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Effect of air pre-oxidization on coal-based activated carbon for methane decomposition to hydrogen

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ABSTRACT

Oxidization is considered to be an indispensable step for coals with thermoplastic properties to act as the precursor of activated carbon (AC). In this work, the effect of oxidization conditions of coal on the texture and surface properties of resultant ACs and their catalytic performances in decomposition of methane to hydrogen were investigated. The results show that the surface oxygen containing groups of the resultant ACs changed, the surface area of ACs increases from 1892 m²/g to 2407 m²/g, and the mesoporosity significantly increases after the precursor coal is pre-oxidized. The ACs from oxidized coals show higher catalytic activities in methane decomposition reaction than that from raw coal. The ACs prepared from oxidized coal at 373 K show the best stability while the AC from the oxidized coal at 573 K for 4 h exhibits the highest initial activity among the ACs. Additionally, the oxidization time has a negative effect on initial activities but little positive influence on stability of ACs when the precursor is oxidized at 373 K. It is thought that the increased mesoporosity is beneficial to the catalytic activity and stability of AC in methane decomposition to hydrogen.

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Introduction

Methane decomposition is considered to be a simple and promising process for hydrogen production without by-products CO and CO₂, which can avoid additional water gas shift and gas separation required in traditional hydrogen production processes. Since the non-catalytic methane decomposition need a high temperature (more than 1473 K) for a reasonable hydrogen production, many researchers introduced metal catalysts, such as Fe [1–4], Co [5,6] and Ni [3,7–12], into the process to decrease the reaction

temperature. However, metal catalysts are easily deactivated because of carbon deposition and the regeneration of the metals is costly, moreover CO₂ will be released again. Contrarily, carbon material, especially activated carbon (AC) and carbon black, has been reported as an effective catalyst for methane decomposition because of its lower cost and higher stability against deactivation [13–16]. And the regeneration of the catalysts by burning carbon on the catalysts surface is unnecessary for the process over carbon materials. Muradov [13] investigated 30 different samples of carbon material, including ACs, carbon blacks, graphite, diamond, carbon fibers and carbon nanotubes and found that the

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catalytic activity of carbons was mostly influenced by their origin, structure and surface area. As for the coal-based AC, the properties of coal significantly affect the catalytic characteristic of ACs. Wei et al. [17] used coal chars from different rank coals as catalysts in methane decomposition. The result showed that the chars from lower rank coal had better catalytic effect. Bai et al. [18] considered that the lignite char has a much higher activity in methane decomposition than bituminous and anthracite ones. Thus, it seems to be a feasible way to obtain suitable AC by changing the properties of raw coals.

Pre-oxidation of carbonaceous raw material was proved to be an important step for preparation of coal-based ACs. The oxidation of precursor significantly changed the properties of resultant AC, especially the pore structure and surface area. Ruiz et al. [19] studied the porous structure of pyrolysis chars from raw and oxidized coal and believed that the pre-oxidation of coals with thermoplastic properties can reduce or eliminate the plastic behavior and make the resultant char develop a suitable porous network during the carbonization step, which is beneficial to a suitable porous structure of AC. Teng et al. [20] also found that the carbonization of the oxidized coal exhibits a broader volatile evolution with respect to temperature, and the resultant char from the oxidized coal has larger specific surface area. Clearly, oxidation treatment improved the interaction between the precursors and activating agent during carbonization or activation step. Thus, the pretreated coal shows an increase in specific surface area and pore volume of the resultant AC. However, few papers were reported on the effects of pre-oxidation of coals on the surface structure and chemistry, and the catalytic characteristics in methane decomposition to hydrogen of the resultant ACs.

In this work, pre-oxidized coal was used to prepare ACs, and their catalytic performances in methane decomposition to hydrogen were investigated. The effect of oxidation temperature and time on structure, surface chemical and activity of resultant ACs was also investigated.

Experimental

Materials

Shenmu coal, a bituminous coal from China, was used as the precursor. The coal was first crushed and sieved to a size fraction of 150–250 μm , and then put into muffle furnace and oxidized at different temperature (373 K, 473 K, 573 K) for different time (4 h, 8 h, 12 h) in air. The oxidized coal was expressed as the corresponding oxidization condition, for example, when the coal was oxidized at 373 K for 4 h, the oxidized coal was named as SM-373-4. The oxidation degree was analyzed by measuring the oxygen content in the coals.

Preparation of carbon product

The raw or pre-oxidized coal was physically mixed with KOH (Shantou Xilong Chemical Technology Co., China) in a mass ratio of 1:2. Thereafter, the mixture containing 5 g coal and 10 g KOH was carbonized in a horizontal furnace under

nitrogen atmosphere with a flow rate of 110 mL/min. The carbonization procedures were as follows: the samples were heated from 298 K to 473 K within 40 min and held for 1 h, then heated to 673 K with a heating rate of 5 K/min and kept for 1 h, further to 873 K with a heating rate of 5 K/min and also held for 1 h, finally to 1173 K within 300 min and kept for 2 h before cooling down, followed by washing, filtrating and drying in sequence. The obtained AC was expressed as AC-T-t, here, T is the oxidization temperature, t refers to oxidization time. For example, AC-373-4 means that the AC was prepared by using the oxidized coal at 373 K for 4 h as precursor.

Characterization

The textural properties of the samples were measured by N_2 adsorption at 77 K with a physical adsorption apparatus (ASAP 2420). The surface area and pore information were obtained by the BET and BJH methods. The micropore volume (V_{mic}) and microporosity were calculated by using t-plot method and the ratio of V_{mic} to total pore volume (V_t), V_{mic}/V_t . X-ray diffraction (XRD) patterns of the samples were measured by a D/MAX-2400 with a Cu $K\alpha$ radiation at 30 kV and 30 mA.

The oxygen containing functional groups on the carbons were investigated by Fourier-transform infrared (FTIR) spectroscopy (EQUINOX55 FTIR spectrometer). The properties of raw and oxidized coals were determined by proximate and ultimate analyses. Thermogravimetric (TG) analysis of the samples was conducted under a N_2 flow of 60 mL/min in a TG analyzer (Mettler Toledo TGA/SDTA851^e) to investigate the pyrolysis characteristics of raw and oxidized coals. TG-MS was carried out under an argon flow of 60 mL/min in a TG analyzer (Mettler Toledo TGA/SDTA851^e) coupled with a quadrupole mass spectrometer (ThermoStarTM) to investigate the evolution of gaseous products.

Methane decomposition reaction

Methane decomposition was carried out in a vertical fixed-bed reactor at 1123 K and atmospheric pressure. The reactor charged with 0.2 g AC catalyst was first heated to 1123 K under nitrogen atmosphere with a flowrate of 40 mL/min, and then the mixture gas of 10 mL/min methane and 40 mL/min nitrogen was introduced instead of pure N_2 . The total volumetric hourly space velocity was set at 15,000 mL/(h \cdot g_{cat}). The gas products were analyzed by an online gas chromatograph (Techcomp, GC7890II) equipped with a thermal conductivity detector (packed with 5A molecular sieve) performed at 423 K and a flame ionization detector (GD502 packed column) performed at 373 K. Methane conversion and hydrogen productivity were calculated by the following formulas:

$$X_{\text{CH}_4} = (F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) / F_{\text{CH}_4,\text{in}} \times 100\% \quad (1)$$

$$Y_{\text{H}_2,\text{out}} = 2(F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) / m \quad (2)$$

where X, Y, F, m represents the conversion (%) of CH_4 , hydrogen productivity (mmol/(g \cdot min)), gas flowrate (mmol/min) and catalyst mass (g), respectively.

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