

$$CaCO_3 = CaO+CO_2,\ \ \Delta H=216.52\mathrm{kJ/mol} \tag{4}$$

The methane conversion is described as:

$$X_{CH_4} = \frac{\varphi_{CH_4,i}V_1 - \varphi_{CH_4,o}V_2}{\varphi_{CH_4,i}V_1} \times 100\% \tag{5}$$

where $F_{CH4,I}$ denote inlet flow of methane, mol/min.

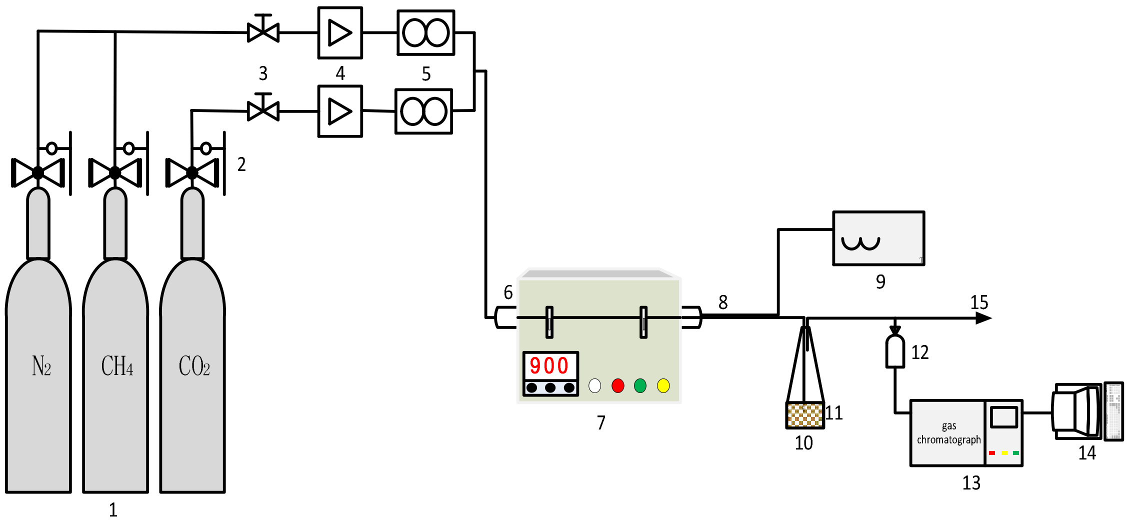

Fig.1 Schematic diagram of the experimental system
1.Nitrogen, methane and carbon dioxide cylinders, 2. Pressure reducing valve, 3. Screw valve, 4. Mass flow metre, 5. Mass flow control, 6. Tube reactor, 7. Electric heating furnace, 8. Thermocouple, 9. Data collector, 10. Gas wash bottle, 11. Molecular sieve,12. Gas sampling bag, 13. Gas chromatograph,14. Computer, 15. Exhaust gas treatment.

3. EXPERIMENTAL RESULTS

3.1 Dolomite composition change

The dolomite decomposition is divided into two stages as the temperature ranges of 680°C-810°C and 810°C-920°C [9]. In order to study the change of dolomite before and after the catalytic recombination reaction, XRD test of dolomite after 1000°C reaction. Powder x-ray diffraction analysis (XRD) slag was performed from Pannacle using an x-ray diffraction system under the following conditions: copper target, K-α radiation source, scattering slit 0.19 mm, tube voltage 40 kV, tube current 40 mA. The scanning range is 2θ=5°-80°, the scanning speed is 38 s/step, and the scanning step is 0.026°.

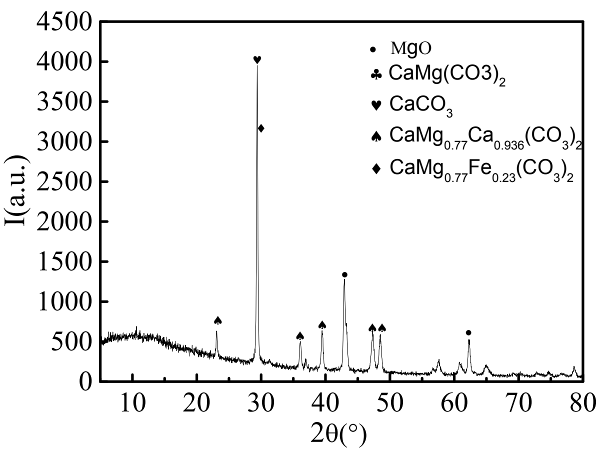

Fig.2 XRD of dolomite decomposition after methane reforming process
(CH_4:CO_2=1)

The XRD results of dolomite decomposition after methane reforming process are shown in Fig. 2. The results show that when dolomite was heated to 1000°C to catalyze the reaction of methane carbon dioxide, all of the magnesium carbonate was decomposed into magnesium oxide, and the calcium carbonate has not completely decomposed.

3.2 Methane conversion under different inlet conditions

Fig. 3 is methane conversion with different bed temperature, where molar ratio CH_4:CO_2=1. Since methane reforming with carbon dioxide is an endothermic reaction, and the reaction proceeds as the temperature increases. As bed temperature increased, the dolomite is gradually decomposed, which causes the increase of carbon dioxide in the reactor. Under the same inlet flow rate, the concentration of carbon dioxide increases, and the main reaction was promoted. In addition, the reverse reaction of water vapor shift reaction is reduced for high concentration of carbon dioxide. For the co-coupling effect of main reaction and side reaction, the methane conversion increases as the bed temperature.

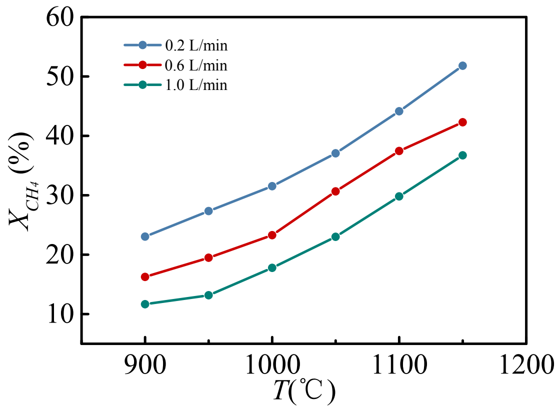

Fig. 3 Methane conversion with different bed temperature
(CH_4:CO_2=1)

Fig. 4 is methane conversion with different reactant flow rate, when the reactant molar ratio CH_4:CO_2=1. Under the same experimental conditions, the increase of reactant flow rate reduces the temperature of the catalyst bed and residence time, and then methane conversion decreases.

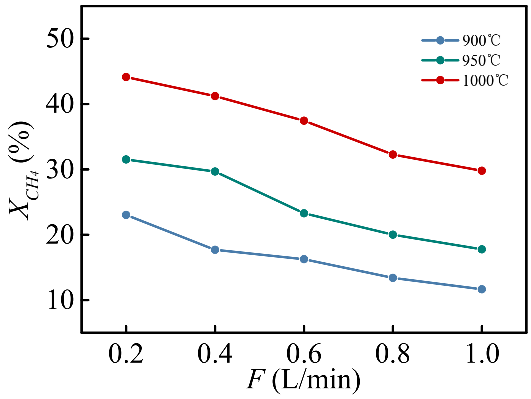

Fig. 4 Methane conversion with different inlet flow rate
(CH_4:CO_2=1)

3.3 *Kinetic analysis*

The Arrhenius empirical formula is the relationship between the rate constant of the reaction and the temperature which can be expressed as:

$$k = Ae^{-E_a/RT} \tag{6}$$

The Arrhenius empirical formula can be transformed into logarithmic form and differential form as:

$$\ln k = \ln A - \frac{E_a}{RT} \tag{7}$$

$$\frac{d \ln k}{dT} = \frac{E_a}{RT^2} \tag{8}$$

Plotting a straight line of ln*k* and 1/T, Ea and A can be obtained from the slope and intercept of the line, respectively.

The temperature dependence of methane reaction rate on slag was studied in the temperature range of 700~1050°C. The conversion rate was measured at a low feed rate (F=200 mL/min) in the micro tubular reactor with dolomite 10g. The geometry of the quartz tube is 900mm long, 20mm outer diameter and 16mm inner diameter. The relationship between reaction rate and temperature is shown in Fig. 5. According to experimental results, the activation energy E_a=99.1kJ·mol^{-1} is obtained.

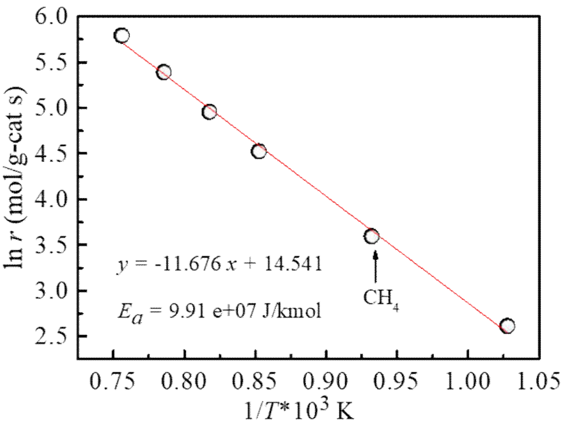

Fig. 5 Arrhenius plot of lnr versus 1/T for CH_4 (CH_4:CO_2=1)

4. CONCLUSION

In this paper, characteristics of methane reforming with carbon dioxide on high temperature dolomite, and the influence of catalyst bed temperature and inlet reactant flow rate on methane conversion were studied. The results show that dolomite can benefit methane reforming with carbon dioxide at high temperature. As the bed temperature increases, the methane conversion increases. When the inlet reactant flow rate increases, the methane conversion decreases. The kinetic equation of methane reforming with carbon dioxide on high temperature was calculated by experimental results, and the activation energy is obtained as 99.1 kJ·mol^{-1}.

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