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Hydrogen production from CO₂ reforming of methane over high pressure H₂O₂ modified different semi-cokes

Guojie Zhang^{a,*}, Jiangwen Qu^a, Yannian Du^a, Fengbo Guo^b, Haixiang Zhao^c, Yongfa Zhang^{a,*}, Ying Xu^a^a Key Laboratory of Coal Science and Technology, Ministry of Education and Shanxi Province, Taiyuan University of Technology, Taiyuan 030024, PR China^b School of Chemical Engineering and Environment, North University of China, Taiyuan 030051, PR China^c Sichuan Provincial Economic and Information Technology Commission, PR China

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ABSTRACT

H₂O₂ was used under different temperatures and pressures to activate three kinds of different semi-cokes. FTIR, BET, SEM and Boehm titration were used to analyze properties of the semi-cokes surfaces, finding that catalytic activities of these semi-cokes after modification by high temperature and high pressure H₂O₂ were improved. FTIR shows that the characteristic infrared absorption peak of functional groups on the semi-cokes surface does not change, but the absorption peak intensity of some functional groups is increased. The strength of –OH absorption peak of Hongce lignite (HCL) semi-coke at 3444 cm⁻¹, carboxyl C=O at 1598 cm⁻¹, aliphatic ether, cyclic ether and other organic functional groups at 1023 cm⁻¹ in the modified Shenmu bituminous(SMB) semi-coke and Jincheng anthracite (JCA) semi-coke are increased significantly. BET finds that the specific surface area and pore volume of three semi-cokes are increased after modification. Boehm titration shows that the basic functional group content in semi-coke is increased after modification, and the net alkali content is increased significantly. Compared with the raw semi-coke, SEM shows that the surface of semi-coke modified with H₂O₂ becomes rough. Modified JCA semi-coke surface pitted with holes, modified HCL and SMB semi-coke surface present porous.

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1. Introduction

CO₂ and CH₄ are the main greenhouse gases, however, also a valuable resource. Global climate change caused by greenhouse gases has aroused wide concern in international society. Not only does CH₄ reforming of CO₂ produce necessary energies and chemical products but also comprehensively improves the energy efficiency. It is an environment-friendly and important way to realize clean conversion and efficient utilization of coal and deal with the emission of greenhouse gas, and thus has been widely studied by many researchers [1–4]. As is well known, noble metals and transition metal are often employed as catalysts to facilitate the production of syngas by CH₄ reforming of CO₂. Noble metals are unsuitable for practical applications because of their prohibitive cost and insufficient long term stability, the transition metal are usually unstable and are easily deactivated, especially by carbon deposition [5–8]. Hence, development and modification of

new catalyst materials with low-cost and high activity have always been a focus research in material science and catalytic field.

In recent years, carbon materials have received a wide attention due to the features of low cost, rich pore structures and high specific surface area. The activity of the catalyst can be regulated by changing the structure of carbon materials and composition of functional groups through modification, as there are various kinds of carbon materials with rich structures and functional groups. Compared with the traditional supported catalysts, rich categories and variable properties of carbon materials not only provide new ways for the preparation of new carbon materials, but also provide opportunities for development of reforming catalyst. Semi-coke, the solid residue obtained by carbonization of coal at below 700 °C, is a carbon material. Based on our previous researches [9–12], it has been found that semi-coke has a significant catalytic effect on syngas generation by CH₄ reforming with CO₂. And properties of the semi-coke surface, such as specific surface area, content of surface functional groups and coal rank, play a main role in the reforming reaction.

Currently, physical and chemical activation are the main ways in carbon material (semi-coke) modification [13,14], mainly including acid and alkali modification, high temperature

* Corresponding authors. Tel.: +86 351 601 8676; fax: +86 351 601 8676.
E-mail addresses: zhgjdoc@126.com, zhangguojie@tyut.edu.cn (G. Zhang), yongfaz@tyut.edu.cn (Y. Zhang).

modification and hydrothermal chemical modification. The activation is mainly achieved through (1) improving the physical properties of semi-coke, i.e. specific surface area, pore volume and diameter; (2) improving the chemical properties of semi-coke, i.e. content of surface functional groups. Hydrothermal chemical modification has been widely applied as the most commonly used methods in material modification [15–17]. However, its application was restricted by large energy consumption, high carbon loss, complicated process and large coverage, etc. Acid, alkali and high temperature modification were adopted in patent [18], and the pore volume and specific surface area of the semi-coke were improved. Zheng achieved semi-coke modification and obtained satisfactory effect in removing SO₂ from flue gases by pressurized hydrothermal modification [19]. Based on the experience obtained from previous researches [12], in this paper, Hongce lignite (HCL) semi-coke, Shenmu bituminous (SMB) semi-coke, and Jincheng anthracite (JCA) semi-coke are modified through hydrothermal reaction at high temperature and high pressure. The impact of H₂O₂ concentration, modification temperature, pressure and time on catalytic activity of semi-coke was studied, and the change of surface properties of semi-coke before and after the modification was analyzed by modern means.

2. Experimental

2.1. Catalyst preparation

WHF-08 type small size high pressure reaction kettle produced by Weihai Automatic Control Reaction Kettle, with the volume of 500 ml, temperature range from room temperature to 600 °C and pressure ranges from 0.1 MPa to 12 MPa, was used for semi-coke modification. Properties of the three different kinds of semi-cokes were shown in the literature [12]. 75 g samples with the grain size of 2–4 mm was put into the reaction kettle, the H₂O₂ according to the solid-to-liquid ratio of 1:2 was added, then the reaction kettle was capped and kept tight sealing. Seal test according to the set pressures was conducted. Then, it was heated up to set the temperature at the 5 °C min⁻¹, and kept a constant temperature for 2 h, and then cooled down to room temperature naturally. The sample was dried for 12 h at 110 °C.

2.2. Boehm titration

Carbon (semi-coke) is complex mixture composed by polycyclic aromatic hydrocarbons, in which aromatic structure of compounds is very stable and does not tend to react [20–24]. However, the oxygen-containing functional groups on the surface have a higher reactivity. So, the type and content of oxygen-containing functional groups in semi-coke have great influence on the semi-coke properties [21–26]. Through

pretreatment, the oxygen-containing functional groups of the structure of semi-coke could be changed, the adsorption and catalytic activity of semi-coke increased [20,21,24–26]. According to the literature and our previous researches [20–26], it found that the surface acidity and basicity of the semi-coke have an important role in the semi-coke performance and catalytic activity. So, the surface acidity and basicity determinations are very necessary in developing new and improving existing semi-cokes materials.

Boehm titration was used to determine the surface acidity and basicity of the samples. The number of basic sites was titrated with HCl. Acidic groups were titrated with bases of different strength: NaOH neutralizes carboxylic, lactonic and phenolic groups; Na₂CO₃ neutralizes carboxylic and lactonic groups; and NaHCO₃ neutralizes only carboxylic groups [27–29]. Weighed 1.0 g of carbon samples (1.0 g) were placed in 100 ml of 0.01 M solution of either HCl or the bases. After sealing and equilibration with gentle agitation for at least 48 h at room temperature, the suspension was filtrated over a filter. Part of the solution was separated and back-titrated with either standard 0.01 M HCl or NaOH. The results were expressed as mmol H⁺ or OH⁻ equivalent per gram carbon.

2.3. Catalyst characterization [9,10]

All samples were degassed at 300 °C for 1 h before measurements to remove impurities of the catalyst surface. The specific surface area of the catalysts was determined by nitrogen adsorption-desorption measurement at -196 °C in Tristar gas adsorption system.

The oxygen-containing function group of the carbonaceous catalysts was determined by means of a VERTEX70 Fourier transformation infrared spectrometer. Scanning area was 4000–400 cm⁻¹. Resolution was 4 cm⁻¹. Wave number accuracy was 0.01 cm⁻¹. Scan time was 16 s.

Scanning electron microscopy (SEM) images of the catalyst surface were performed with a scanning electron microscope JSM-4800 (Japan, JEOL, Ltd.). Gold was sputtered onto the catalysts to ensure sufficient conductivity.

2.4. Catalytic activity measurements

The catalytic activity experiments were carried out at a normal pressure in a lab-scale multiphase flow reactor. The flows of feed gas were exactly controlled by mass flow controllers. About 1.0 g of the catalyst was used in the reaction. The flow rates of CO₂ and CH₄ were 36 ml min⁻¹, CH₄/CO₂ was about 1. The temperatures at the top and the bottom of the catalyst bed were monitored with a platinum-rhodium thermocouple. After reaching steady-state 30 min, the product gas was analyzed by gas chromatography (GC-950 to measure CO₂, CH₄

Table 1

Content of acidic and basic groups of semi-cokes [modification conditions: temperature 300 °C, pressure 8 MPa, time 4 h, H₂O₂ concentration 5%].

Sample		Before activated, mmol g ⁻¹	After activated, mmol g ⁻¹
HCL semi-coke surface group	Basicity	0.195	0.343
	Acidity	0.051	0.064
	Total	0.246	0.407
SMB semi-coke surface group	Basicity	0.173	0.261
	Acidity	0.047	0.062
	Total	0.220	0.323
JCA semi-coke surface group	Basicity	0.119	0.213
	Acidity	0.038	0.046
	Total	0.157	0.259

Table 2

Surface area, volume and average pore diameter of semi-cokes [modification conditions: temperature 300 °C, pressure 4 MPa, time 4 h, H₂O₂ concentration 5%].

Sample	Micro pore area (m ² g ⁻¹)	Micro pore volume (cm ³ g ⁻¹)	Average pore diameter (nm)
HCL semi-coke	47.8	0.021	2.976
SMB semi-coke	39.3	0.018	3.421
JCA semi-coke	5.6	0.007	5.376
Modified HCL semi-coke	139.1	0.063	1.983
Modified SMB semi-coke	123.3	0.069	2.168
Modified JCA semi-coke	89.7	0.046	2.364

and CO, GC-9890 to measure H₂), produced by Shanghai Linghua Co., Ltd. Prior to analysis, the effluent was passed through a water-trap at 0 °C to remove the reaction water. The error of each data point was less than 3%, and experiments with large

errors were rejected. And the product gas flow was measured by a soap foam flow meter. Without specification, the time used in the x axis is reaction time in the manuscript. The calculation equation of CH₄ and CO₂ conversions was followed:

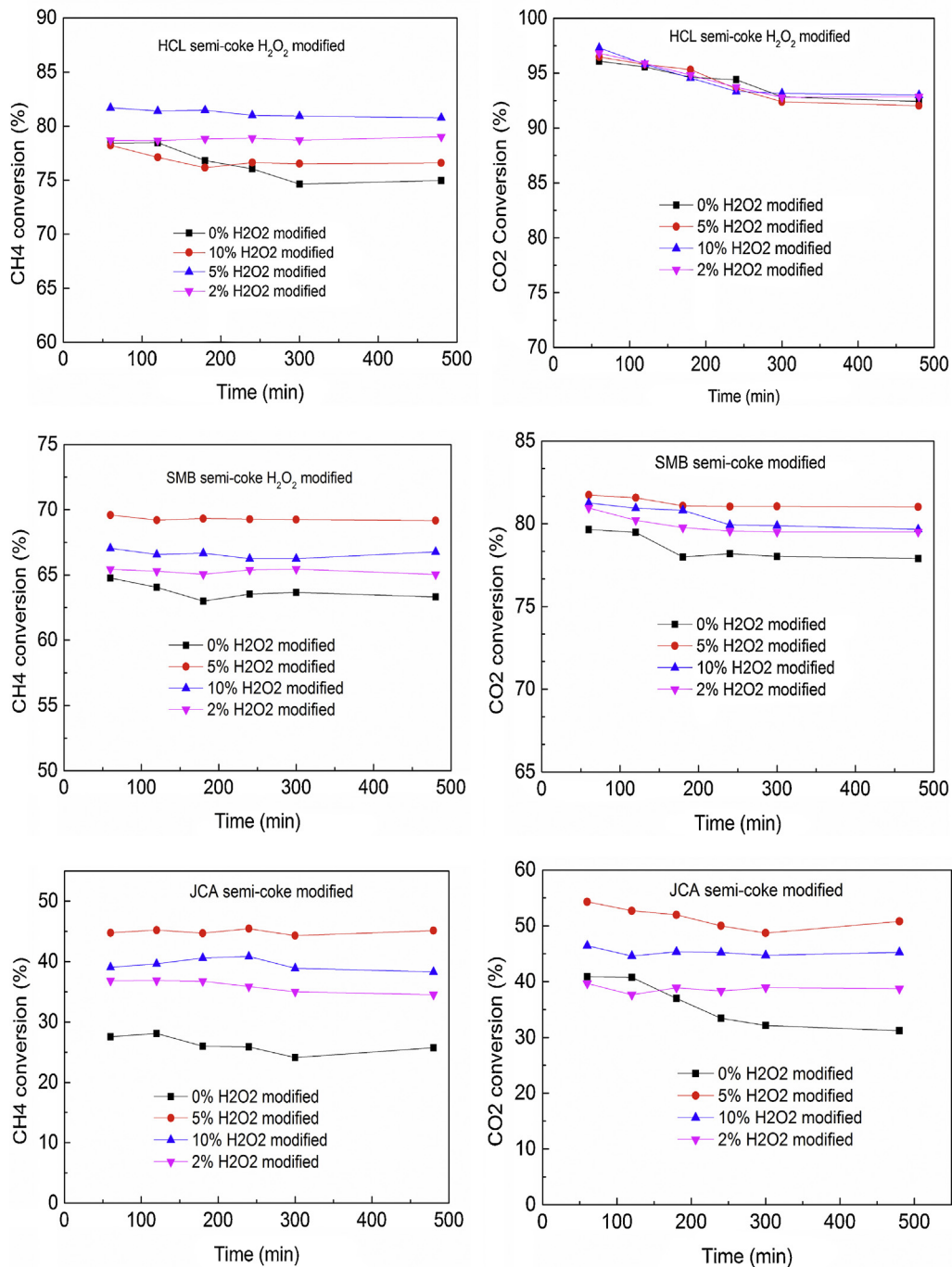


Fig. 1. Effects of H₂O₂ concentration.

$$X_{CH_4} = \frac{F_{CH_4 in} \times F_{CH_4 in} - F_{CH_4 out} \times F_{CH_4 out}}{F_{CH_4 in} \times F_{CH_4 in}} \times 100$$

$$X_{CO_2} = \frac{F_{CO_2 in} \times Y_{CO_2 in} - F_{CO_2 out} \times Y_{CO_2 out}}{F_{CO_2 in} \times Y_{CO_2 in}} \times 100$$

where X is the conversion of the CH₄ or CO₂, F is the gas flow rate of in and out, ml min⁻¹, Y is the different fraction volume percentage, subscript in: the inlet, subscript out: the outlet.

3. Results and discussion

3.1. Catalysts characterization

3.1.1. FTIR

According to Fig. 5, after hydrothermal reaction and modification in high temperature and high pressure H₂O₂, the characteristic absorption peak of functional groups on the semi-coke surface does not change, but the absorption peak intensity of some functional groups increases. It also can be seen that strength of -OH absorption peak of the modified HCL semi-coke

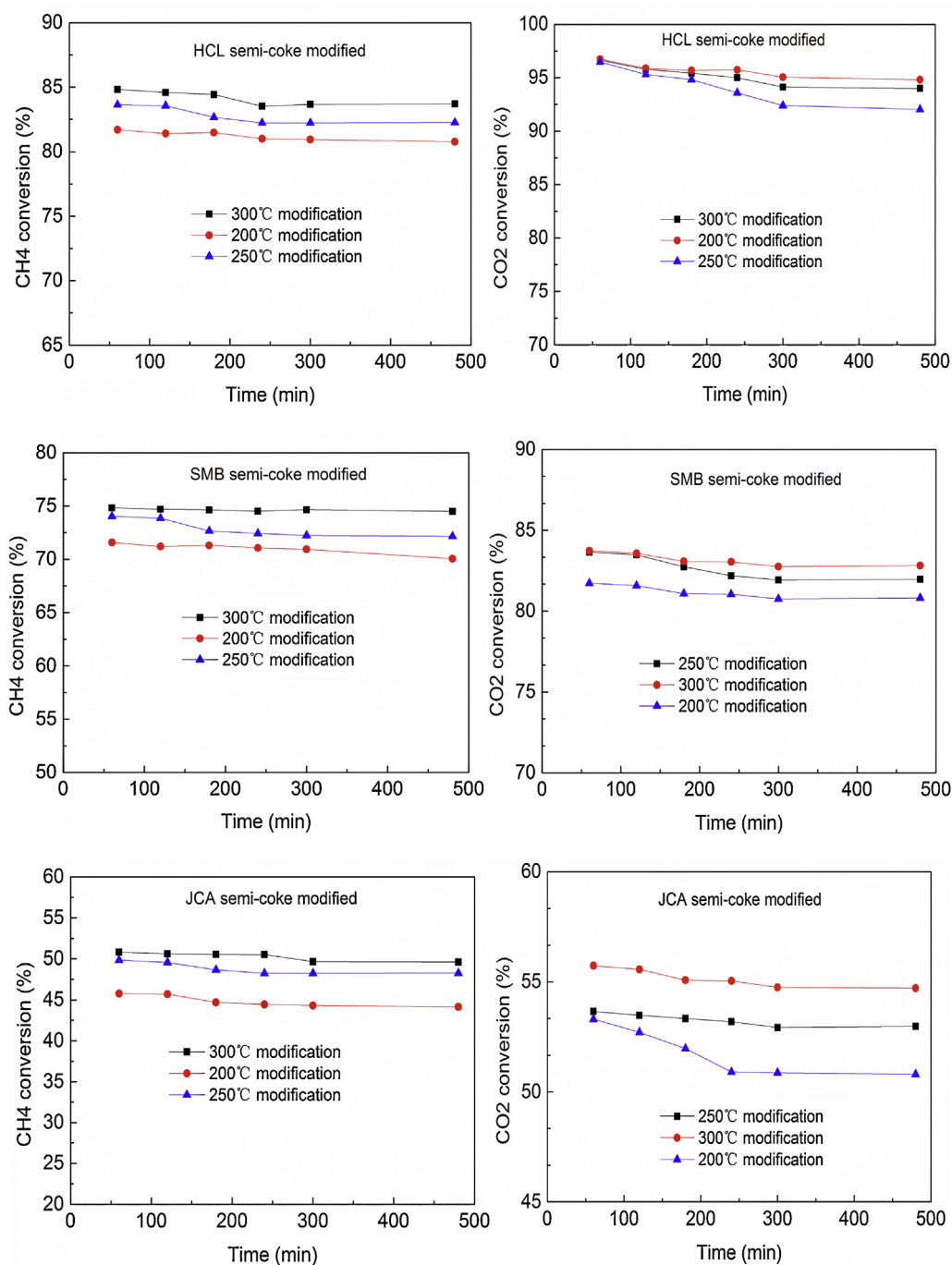


Fig. 2. Effects of modification temperature.

is enhanced obviously at 3444 cm^{-1} . The contents of carboxyl C=O at 1598 cm^{-1} , aliphatic and cyclic ether, and other organic functional groups at 1023 cm^{-1} in the modified SMB semi-coke and JCA semi-coke is increased significantly. The strength of the modified JCA semi-coke carboxyl C=O absorption peak shows a significant increase at 1598 cm^{-1} . The previous researches have shown that aliphatic ether, cyclic ether and other organic functional groups on the surface of semi-coke are the active substance of reforming reaction, which could reduce the activation energy of reforming reaction and improve the activity of catalyst [9–12]. After hydrothermal reaction and modification in high temperature and high pressure H_2O_2 , the content of the reactive functional groups increases, which can improve the activity of carbon materials catalysts [30,31].

3.1.2. Boehm titration

According to Table 1, the contents of the three semi-coke acid base functional groups are: HCL semi-coke > SMB semi-coke > JCA semi-coke, which is associated with coal rank of the semi-coke types. Hongce Lignite (HCL) has larger volatiles and contents of organic matter functional groups. After high temperature and high pressure H_2O_2 modification, the contents of three kinds of semi-coke acid–base functional groups increase. The surface acidic functional groups of HCL, SMB and JCA semi-cokes are increased by 0.013 mmol g^{-1} , 0.015 mmol g^{-1} and 0.008 mmol g^{-1} ; alkaline functional groups are increased by 0.148 mmol g^{-1} , 0.088 mmol g^{-1} and 0.094 mmol g^{-1} . The content of alkaline functional groups shows a significant increase than that of the acidic functional groups, and the increasing of net alkali of semi-coke

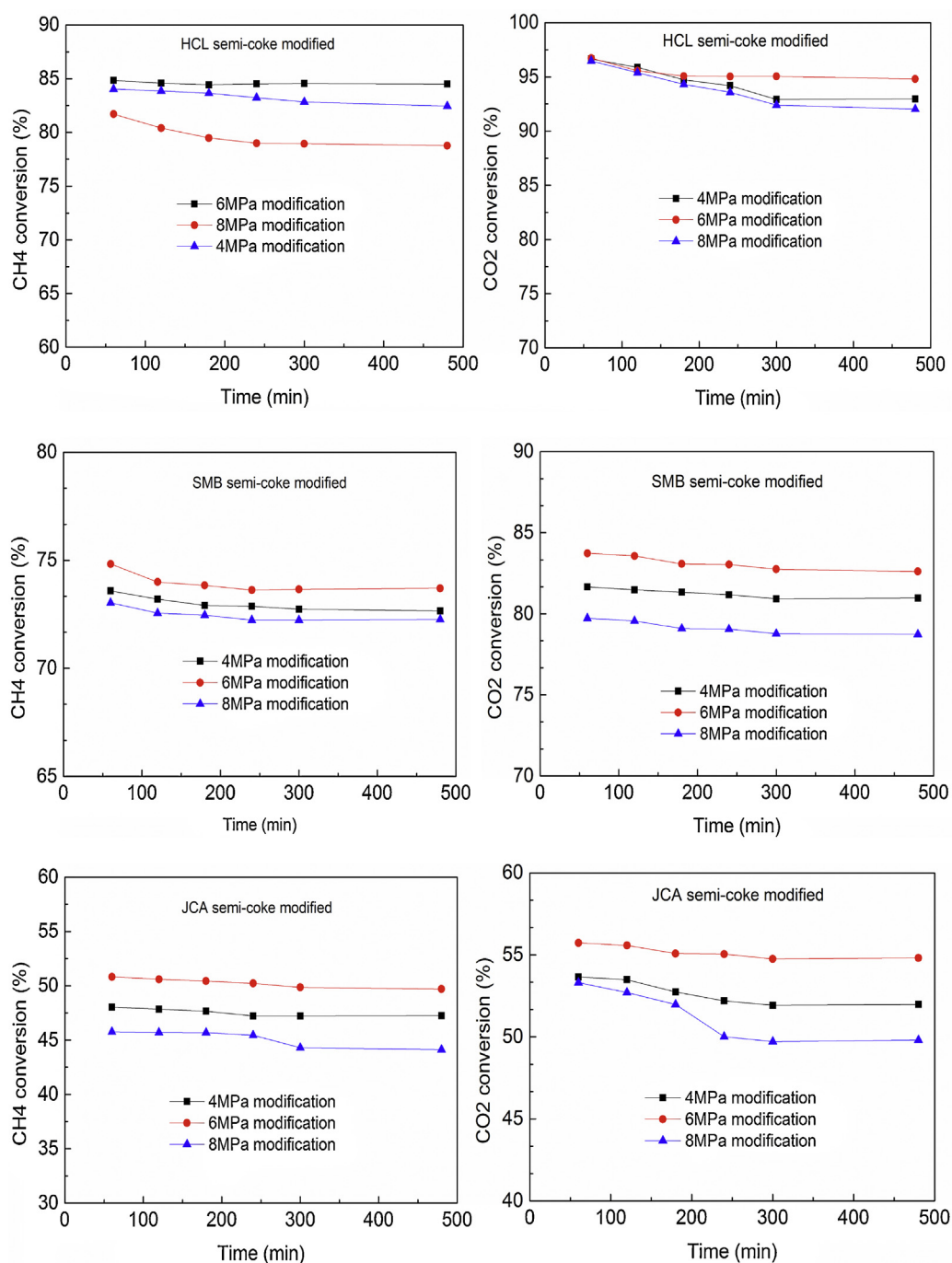


Fig. 3. Effects of modification pressure.

is especially significant [32–34]. Alkaline functional groups of the semi-cokes can help CO₂ adsorption and activation [32–36]. The newly-produced alkaline functional groups after modification increase the contact time between the reaction gas and the semi-coke active site, and therefore improving the catalyst performance [33–36].

3.1.3. Specific surface area and pore volume

According to Table 2, the specific surface area and pore volume of three semi-cokes increase after modification. JCA semi-coke shows an obvious greater specific surface area increase than HCL and SMB semi-cokes. The specific surface area and pore volume were increased by hydrogen peroxide activation. This is due to the

fact that H₂O₂ can react with the carbon particles of the semi-coke surface [37–40]. The higher H₂O₂ concentration is, the more intense the oxidation reaction between H₂O₂ and semi-coke becomes; the more micro-pores in the semi-coke can be formed, and the bigger the specific surface area of the semi-coke increases. Secondly, under the high pressure condition, due to the differential pressure between inside and outside of the pore jammed originally within the semi-coke, some of the jammed pores can be opened [38–41]. In addition, under the high temperature and high pressure condition, the small amount of tar in semi-coke is dissolved. It further increases the surface area and pore volume of semi-coke. The results show that H₂O₂ plays a role in opening micro-pores and enlarging them.

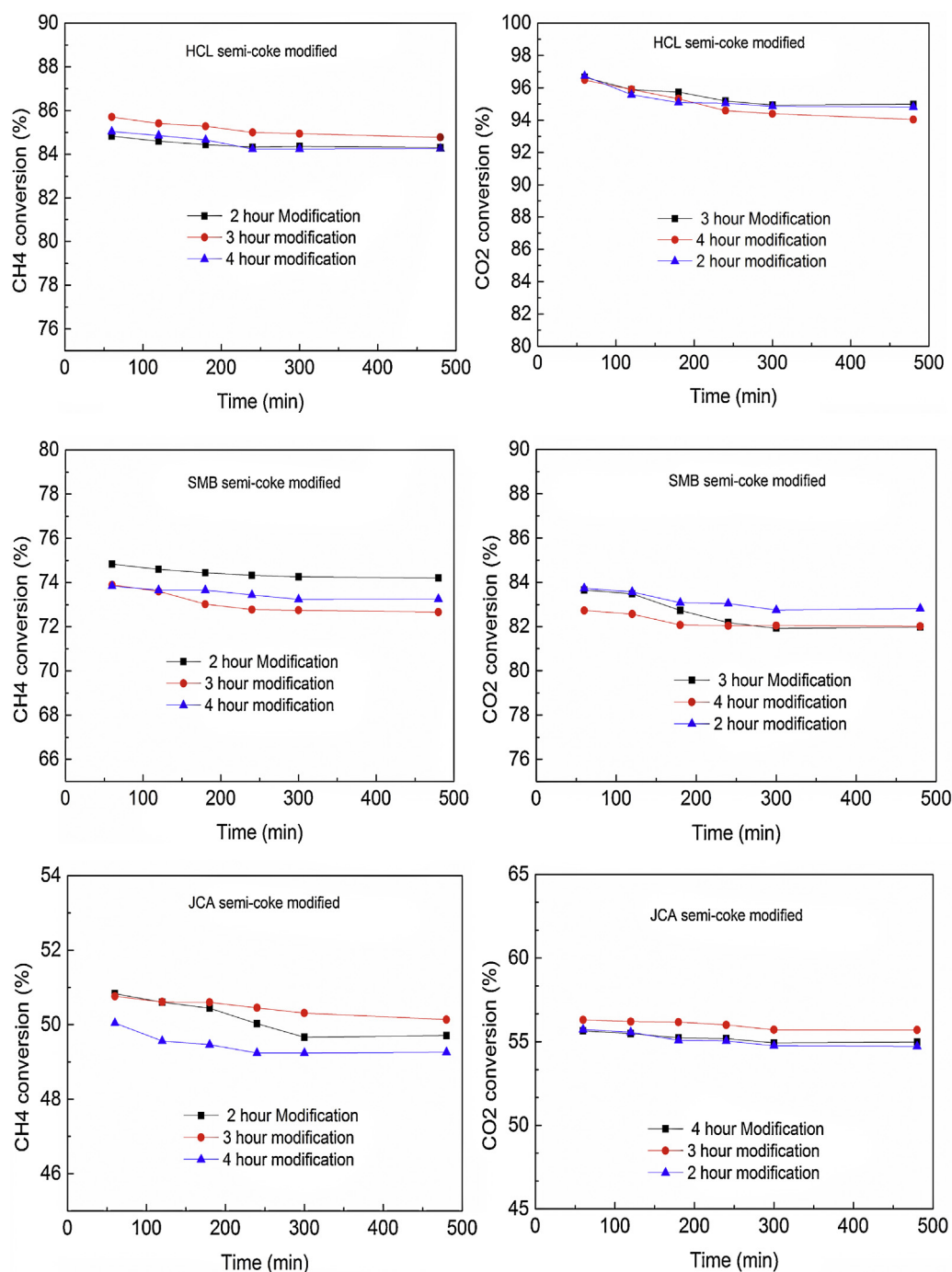


Fig. 4. Effects of modification time.

3.1.4. SEM

It can be seen from Fig. 6, after modification with H_2O_2 , the surface appearance of the three kinds of semi-coke was changed greatly. It was found that the result agglomerated, then the agglomerate is piled up on the surface of HCL semi-coke after modification with H_2O_2 . Surface porosity of the modified SMB semi-coke is relatively more developed than that before modification. The macro-porous structure changes into uniformly the micro-porous structure with large amount, which increases the surface area of the semi-coke. The surface of the modified JCA semi-coke becomes uneven, and shows the leaf layer structure. Overall, high temperature and high pressure H_2O_2 modification has obvious influence on the semi-coke pore structure. H_2O_2 oxidation fueled the oxidation of carbon and ash on the surface of semi-coke, forming more micro-pores. It is consistent with the data in Table 2.

3.2. Catalytic activities

3.2.1. Effects of H_2O_2 concentration

From Fig. 1, it also can be seen that the catalytic activities of the three semi-cokes with different coal ranks were obviously improved after H_2O_2 modification at high temperature and high pressure. The results show, at 240 min, that CH_4 conversion is 35%,

45% and 40% over modified JCA semi-coke (by 2%, 5% and 10% H_2O_2 modification) respectively, which are higher than that over non-modified JCA semi-coke (25%). CO_2 conversion is 38%, 50% and 45% over modified JCA semi-coke (by 2%, 5% and 10% H_2O_2 modification) respectively, which is 5%, 17% and 12% higher than that over non-modified JCA semi-coke (33%). CH_4 and CO_2 conversions are about 6% and 2% higher than that non-modified SMB semi-coke over 5% H_2O_2 modified SMB semi-coke respectively. CH_4 and CO_2 conversions change less than 5% that non-modified HCL semi-coke under 5% H_2O_2 modified HCL semi-coke. Under the same modified conditions, catalytic activity of JCA semi-coke is greatly improved after modification by H_2O_2 . Before and after H_2O_2 modification, catalytic activity of HCL semi-coke changes relatively less.

In addition, it can be seen from the figure that CH_4 has a better conversion results than CO_2 over H_2O_2 modified semi-coke, and the optimal modification concentration of H_2O_2 is 5%. This is due to that the contents of alkaline functional groups increase significantly after the semi-coke experienced hydrothermal reaction in high temperature and high pressure H_2O_2 , as shown in Table 1. On the one hand, the alkaline functional group is favorable for CO_2 adsorption and capture; on the other hand, the alkaline functional group can dissociate unsaturated oxygen to eliminate carbon deposition in the process of reforming reaction, thereby

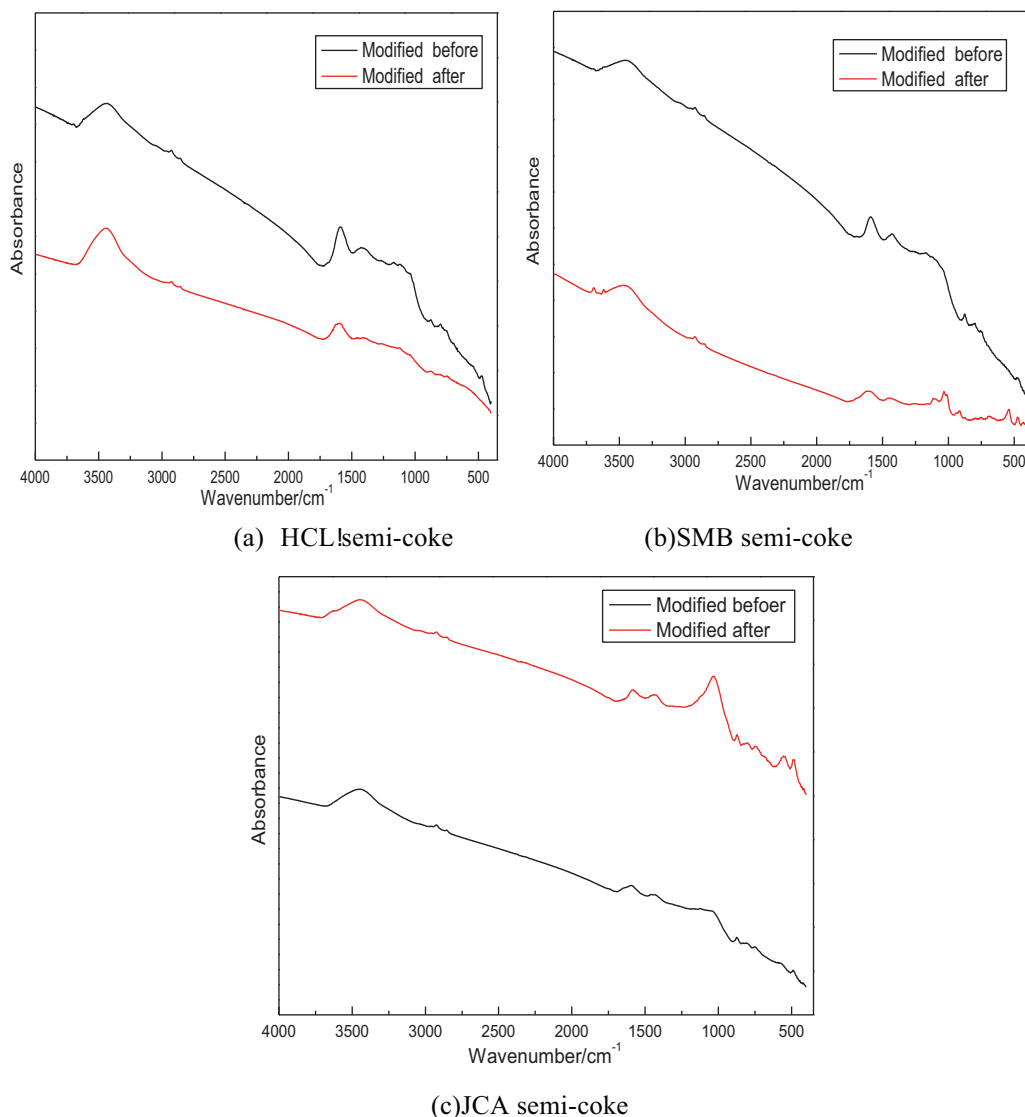


Fig. 5. FTIR of semi-coke before and after modified.

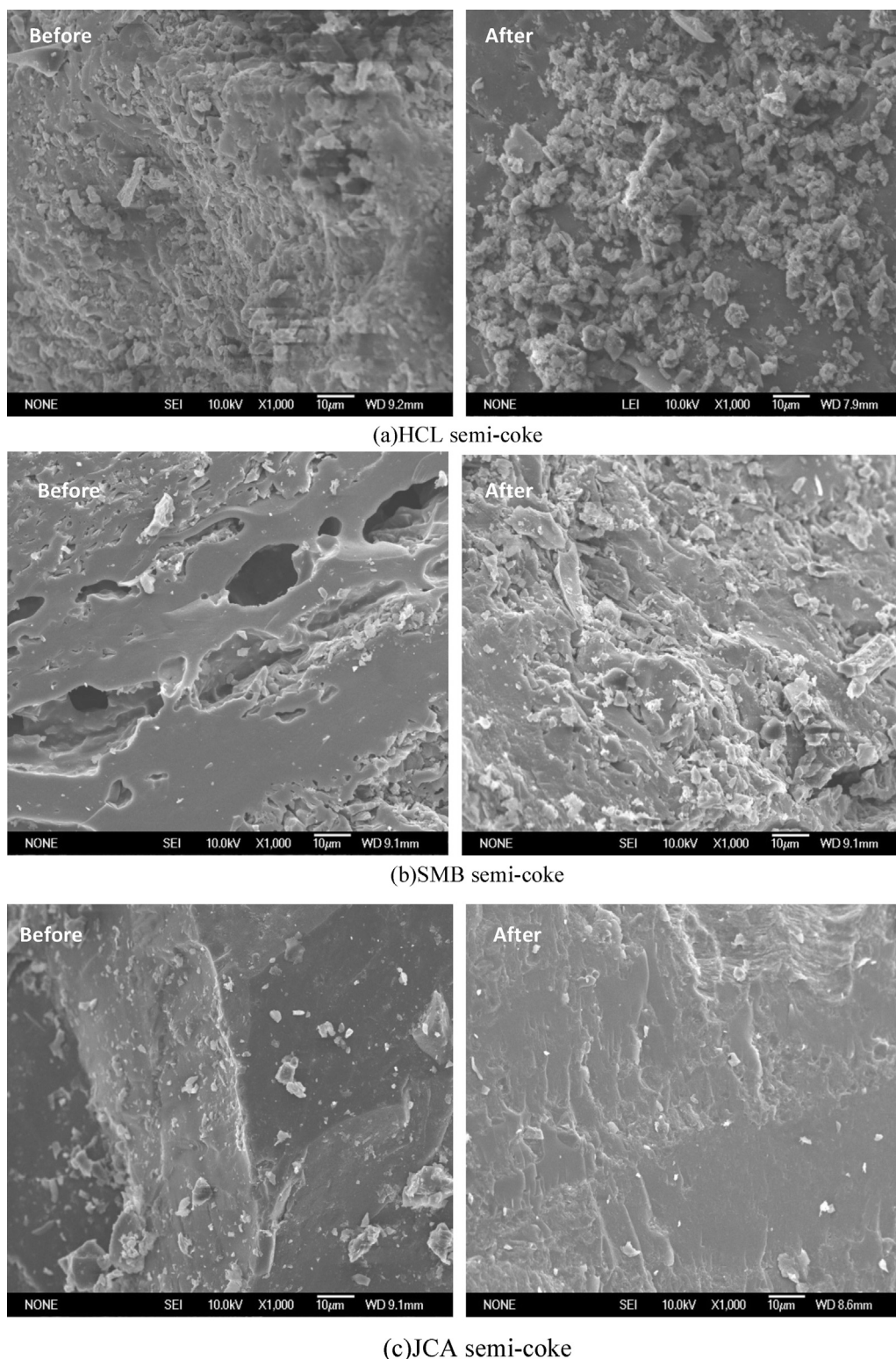


Fig. 6. SEM image of semi-coke before and after modification.

improvement in the resistance to carbon deposition and stability [28,42–46]. In addition to that, H_2O_2 modification can increase the specific surface area of the carbon materials, as shown in Table 2. Therefore, the contact area time between reaction gas and semi-coke are increased, which is beneficial to CH_4 reforming with CO_2 [47]. It was also found that the higher concentration of H_2O_2 is of benefit to the catalytic activities, but too high concentration of H_2O_2 causes strong oxidation with semi-coke, and damaged the

micro-porous semi-coke, surface area decrease [48]. Thus, the contact time of the reaction gas with semi-coke decreases, the catalytic activity decreases.

3.2.2. Effects of modified temperature

According to Fig. 2, CH_4 and CO_2 conversions increase with the modified temperature. The results show, at 240 min, that CH_4 conversion is 45%, 48% and 50% over modified JCA

semi-coke (by 200 °C, 250 °C and 300 °C H₂O₂ modification) respectively. CO₂ conversion is 53%, 50% and 55% over modified JCA semi-coke (by 200 °C, 250 °C and 300 °C H₂O₂ modification), respectively. Under the modified SMB semi-coke and HCL semi-coke, the change of CH₄ and CO₂ conversions is the same. With the rise of modified temperature, thermal decomposition of H₂O₂ and oxidation of semi-coke become stronger, the free radical entering into the internal semi-coke become more. These are favorable for the increase of semi-coke oxygen-containing functional groups, and are conducive to the semi-coke activation. The higher modified temperature corresponds with stronger reaming effect of H₂O₂. Meanwhile, modification with higher temperature can dissolve some organic matter and tar contained on the semi-coke surface, which increase the specific surface area and the contact time between the reaction gas and semi-coke, and improve the reaction efficiency. In addition, the impact of modified temperature on semi-coke is associated with the boiling point of the additives (hydrogen peroxide) [30,48,49]. When the modified temperature gets close to the boiling point of hydrogen peroxide, the activation effect is optimum [30,31,48,49].

3.2.3. Effects of modified pressure

According to Fig. 3, when the modified pressure is from 4 MPa up to 8 MPa, the result of the analysis shows that CH₄ and CO₂ conversion increase first and then decrease. At 240 min and under the SMB semi-coke, when the modified pressure is increased from 4 MPa to 6 MPa, CH₄ and CO₂ conversions have improved to 74% and 80% (72% and 80% under 4 MPa), respectively. When the modified pressure is further increased to 8 MPa, CH₄ and CO₂ conversions are reduced, down to 71% and 79%. It is mainly because higher pressure could enhance H₂O₂ oxidation, which can be increase of the content of the alkaline groups and oxygen containing functional groups on the semi-coke surface, and the semi-coke catalytic activity increases. Secondly, pressure increase can realize oxidation hydrolysis of ash and organic volatiles jammed in the semi-coke pore, increase the specific surface area, and improve the reforming reaction efficiency. However, if the pressure is too large, exceeding the mechanical strength of semi-coke, some micro-pores and mid-pores will be damaged. Therefore, the specific surface area of catalyst reduces, and the reaction conversion decreases.

3.2.4. Effects of modified time

According to Fig. 4, prolong of the modified time exerts little effect on improvement of the catalytic activity. The results show, at 240 min, that CH₄ conversion is 50%, 50% and 51% over modified JCA semi-coke (by 2 h, 3 h and 4 h H₂O₂ modification) respectively. CO₂ conversion is 55%, 55% and 56% over modified JCA semi-coke (by 2 h, 3 h and 4 h H₂O₂ modification), respectively. Meanwhile, under the actions of SMB semi-coke and HCL semi-coke, conversion tendency of CH₄ and CO₂ is the same. This is possible because the decomposition of H₂O₂ is relatively fast at the high temperature. H₂O₂ decomposition achieves a balance after 2 h high temperature and high pressure modification [30,31,48,49]. The continuously extending the modified time does not an obvious improvement in semi-coke activity. Optimized modified time is 2 h.

4. Conclusions

Three kinds of different semi-cokes are modified by H₂O₂ hydrothermal activation under high temperature and high pressure. After modification, the semi-coke surface is changed: HCL semi-coke and SMB semi-coke show cavernous structure; JCA semi-coke shows potholed surface compared with before modifi-

cation. In addition, their specific surface areas and pore volumes increase after modification. It indicates that high pressure H₂O₂ modification has a certain reaming effect on semi-coke, and H₂O₂ modification can open the jammed pores in the semi-coke. According to the results of Boehm titration, the content of alkaline and acidic functional groups in three kinds of modified semi-coke increases, and the content of alkaline functional groups increases obvious than that of the acidic functional groups. FTIR characterization finds no new functional group's characteristic peak, but strength of some peak enhances obviously. The content of -OH absorption peak of HCL semi-coke at 3444 cm⁻¹, carboxyl C=O at 1598 cm⁻¹, and aliphatic ether, cyclic ether and other organic functional groups at 1023 cm⁻¹ in the modified SMB semi-coke and JCA semi-coke increases significantly. The optimized modified condition is: H₂O₂ concentration of 5%, modification temperature of 300 °C, a pressure of 6 MPa and time of 2 h.

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