Effect of Thermal Extraction on Coal-Based Activated Carbon for Methane Decomposition to Hydrogen

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ABSTRACT: After coal is treated by thermal solution of solvent, a certain amount of thermal solution oil and residue can be obtained, and the macromolecular network structure in coal can also be relaxed. These will inevitably affect the emission of harmful gases and distribution of the pore structure when the residue is made into activated carbon (AC). In this paper, the effects of thermal solution pretreatment on the microcrystalline structure, surface properties, pore structure of resultant ACs at different temperatures, and their catalytic performances in methane decomposition to hydrogen were investigated. The results show that the surface oxygen-containing functional groups of the residue-based ACs are changed, and the specific area of ACs increases from 1730 to 2652 m²/g with the increase in activated temperature. The pore diameter distribution of ACs also is changed. In the process of methane decomposition to hydrogen, the residue-based ACs show higher catalytic activity than coal-based ACs. AC-1123-1 and AC-1123 show the best stability, while AC-823-1 has the highest initial activity. With the increase in activated temperature, residue-based ACs show higher activity and stability, and partial fibrous carbon is deposited on the surface of ACs after the reaction. It is thought that increased mesoporosity is beneficial to the catalytic activity and stability of AC in methane decomposition to hydrogen, and the reduction of surface oxygen-containing functional groups contribute to the formation of fibrous carbon on the surface of AC after the reaction.

1. INTRODUCTION

Hydrogen is not only an important raw material in chemical production but also a kind of clean fuel. Many scholars were committed to obtaining hydrogen from hydrocarbons or water by means of thermochemistry and electrochemistry.¹ Up to now, steam methane reforming (SMR) technology is generally used to produce hydrogen in industrial production. However, a large amount of carbon dioxide (CO₂) will be generated in this process. In order to remove the CO₂, purification devices must be added, which will lead to a significant rising cost of hydrogen production.²

Catalytic methane decomposition (CMD) is a hydrogen production method with simple process and byproduction of carbon materials. This process has attracted the attention of researchers because there is no generation of CO and CO₂. Many metal catalysts (such as Fe,³–⁵ Co,⁶–⁹ Ni,¹⁰–¹³ etc.) had been applied in the process of transformation and had been proven by studies that these catalysts can effectively promote the methane decomposition to hydrogen. However, carbon deposition is easy to be generated in the process, which leads to the deactivation of metal catalyst. The regeneration cost of the catalyst is often expensive, and this process will release a large amount of CO₂ again. These factors will greatly limit the industrial application of this technology. In view of metal catalyst’s disadvantage, carbon materials are considered to be most alternative catalyst. Compared with the metal catalyst, they are low cost and have strong characteristics such as high temperature resistance and high sulfate resistance, and the used catalyst of carbon materials can be directly used in the preparation of high specific volume electrodes and so on. Besides, it may also avoid the high cost of catalyst activation and large production of CO₂.¹⁴,¹⁵ Muradov¹⁶ studied the catalytic effect of 30 different carbon materials, including activated carbon, carbon black, graphite, diamond, carbon
fiber, carbon nanotube, etc., and found that the catalytic activity of carbon materials is significantly related to their source, structure, and surface area. Most researchers stated that there is no linear relationship between the surface area of carbon materials and its initial catalytic activity.\textsuperscript{17–20} It is generally believed that mesoporous\textsuperscript{21,22} and hierarchical porous carbon materials\textsuperscript{23} usually show higher and more stability in CMD than microporous carbon materials. The properties of raw coal greatly affect the catalytic activity of coal-based activated carbons (ACs). Wei et al.\textsuperscript{24} studied the catalytic performance of AC from raw coal of different ranks, and the results showed that coal coke from low-rank coal had better catalytic activity. Bai et al.\textsuperscript{25} also believed that the catalytic activity of lignite coke was better than that of bituminous coal and anthracite. These results show that it is a feasible scheme to use appropriate methods to pretreat raw coal so as to obtain suitable AC for methane decomposition to hydrogen.

The thermal solution of solvent stood out from many methods of improving quality and utilization of coal because of its mild reaction condition, high energy conversion rate, efficient multilevel utilization of coal, and so on. However, in the process of thermal solution of solvent, most researchers paid more attention to promoting the efficiency of extraction and utilization of extraction. In fact, the resource utilization of a large number of extraction residues is also a very worthy research direction. Li et al.\textsuperscript{26} studied the gasification performance of eight kinds of thermal solution upgrading low-rank coal coke, and the results showed that the gasification performance of thermal solution upgrading coal coke was better than that of raw coal coke. Cai\textsuperscript{27} studied that thermal solution upgrading coal was prepared from mesoporous carbon by using the method of CO\textsubscript{2} physical activation and KOH chemical activation. The results showed that the surface area and pore volume of mesoporous carbon prepared by the extracted residue were better than that prepared by raw coal under the same condition. The mesoporosity of carbon materials was the highest at 800 °C and a KOH/extracted residue mass ratio of 2:1, and the highest specific surface area was 2100 m\textsuperscript{2}/g. This showed that the thermal solution pretreatment of coal can improve the interaction between the precursor and activator in the carbonization and activation stage. However, there are few reports on the influence of thermal solution pretreatment of coal on the surface and chemical properties of ACs prepared at different temperatures and catalytic methane decomposition to hydrogen.

In view of this, the raw coal and extraction residue of raw coal were used to prepare ACs at different activation temperatures. The effects of thermal solution pretreatment on structure and surface properties and reactivity of ACs for methane decomposition to hydrogen were studied.

2. EXPERIMENTAL SECTION

2.1. Preparation and Thermal Solution of Coal Samples. Datong raw coal (DT), a long-flame coal from China, was used as the precursor. The DT was crushed, ground, and sieved to a size less than 0.5 mm. Then, the DT was put into a vacuum drying oven (383 K) for 2 h and subsequently gathered in a dryer for standby.

Five grams of DT and 150 mL of benzene solvent were mixed and put into a 500 mL high-pressure reaction kettle. The bolts of the reaction kettle were fixed in, and then a certain amount of nitrogen atmosphere was repeatedly accessed to the reaction kettle to discharge internal air. A 4 MPa nitrogen atmosphere was injected in the kettle, and the valve was closed. After the agitator blade was opened, the reaction kettle was heated to 563 K at the heating rate of 5 K/min, and the final pressure was kept at 9 MPa. When thermostatic mixing was up to 2 h, the kettle was cooled to room temperature, and all thermal extracted products were taken out. The thermal extracted products were cleaned with ethanol solvent in a Soxhlet extractor. The liquid products were separated by vacuum distillation to get the thermal extracted oil and ethanol solvent. The solid products were washed with hot water to get the thermal extracted residue of DT (RR). This process was different from the existing thermal solution pretreatment process.\textsuperscript{28} The following aspects were described: (i) The selected temperature was lower than the temperature of the general thermal solution process (633 K), which was before the pyrolysis temperature of coal; (ii) benzene (\(T_c = 562.1 \, K, P_c = 4.83 \, \text{MPa}\)) was in a supercritical state under the conditions of selected temperature and pressure; and (iii) nearly all ash contents were retained in the RR because of its positive role on the preparation of AC.\textsuperscript{29}

2.2. Preparation of AC. DT or RR was mixed with activator KOH (Tianjin Damao Chemical Reagent Factory) at a mass ratio of 4:1. A certain amount of deionized water and ethanol were added to the mixture and mechanically stirred in a crucible for 24 h. The crucible was placed in a vertical carbonization furnace, and the nitrogen flow rate was set at 200 mL/min. The process of carbonization was set as follows: the sample was heated from 298 to 473 K within 35 min and was held for 1 h. Then, it was sequentially heated to the target temperatures (823, 923, 1023, and 1123 K) with a 5 K/min heating rate and was held for 2 h. The reaction equipment was cooled to room temperature with 50 mL/min nitrogen, and the AC was collected. The carbonized material was soaked in 3 M hydrochloric acid for 24 h and was mixed by a magnetic blender for 6 h. In the end, the AC was washed with deionized water and filtered to neutral, and then it was dried under 423 K for 2 h. The AC was prepared from DT at an activation temperature of 823 K; AC-823-1 meant the AC prepared by RR. For example, AC-823 meant the AC prepared from DT at an activation temperature of 823 K; AC-823-1 meant the AC prepared by RR at an activation temperature of 823 K.

2.3. Structural Characterization of Activated Carbon. The structure properties of ACs were determined by an ASAP 2420 automatic nitrogen adsorption instrument at 77 K. The surface area and pore structure information were calculated by BET (Brunauer–Emmett–Teller) and BJH (Barrett–Joyner–Halenda) methods. The micropore volume (\(V_{\text{micro}}\)) and microporosity were calculated by the \(t\)-plot method and the ratio of \(V_{\text{micro}}/V_t\). The X-ray diffraction (XRD) patterns of ACs were measured by a D/MAX-2400 X-ray diffractometer with Cu K\(\alpha\) radiation at 30 kV and 30 mA. The surface functional group structures of the ACs were measured by a Thermo Fisher Fourier transform infrared analysis spectrometer. The properties of DT and RR were measured by industrial and elemental analyzers. The element compositions of DT and RR were measured by an XRF instrument of SR3400 type made in Germany. The surface morphology of ACs was measured by a scanning electron microscope (Zeiss EV018).

2.4. Methane Cracking Reaction. The methane cracking reaction was conducted in a vertical fixed-bed reactor at 1123 K and atmospheric pressure. First, 0.2 g of AC was filled in the
reactor, and then nitrogen atmosphere with a flow rate of 40 mL/min was introduced and heated to 1123 K. The mixture gas of 10 mL/min methane and 40 mL/min nitrogen was introduced to replace the pure nitrogen. The total volume hourly space velocity were set at 15,000 mL/(h·gcat). The gas products were analyzed by an online gas chromatograph (Techcomp, GC7890II) equipped with a thermal conductivity detector running at 423 K (5 Å molecular sieve filled column) and a hydrogen flame detector running at 373 K (GDX502 filled column). Methane conversion and hydrogen productivity were calculated by the following formulas:

\[ X_{CH_4} = \frac{F_{CH_4\text{in}} - F_{CH_4\text{out}}}{F_{CH_4\text{in}}} \times 100\% \]  

\[ Y_{H_2\text{out}} = \frac{2(F_{CH_4\text{in}} - F_{CH_4\text{out}})}{m} \]

where \( X, Y, F, \) and \( m \) represent the conversion rate of methane (%), hydrogen productivity (mmol/g·min), gas flow rate (mmol/min), and catalyst mass (g), respectively.

3. RESULTS AND DISCUSSION

3.1. Effect of Thermal Solution Pretreatment on Properties of ACs at Different Activation Temperatures.
When DT was treated by the thermal solution of solvent, a certain amount of thermal extraction oil and RR could be obtained. The thermal solubility could reach 26.2%. The industrial analysis, elemental analysis, and ash content analysis of DT and RR are shown in Table 1. Obviously, the volatiles and ash content of RR decrease by 2.6% and 3.7%, respectively, and the content of fixed carbon increases by 2.6%. The corresponding elemental analysis also shows that the contents of carbon increase a little, but the content of other elements decrease slightly. Ash analysis shows that all of the main elements, such as Si, Al, Fe, Ca, and Mg, decrease slightly. This shows that only a part of small molecules in RR is removed, and the macromolecular structure in it rarely has been influenced. Most of the ash has been retained in RR.

In order to further study the effects of thermal solution pretreatment on the ACs prepared by KOH activation, the ACs were prepared at different carbonization temperatures (823, 923, 1023, and 1123 K) for DT and RR. The yields of ACs prepared at different temperatures are shown in Table 2. As can be seen from Table 2, the yields of ACs produced by DT and RR at different temperatures gradually decrease with the increase in temperature; especially, the yields of AC-1123 and AC-1123-1 are only 30.8% and 7.14%, respectively. This indicates that the thermal solution pretreatment of DT can make the structure of coal looser, thus promote the reaction between activator KOH and carbon elements, and increase the consumption of RR.

The structure and properties of ACs prepared at different temperatures are shown in Figure 1 and Table 2. As can be seen from Figure 1, the isotherms of AC-823, AC-923, and AC-823-1 are nearly parallel to the axis of P/P₀, which show that these samples are multi-micropore materials. The isotherms of other ACs exhibit a type IV curve, which show that these samples contain many mesoporous materials. The pore diameter profiles of ACs show that the mesopores are mainly concentrated in 3–5 nm. The pore structure parameters of ACs are shown in Table 2. It can be found that the specific surface area and pore volume of AC-823-1, AC-923, and AC-923-1 are higher than those of AC-823, AC-923, and AC-1023, while the specific surface area and pore volume of AC-1123-1 are lower than those of AC-1123. This indicates that thermal solution pretreatment can promote the increase in specific surface area and pore volume of ACs. When the temperature reaches 1123 K, excessive reaction can cause partial pores of AC to collapse, resulting in the decrease in surface area and pore volume. The Vₘic/Vₜ of AC-823-1 and AC-1023-3 are higher than those of AC-823 and AC-1023, indicating that the thermal solution pretreatment mainly promote the raising of micropores at 823 and 1023 K. However, the Vₘic/Vₜ of AC-923-1 is lower than that of AC-923, indicating that the thermal solution pretreatment mainly promote the rising of mesopores at 923 K. The Vₘic/Vₜ of AC-1123-1 and AC-1123 are both 0, indicating that pores of AC-1123-1 and AC-1123 are all mesoporous. In summary, the thermal solution pretreatment further promotes the opening pore of ACs at different temperatures, and the distribution of pore has an important correlation with temperature.

The infrared spectra of ACs prepared at different temperatures are shown in Figure 2. As can be seen from Figure 2, The ACs under the same carbonization condition have the same kind of surface groups. The broad band from 3000 to 3400 cm⁻¹ can be assigned to the O–H stretch for hydroxyl groups. This band can be found at all samples; however, the intensities of the bands in ACs prepared by RR decrease with increasing carbonization temperature. This indicates that the contents of the hydroxyl groups in DT could partially be removed by the thermal solution pretreatment. The band at 2970 cm⁻¹ can be attributed to C–H symmetric and asymmetric stretching vibration. The intensity of the bands in ACs prepared by RR is less. This indicates that the contents of aliphatic groups in DT could be removed by the thermal solution pretreatment. The broad band from 900 to 1300 cm⁻¹ can be attributed to alcohol and phenolic C–O bond stretching vibration and O–H bending vibration, and the intensities of the bands in ACs prepared by RR decrease with increasing carbonization temperature. This indicates that the contents of alcoholic and phenolic groups in DT could partially be removed by the thermal solution pretreatment. In general, the bands at 1660 and 1719 cm⁻¹ are associated with C=O and O–H stretching vibration, which are the characteristic peaks for carboxylic acid functional groups. The intensity of the band has a negligible change in all the samples. The bands at 500–600, 1000–1100, and 3600–3700 cm⁻¹ are attributed to the characteristic peaks of minerals.

However, the ACs do not show these absorption peaks, indicating that the minerals in ACs are mostly removed by hydrochloric acid in the preparation process. It can be concluded that the thermal solution pretreatment may further remove alcoholic and phenolic groups in DT, which leads to the decrease in these groups in ACs prepared by RR at different temperatures. The minerals in ACs are mostly removed by hydrochloric acid in the preparation process.

The XRD patterns of ACs prepared from DT and RR are shown in Figure 3. It is generally believed that the peaks of carbon materials are 26° and 44°, corresponding to the C(002) and C(101) crystal planes, respectively. The intensity or area ratio of the two diffraction peaks reflects the order degree of carbon graphite layers, and the lower ratio represents the more ordered structure. The XRD peak intensity C(101)/C(002) ratios of ACs prepared from DT and RR are shown in Table 3. It can be seen that C(101)/C(002) ratios of AC-823 and AC-923 are lower than those of AC-823 and AC-923, indicating that the AC-823 and AC-923 have a higher graphitization degree and a more ordered structure. The C(101)/C(002) ratio of AC-1023-1 is higher than that of AC-1023-3, indicating that the AC-1023-1 has a lower degree of
graphitization and a more disordered structure. The C(101)/C(002) ratios of AC-1123-1 and AC-1123 are the same. In summary, it can be concluded that the effect of thermal solution pretreatment on the crystal structure is related with the carbonization temperature.

The SEM analysis of ACs prepared by DT and RR at different temperatures are shown in Figures 4 and 5, respectively. It is clearly observed that the carbon layer of the ACs from RR becomes thinner as the carbonization temperature increases, especially those of AC-923-1 and AC-1123-1 as seen in Figure 5b,d, which have almost hyaline morphological characteristics. The surface of ACs from RR becomes bumpier than that of ACs from DT, which may be caused by the consumption of carbon by the reaction between coal and KOH.

3.2. Effect of Thermal Solution Pretreatment on Methane Decomposition to Hydrogen. The effect of thermal solution pretreatment on the ACs for methane decomposition to hydrogen is shown in Figure 6. It can be found that ACs prepared by RR exhibit better catalytic stability and initial activity than ACs prepared by DT. The initial methane conversion has no direct relationship with the increasing surface area of the ACs prepared by DT and RR at different carbonization temperatures in this work. All the ACs prepared from RR have higher initial activity than the ACs from DT, which may be caused by the consumption of carbon by the reaction between coal and KOH.

Table 3. Intensity Ratio of C(101) to C(002) in XRD from Activated Carbon of the Raw Coal and Thermal Extracted Coal at Different Temperatures

| sample          | AC-823 | AC-823-1 | AC-923 | AC-923-1 | AC-1023 | AC-1023-1 | AC-1123 | AC-1123-1 |
|-----------------|--------|----------|--------|----------|---------|-----------|---------|-----------|
| intensity ratio of C(101) to C(002) | 0.52   | 0.51     | 0.54   | 0.47     | 0.45    | 0.47      | 0.54    | 0.54      |
on the initial activity and the stability of ACs, which are associated with the change of chemical properties and mesoporosity of ACs. The time dependence of hydrogen production rate is similar to that for methane conversion. This is mainly because the methane is mainly converted to hydrogen and solid carbon, and only very small amounts of ethylene and ethane are generated in the process of methane decomposition to hydrogen for ACs. The selectivity of hydrogen in this work is greater than 98%; thus, the change of the hydrogen selectivity and the yield of ethane and ethylene are no longer discussed.

3.3. Carbon Fiber Formation. The SEM analyses of spent ACs are shown in Figure 7. As can be seen from the figure, a certain amount of octopus fibrous carbon appear on the surface of AC-823, AC-923, and AC-1023, while a large amount of fibrous carbon appear on the surface of AC-1123. A large amount of fibrous carbon appear on the surface of AC-823-1, AC-923-1, and AC-1023-1, while a small amount of octopus fibrous carbon appear on the surface of AC-1123-1. Generally, fibrous carbon can be formed on the surface of metal catalyst during the process of methane decomposition to hydrogen. The main reason is that the driving force formed by the significant carbon concentration gradient on the front and rear surfaces of metal particles made the carbon deposit grow as fibers. However, it has been rarely reported that carbon for methane decomposition to hydrogen forms fibrous deposits on the surface. Some studies suggested that residual minerals in carbon (generally 1–12 wt %) did not lead to the formation of fibrous carbon deposits. Zhang et al. believed that the low concentration of oxygen-containing functional groups on the surface of carbon play a key role in the formation of fibrous carbon. It can be seen from the above results that the amount of oxygen-containing functional groups of ACs prepared by RR at different temperatures decreases, resulting in more fibrous carbon on the surface of AC-823-1, AC-923-1, and AC-1023-1. The amount of fibrous carbon produced on the surface of AC-1123-1 is less than that on the surface of AC-1123, which is possibly caused by the average pore size of AC-1123-1 becoming larger.

4. CONCLUSIONS

The ACs were prepared from DT and RR at different carbonization temperatures and used for methane decomposition to hydrogen. The amount of oxygen functional groups in ACs prepared by RR is lower than that in ACs prepared by DT, while the number of specific surface area and mesoporous is higher. The ACs prepared by RR exhibit better catalytic stability and initial activity than ACs prepared by DT. The AC-1123-1 and AC-1123 show the best reaction stability in the process of methane decomposition to hydrogen, while AC-823-1 shows the highest initial reaction activity. More carbon fibers appear on the ACs prepared by the RR surface after the reaction (except for AC-1123-1).

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Figure 6. (a) Methane conversion and (b) hydrogen productivity in methane decomposition over ACs from raw coal and thermal extracted coal at different temperatures.

Figure 7. SEM images of spent ACs over methane decomposition. (a–d) Spent ACs from raw coal. (e–h) Spent ACs from thermal extracted coal.
Notes
The authors declare no competing financial interest.

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