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Article

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Dry re-forming of methane to synthesis gas over lignite semicokes catalyst at high pressure



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ABSTRACT

Dry re-forming of methane has been carried out in a high temperature–pressure reactor at different pressures, using Hongce lignite semicokes catalyst. The results show that CH₄ and CO₂ conversions are decreased as the reaction pressure increased, but both of them kept basically stable when the reaction pressure is between 0.3 and 1 MPa. The comparison shows that the effects of the temperature and the flow of reactant gas on dry re-forming of methane are consistent with between high pressure and atmospheric pressure. The ratio of CO/H₂ decreased as the ratio of CH₄/CO₂ increased, yet the value of CO/H₂ is always more than 1 at different pressures. Hongce lignite semicokes catalyst is characterized by FTIR, XRD, SEM and BET, and the analysis results revealed that the physical specific adsorption peak of CO₂ at 2350 cm^{−1} is strengthened significantly at different pressures, the micropore area and volume of Hongce lignite semicokes reduced from 40.2 m² g^{−1} and 0.019 cm³ g^{−1} to 34.9 m² g^{−1} and 0.017 cm³ g^{−1}, respectively. Hongce lignite semicokes catalyst exhibited better activity and stability within 0.3–1 MPa range.

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1. Introduction

The excess emission of greenhouse gases (such as carbon dioxide and methane) not only contribute to global warming but also cause serious environmental problem, these have become a critical issue of international community attention (Minx et al., 2011; Jotzo et al., 2012; Ashik et al., 2015). Therefore, the abatement of carbon emission and the use of carbon dioxide and methane have been a one of the most important subjects in the fields of energy and environment (Christopher and Dimitrios, 2012; Dion et al., 2011). It is widely studied and confirmed that dry re-forming of methane is an effective way for methane and carbon dioxide conversion and utilization (Fischer and Tropsch, 1923; Zhang et al., 2014; Ha et al., 2010).

Current, transition metals and precious metals catalysts have been studied for dry re-forming of methane at atmospheric pressure, but they still have major defects among which transition metals catalysts are poor stability and easier deactivation as well as precious metals catalysts are costly and these resources are finite, therefore, these will restrict industrialization process (Silva et al., 2013; Gnanamani et al., 2011; Sun et al., 2010; Guo and Zhang,

2012; Kang et al., 2013; Pan et al., 2010; Xie et al., 2013; Yao et al., 2011). Carbon material as a catalyst for dry re-forming of methane was also investigated, our groups previous work revealed that the three kinds of semicokes (Hongce lignite, Shenmu bituminous coal and Jincheng anthracite) have a significantly catalytic function for dry re-forming of methane, and the catalytic stability and activity can be enhanced evidently by activating with H₂O₂ and NH₄OH activated at high temperatures and high pressures (Guo et al., 2013, 2012, 2014). The catalytic function, the reaction parameters, the reaction mechanism and kinetics of dry re-forming of methane were widely researched at atmospheric pressure, but the relevant report was less at high pressure (Wang and Xu, 2005; Wang et al., 2005; Zhang et al., 2011).

Dry re-forming of methane was a volume increase reaction, which the increasing of reaction pressure has a passive influence on dry re-forming of methane according to thermodynamics of chemical reaction (Zhu, 2012). On the contrary, The reaction pressure comprises the reactant gas, it is beneficial for the adsorption of methane and carbon dioxide on the Hongce lignite semicokes surface, in which both methane and carbon dioxide conversions were improved further. Generally also in the industry the syngas was produced under high pressure condition. For these reasons, in order to get an optimum pressure range can meets the requirements of industrial production, dry re-forming of methane over semicokes was investigated at high pressure.

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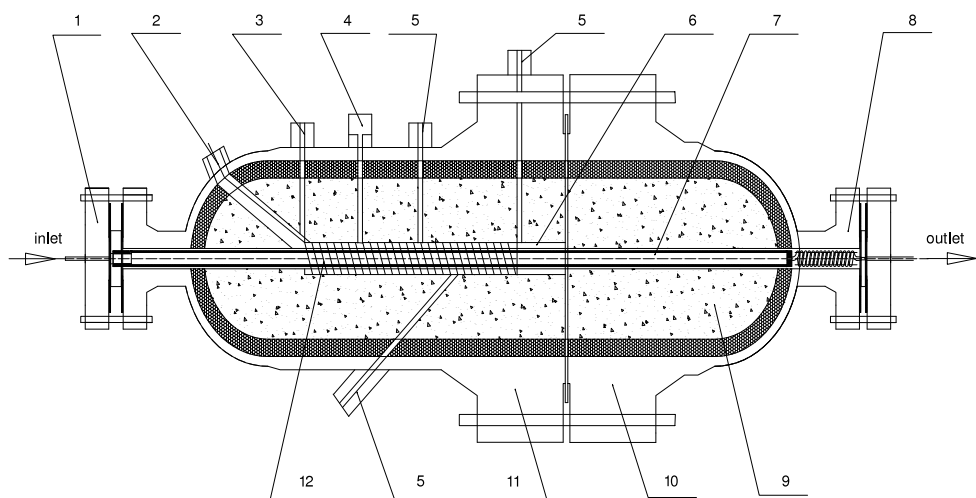


Fig. 1. Schematic diagram of high temperature–pressure reactor: (1) reactant gas (CH_4 and CO_2) inlet, (2) heating power cord, (3) under pressure gas (N_2 gas) inlet, (4) safety valve, (5) thermocouple, (6) equilibrium pressure zone, (7) stainless steel tube reactor, (8) product gas (H_2 and CO) outlet, (9) insulation layer, (10) right reactor shell, (11) left reactor shell, (12) heating apparatus.

In this paper, the high temperature–pressure reactor was designed and made according to the idea of “high temperatures zone equilibrium pressure, low temperatures zone under pressure”. The effects of reaction temperature, reaction pressure, the flow of reactant gas and the ratio of CH_4/CO_2 on catalytic activity of Hongce lignite semicokes catalyst were analyzed systematically, and the surface properties of Hongce lignite semicokes catalyst before and after reaction were extensively characterized, using: Fourier transform infrared (FTIR), X-ray diffraction (XRD), specific surface area (BET) and scanning electron microscopy (SEM).

2. Experimental section

2.1. Preparation of semicokes

Under a N_2 atmosphere, semicokes catalyst was made by the dry distillation of Hongce lignite at a constant temperature of $500\text{ }^\circ\text{C}$ and a heating rate of $10\text{ }^\circ\text{C min}^{-1}$ for 150–180 min.

2.2. Dry re-forming of methane

The dry re-forming of methane was conducted in a high temperature–pressure reactor at the temperature of $700\text{--}850\text{ }^\circ\text{C}$ and a heating rate of $20\text{ }^\circ\text{C min}^{-1}$, pressure of 0.1–3 MPa, CH_4/CO_2 ratio of 1:2–2:1, total flow of $300\text{--}540\text{ ml min}^{-1}$ and 20.0 g of Hongce lignite semicokes. The output flows of CH_4 and CO_2 were controlled through the control panel, and the reaction pressures were provided from high-pressure cylinders. the catalyst was placed in the middle of the corundum tube reactor, which was filled with broken tiles on both ends to guarantee that the catalyst was in the constant temperature area of the reactor. Fig. 1 presents a schematic diagram of high temperature–pressure reactor.

2.3. Characterization

Fourier transform infrared (FTIR) spectrum of Hongce lignite semi-cokes before and after reaction were gained by a FTS-165 infrared spectrometer, detection range of $400\text{--}4000\text{ cm}^{-1}$. The images of SEM were obtained using a JSM-6700F scanning electronic microscope at an acceleration voltage of 0.5–30 kV and the resolution of 1.0 nm (15 kV) and 2.2 nm (1 kV). X-ray diffraction (XRD) patterns were acquired with a Rigaku D/max 2500 X-ray Diffractometer, using $\text{Cu K}\alpha$ radiation ($\lambda = 1.54056\text{ \AA}$), at tube

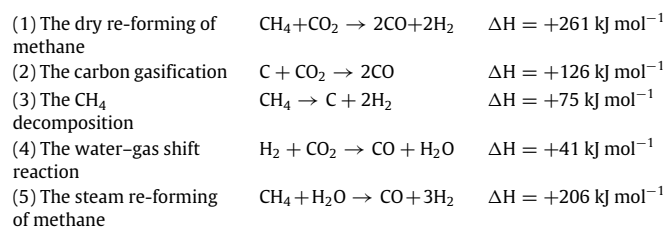
voltage of 40 kV, tube current 100 mA, scan rate of 8° min^{-1} , scanning step 0.01° and scan rang of $5\text{--}85\text{ }^\circ\text{C}$. The specific surface area (BET) was measured by a NOVA 1200e physical adsorption apparatus, the adsorbent was activated in a pure O_2 at $550\text{ }^\circ\text{C}$ for 3 h and cooled down to room temperature, then the sample was activated in a vacuum at $340\text{ }^\circ\text{C}$ for 3 h.

3. Results and discussion

3.1. Effect of the pressure

Fig. 2 displays the effect of pressure on Hongce lignite semicokes catalytic activity. As shown in Fig. 2(a) and (b), although CH_4 and CO_2 conversions were decreased as the reaction pressure increased, but both of them kept basically stable when the reaction pressure was between 0.3 and 1 MPa. After dry re-forming of methane reaction had been conducted for 180 min, the conversions of CH_4 and CO_2 were kept around 45.0% and 55%, respectively, when the reaction pressure was increased from 0.3 MPa to 1 MPa. Under the same condition state above, CH_4 and CO_2 conversions were 54.6% and 62.8% at the normal pressure. When reaction pressure was exceed to 2 MPa, CH_4 and CO_2 conversions were rapidly down to below 30%. The comparison shows that Hongce lignite semi-cokes catalyst have good activity and stability at the pressure of 0.3–1 MPa. It can be observed from Fig. 2(c) and (d) that the CO and H_2 yields also showed the same trend, at the reaction pressure was 1 MPa, the yields of CO and H_2 were 67.4% and 45.4%, respectively, after dry re-forming of methane reaction had been conducted for 180 min.

Dry re-forming of methane at high pressure was a complicated chemical reaction systems, the main chemical reactions were as follows:



In the five reactions above, the reactor (1)–(5) are all volume increase reaction, therefore increasing the reaction pressure is not helpful for those reactions, that is, it is not beneficial for the

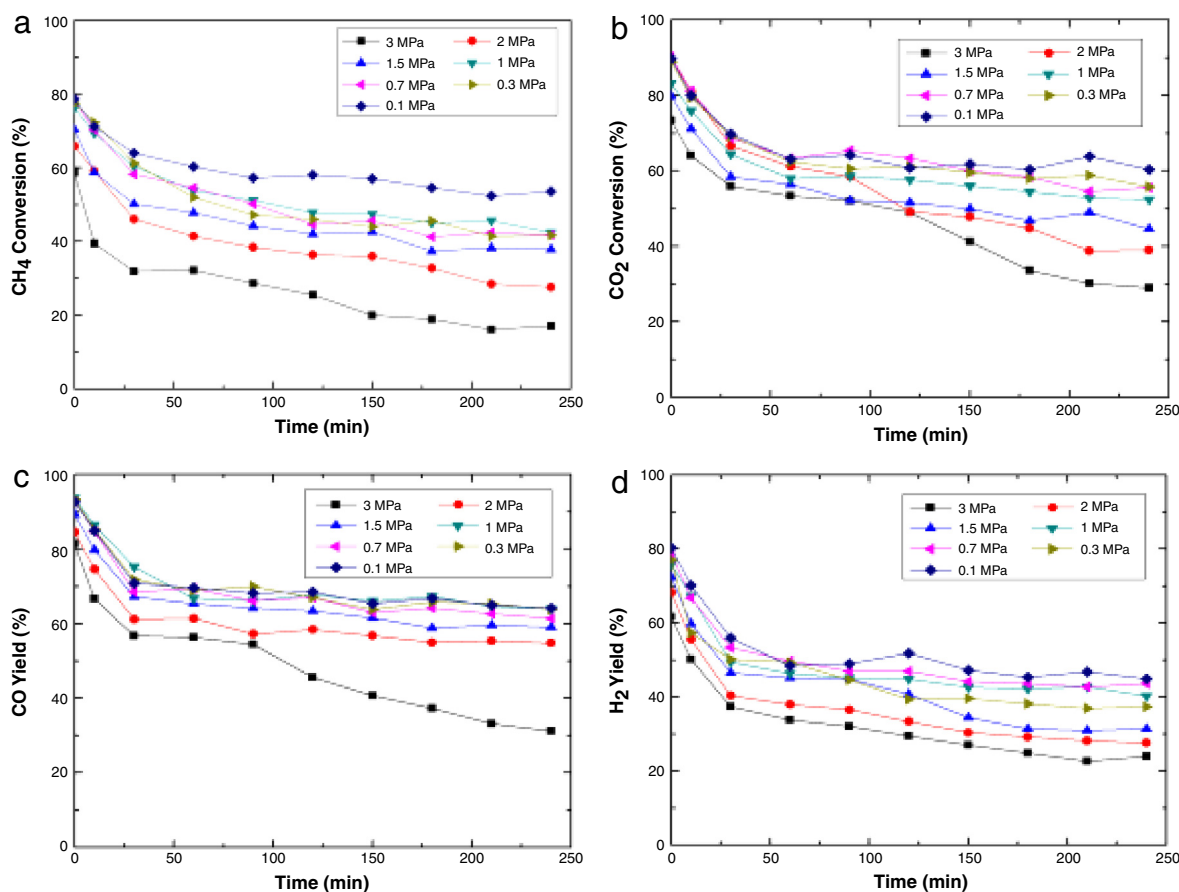


Fig. 2. Methane conversion (a), carbon dioxide conversion (b), carbon monoxide yield (c), and hydrogen yield (d) versus pressures (reaction condition: 800 °C, CH₄/CO₂ ratio of 1:1, total flow of 360 ml min⁻¹ and pressures of 0.1–3 MPa).

dry re-forming of methane and Carbon deposition gasification. At the same time, the higher the reaction pressure, the greater rate of carbon deposition formation than that of carbon gasification. Carbon deposition would be deposited on the Hongce lignite semicokes surface which pore structure was gradually blocked, the active site was embedded and reduced the opportunities of the reactant gas to contact Hongce lignite semicokes catalyst, causing a gradual deactivation of Hongce lignite semicokes, this is the possible reason for reduce conversions of CH₄ and CO₂. On the other hand, increasing the reaction pressure, the volume of the reactant gas was compressed and the productivity was improved. The adsorption of CH₄ and CO₂ on the Hongce lignite semicokes surface was enhanced, as well as the contact probability of reactant gas and catalyst active sites was improved. So dry re-forming of methane positive reaction is promoted. Also, the water–gas shift reaction (4) was accelerated with increased in the reaction pressure because of this reaction was an equal volume reaction, and a portion of H₂ of the generating gas was reacted, it leads to CO yield was higher than that of H₂. The co-effect of the two factors discussed above, the reaction system would be reach a new equilibrium. Considering the above factors comprehensively, the adequate reaction pressure is 0.3–1 MPa.

3.2. Effect of the temperature

Fig. 3 illustrates the effect of temperature on Hongce lignite semi-cokes catalytic activity. When the temperature was increased from 700 °C to 850 °C, CH₄ and CO₂ conversions were increased from 36.6% and 48.3% to 61.6% and 78.7%, respectively, after dry

re-forming of methane reaction had been conducted for 180 min. CH₄ and CO₂ conversions were increased with an increasing of reaction temperature at high pressure, the experiment showed that the law was agreement with the result between high pressure and atmospheric pressure (Guo et al., 2013). The reason was that dry re-forming of methane was a strongly endothermic reaction, and increasing the reaction temperature had a positive effect. The carbon gasification (2) also was an endothermic reaction and increasing the reaction temperature which eliminated carbon deposition for the CH₄ decomposition (3). In the dry re-forming of methane over Semi-coke reaction system, the main source of carbon deposition is CH₄ decomposition (3). It could be reduced the amount of catalytic activity site which was covered, both high activity and stability were obtained. It was consistent with Zhang et al. results (Zhang et al., 2010).

As shown in Fig. 3, the yield of CO was higher than that of H₂ and the conversion of CO₂ was higher than that of CH₄ at the same reaction conditions. The water–gas shift reaction (4) is an endothermic reaction as well as an equal volume reaction; therefore, with an increasing temperature, the reaction (4) had a higher the reaction rate compared with other reactions at high pressure, it leading to increase in a consumption of H₂ and CO₂.

3.3. Effect of the flows of reactant gas

The effect of the flow of reactant gas on Hongce lignite semi-cokes catalytic activity was shown in Fig. 4. The conversions of CH₄ and CO₂ and the yields of CO and H₂ decreased with the increase in the flow of reactant gas. When the flows of reactant gas was raised

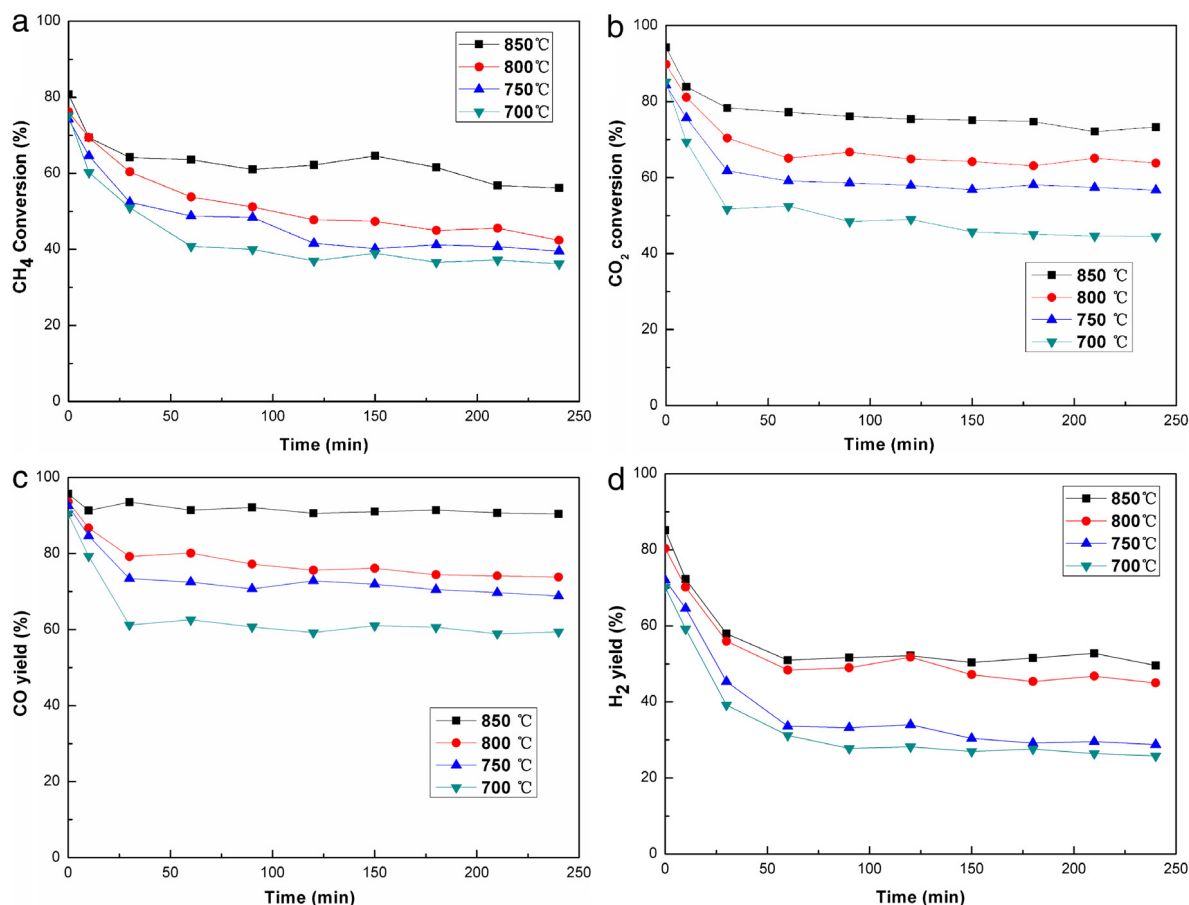


Fig. 3. Methane conversion (a), carbon dioxide conversion (b), carbon monoxide yield (c), and hydrogen yield (d) versus temperatures (reaction condition: pressures of 1 MPa, CH₄/CO₂ ratio of 1:1, total flow of 300 ml min⁻¹ and 700–850 °C).

from 300 ml min⁻¹ to 540 ml min⁻¹, the CH₄ and CO₂ conversions reduced from 71.6% and 76.7% to 41.6% and 44.2%, respectively, the CO and H₂ yields reduced from 93.6% and 56.4% to 76.4% and 31.1%, respectively, after the dry re-forming of methane reaction had been conducted for 180 min. It can be observed that the yield of CO was more than that of H₂, which further evidenced that the water–gas shift reaction (4) was taking place during the dry re-forming of methane process.

With a decreasing the flow of reactant gas, the contact time of the reactant gas with catalytic activity sites had lengthened, as same as, it was propitious for the reactant gas to the adsorption on the surface of Hongce lignite semicokes at high pressure, the more the reactant gas could diffuse deeply into the interior pores of Hongce lignite semicokes and had enough time to react with more the catalytic activity sites, thus impel the proceeding of dry re-forming of methane. When the flow of reactant gas reached a certain level, the contact between the reactant gas and the catalytic activity sites reached a saturated state, the conversions of CH₄ and CO₂ did not continually increased. While the flow of reactant gas was increased continuously, a portion of reactant gas would be flowed out with the product gas because it had no time to react, which resulted in reactant gas wasted.

3.4. Effect of ratios of CH₄/CO₂

The effect of ratios of CH₄/CO₂ on CO/H₂ was given in Fig. 5. The ratio of the CO/H₂ decreased as the ratio of CH₄/CO₂ increased which showed the same trend at the different temperatures. At temperature of 850 °C, the value of CO/H₂ was reduced form

2.84 to 1.76 with increase in the CH₄/CO₂ ratio form 1:2 to 2:1, and the value of CO/H₂ was always more than 1 at the different temperatures. So the value of CO/H₂ could be adjusted in different CH₄/CO₂ ratio to meet different demands. From the point of view of chemical reaction equilibrium, with an increasing the CH₄ content in reaction systems, the CO yield and CO₂ conversion both improved, while with an increasing the CO₂ content in reaction systems, the H₂ yield and conversion CH₄ could be improved. The content of CO was higher than that of H₂, because the high pressure was conducive to the water–gas shift reaction (4). Meanwhile, the CH₄ content increased was beneficial to the CH₄ decomposition (3), and yet it was not unfavorable to the carbon gasification (2), which causing to the rate of carbon deposition formation exceeded the rate of carbon deposition elimination, and then the carbon was deposited on the surface and filled part of the interior pore of Hongce lignite semicokes, in this way, the catalytic activity was lowered.

4. Surface properties of Hongce lignite semicokes at different pressures

4.1. Fourier transform infrared (FTIR) analysis

Fig. 6 was the Fourier transform infrared of Hongce lignite semicokes before and after the reaction. After the reaction, the physical specific adsorption peak of CO₂ at 2350 cm⁻¹ was strengthened significantly at different pressures, which further proved that an increasing pressure could be promoted CO₂ adsorption on the surface of Hongce lignite semicokes, as well as

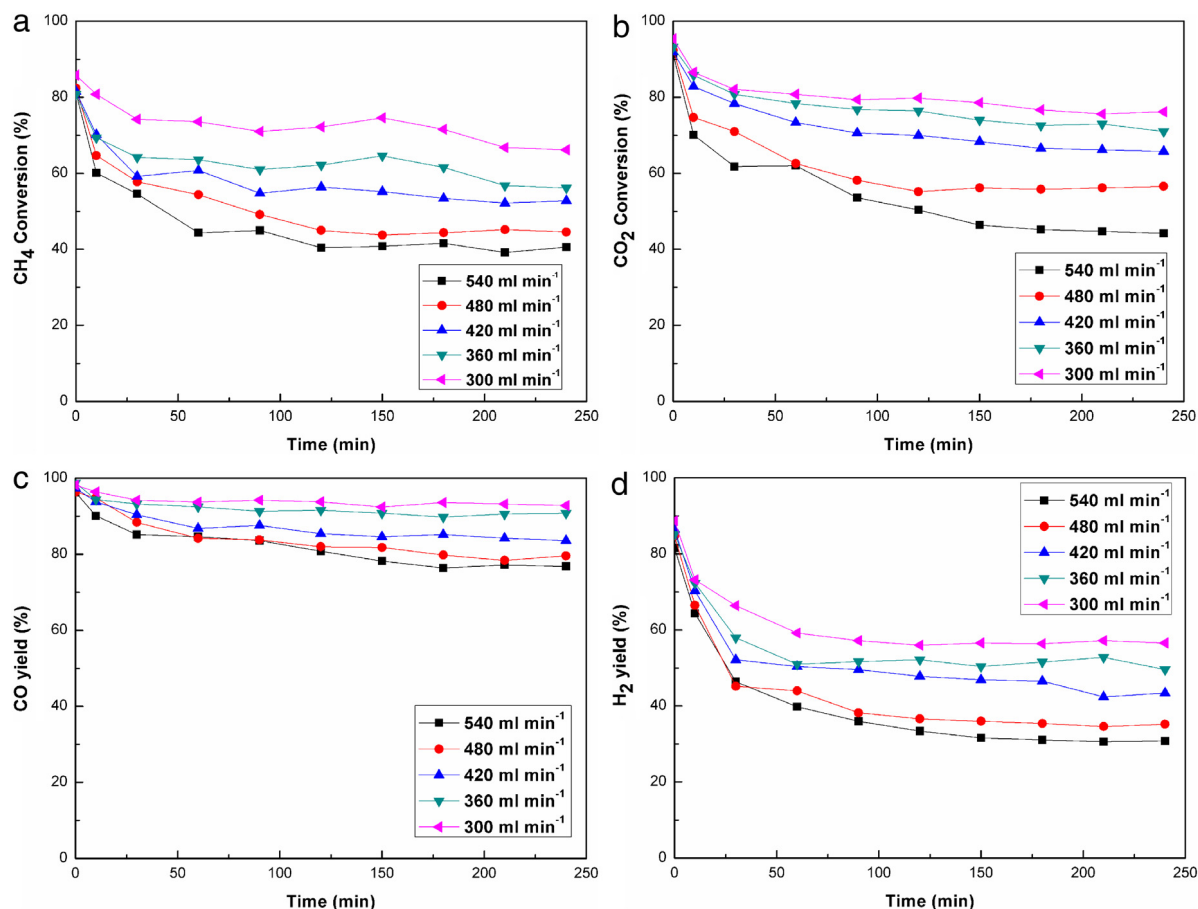


Fig. 4. Methane conversion (a), carbon dioxide conversion (b), carbon monoxide yield (c) and hydrogen yield (d) versus the flows of reactant gas (reaction condition: pressure of 1 MPa, CH_4/CO_2 ratio of 1:1, total flows of 300–540 ml min^{-1} and 850 °C).

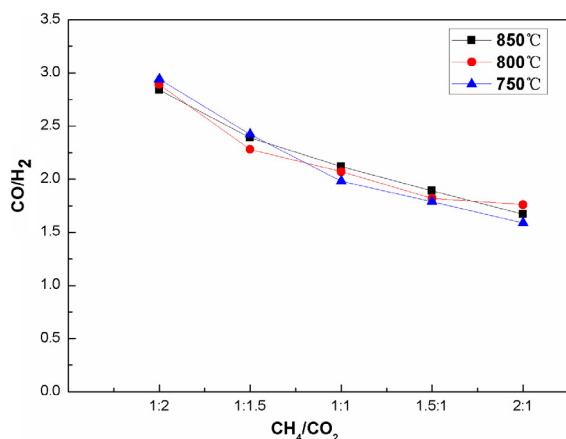


Fig. 5. The value of CO/H_2 versus the ratio of CH_4/CO_2 (reaction condition: pressure of 1 MPa, CH_4/CO_2 ratio of 1:2–2:1, total flow of 360 ml min^{-1} and 750–850 °C).

shown that the dry re-forming of methane was a two step process, namely, the first step was to adsorb reaction of CH_4 and CO_2 with Hongce lignite semicokes, secondly, the interaction between CH_4 with CO_2 . When the reaction pressure was in the range of 0.1–1 MPa, the specific absorption peak of C–O and O–H at 1700 cm^{-1} were obviously diminished, yet it was much the same as before reaction when the pressure was exceed 1.5 MPa. The infrared spectra indicated that the dry re-forming of methane was difficult when the pressure was up to 1.5 MPa, which it was consistent with experimental result.

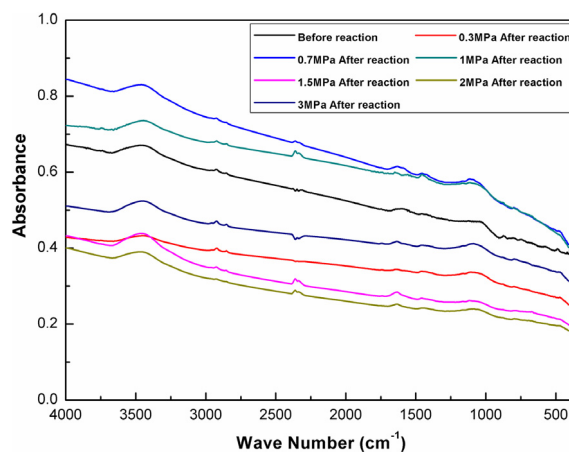


Fig. 6. FTIR of Hongce lignite semi-coke before and after reaction at different pressures.

4.2. Micropore area, volume, and pore diameter

Table 1 was the micropore area, volume, and pore diameter of Hongce lignite semicokes before and after reaction. After the reaction, the micropore area and volume of Hongce lignite semicokes both decreased as the reaction pressure increased, but pore diameter increased. When the reaction pressure increased from 0.1 MPa to 1 MPa, the micropore area and volume of Hongce lignite semicokes were reduced from $40.2 \text{ m}^2 \text{ g}^{-1}$ and $0.019 \text{ cm}^3 \text{ g}^{-1}$ to $34.9 \text{ m}^2 \text{ g}^{-1}$ and $0.017 \text{ cm}^3 \text{ g}^{-1}$, respectively,

Table 1
Micropore areas, volumes, and average pore diameters of Hongce lignite semi-cokes.

Sample	Micropore area ($\text{m}^2 \text{g}^{-1}$)	Micropore volume ($\text{cm}^3 \text{g}^{-1}$)	Average pore diameter (nm)
Before reaction	47.8	0.021	2.976
0.1 MPa after reaction	40.2	0.019	3.415
0.3 MPa after reaction	38.5	0.018	3.765
0.7 MPa after reaction	37.1	0.018	3.806
1 MPa after reaction	34.9	0.017	3.947
1.5 MPa after reaction	27.6	0.014	4.372
2 MPa after reaction	21.7	0.011	4.611
3 MPa after reaction	18.4	0.008	4.868

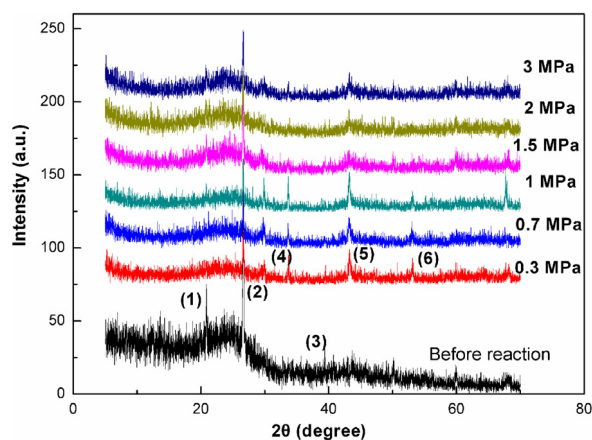


Fig. 7. XRD patterns of Hongce lignite semi-cokes before and after reaction at different pressures: (1) SiO_2 , (2) carbon, (3) $\text{Na}_3\text{MnPO}_4\text{CO}_3$, (4) CuV_2O_6 , (5) KCrO_3F , and (6) $\text{B}_{0.47}\text{C}_{0.23}\text{O}_{0.30}$.

that is, the pressure has been less effect on catalytic activity with 0.1–1 MPa range, it also indicated that the catalytic activity still remained stable.

After that, the micropore area and volume of Hongce lignite semicokes both decreased rapidly as the pressure going up, due to the rate of the CH_4 decomposition (3) was greater than that of the carbon gasification (2), which increased the amount of carbon deposition, and resulted in a large amount of micropore of Hongce lignite semicokes was covered by carbon deposition, which shown that the catalytic activity was degraded.

4.3. X-ray diffractometer (XRD) analysis

X-ray diffraction of Hongce lignite semicokes was shown in Fig. 7. In this spectrum, the diffraction peaks at 26.8° and 21.25° are graphite and SiO_2 , respectively. After the reaction, $\text{Na}_3\text{MnPO}_4\text{CO}_3$ species had almost completely diminished, as well as the species of CuV_2O_6 and KCrO_3F both reduced gradually with an increasing pressure, when the reaction pressure was up to 1.5 MPa. Those alkaline earth metals had a catalyst for the dry re-forming of methane, the volatilization of alkaline earth metals led to loss of catalytic components and lower CO_2 adsorptive capability, which was also one of factors that the catalytic activity of Hongce lignite semicokes was decreased.

4.4. SEM images

Scanning electron microscopy (SEM) of Hongce lignite semicokes was given in Fig. 8. Before the reaction, surface morphologies of Hongce lignite semicokes presented obvious layered structure and the edges of these wrinkles were quite smoothing from the $1 \mu\text{m}$ scale plate on the images. After the reaction, the small granular objects were gradually set on the surface of Hongce lignite semicokes, and the number of the pore structure features of Hongce

lignite semicokes petered out and then disappeared fully with an increasing the pressure. The surface of Hongce lignite semicokes was entirely covered with carbon deposition, especially when the reaction pressure was between 2 and 3 MPa. The result was in correspondence with that of Table 1.

Moreover, it can be seen that, carbon deposition would be form aggregation on the surface of Hongce lignite semicokes as the reaction pressure increased, in the meantime, this trend from decentralize to centralize. On one hand, because of increasing pressure is not propitious for the carbon gasification (2) process, which reduced the elimination rate of carbon deposition. On the other hand, high pressure was beneficial to enhance the bulk density of carbon deposition, and then a compact passivated layer could be formed on the surface of Hongce lignite semicokes, it was separated the contact between reactant gas and the catalyst active site, which resulted in the activity of Hongce lignite semicokes was reduced or even inactivated.

5. Conclusions

Our groups have been designed and made a high temperature–pressure reactor base on the idea of “high temperatures zone equilibrium pressure, low temperatures zone under pressure”. The effects of reaction temperature, reaction pressure, the flow of reactant gas, and the ratio of CH_4/CO_2 on catalytic activity of Hongce lignite semicokes for dry re-forming of methane were investigated. The results showed that CH_4 and CO_2 conversions were kept basically stable when the reaction pressure was between 0.3 and 1 MPa, under the experimental condition, the adequate reaction pressure was 0.7–1 MPa. The conversion of CO_2 was higher than that of CH_4 , and the yield of CO was higher than that of H_2 , because increasing the reaction pressure was conducive to the water–gas shift reaction as compared to other reactions. When the reaction pressure increased from 0.1 to 1 MPa, the specific absorption peak of C–O and O–H at 1700 cm^{-1} are both significantly reduced. The SEM images showed that carbon deposition gradually set on the surface of Hongce lignite semicokes as the pressure increased, and the pore of catalyst was entirely covered when the reaction pressure was between 2 and 3 MPa. The characterization analysis of Hongce lignite semicokes proved that the dry re-forming of methane, first as CH_4 and CO_2 were adsorbed, and then the interaction between CH_4 and CO_2 on the surface of Hongce lignite semicokes. And provided further evidence that Hongce lignite semicokes catalyst have good activity and stability at the pressure of 0.3–1 MPa.

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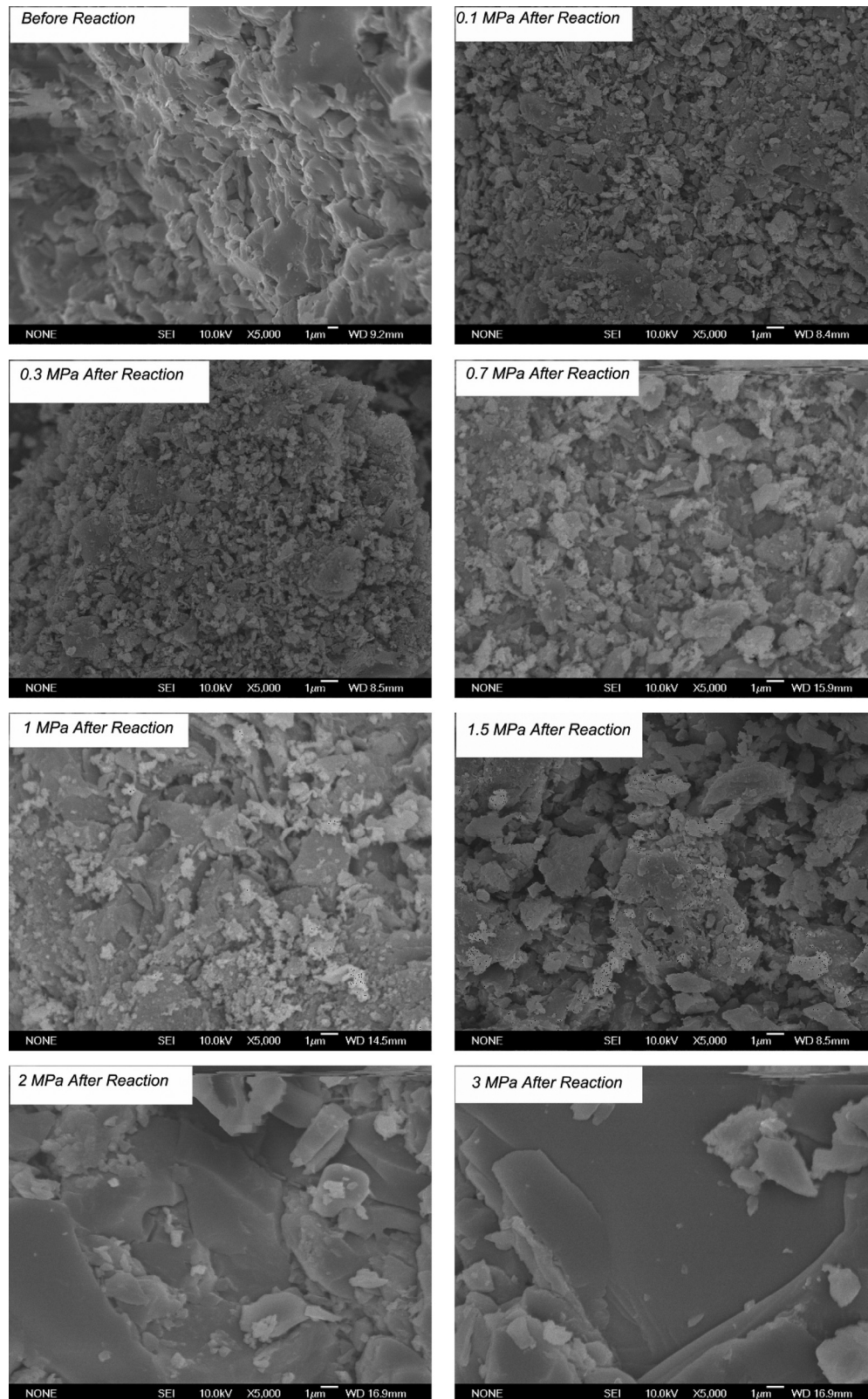


Fig. 8. SEM images of Hongce lignite semicokes before and after reaction at different pressures.

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