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Research article

Effect of $Ca(NO_3)_2$ addition in coal on properties of activated carbon for methane decomposition to hydrogen

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A B S T R A C T

Activated carbon (AC) was prepared from a subbituminous coal with addition of $Ca(NO_3)_2$ by KOH activation, and used for catalytic methane decomposition to produce hydrogen. The effects of calcium addition amount on the structure and catalytic performance of the resultant ACs were investigated. As the addition of $Ca(NO_3)_2$, the surface area and pore volume of ACs increase significantly compared with that of AC without addition, especially the mesoporous surface area improved from 480 m^2/g to 1119 m^2/g. Almost hyaline structure of carbons are obtained when a high amount of calcium is added into the coal. The addition of calcium in coal leads to the significant increase of methane conversion over the resultant carbon catalysts, and when the calcium addition amount is 15 wt%, the prepared AC has the highest mesoporous surface area and the best stability. No direct relationship was found between specific surface area and the activity of carbons, but the mesopores benefit the stability of ACs in methane decomposition. Carbon fiber was produced on AC from the coal with addition of calcium compared with the aggregated carbon on that from coal without addition of calcium.

1. Introduction

Catalytic methane decomposition (CMD) is considered as a simple and promising process for hydrogen production because no by-products CO and CO_2 are produced, thus extra water-gas shift reaction and gas separation required in traditional hydrogen production processes can be avoided. Compared with metal catalysts, such as Fe [1–3], Ni [4–7] and Co [8–10], which is easily deactivated by the carbon deposition, carbon catalysts, especially activated carbon (AC), received considerable attention because of their high surface area, pore volume, better tolerance to sulfur and other poisonous impurities in the feedstock and resistance to higher temperature in CMD [11–16]. AC has a higher initial activity in methane decomposition but poorer stability, while the carbon black has a lower initial activity but better stability [11,12]. Many researches have reported that the activity of carbon materials strongly depended on their surface chemistry and texture properties [15,17–19]. Moliner et al. [17] claimed that the initial rate of methane decomposition was related mainly to the concentration of oxygen functional groups on the catalyst surface. Serrano et al. [20] reported for the first time that ordered mesoporous carbons CMK-3 and CMK-5 have higher and more stable activity than commercial AC and carbon black catalysts. Shilapuram et al. [21,22] also studied the catalytic performance of ordered mesoporous carbon nanorods CMK-3 and ordered mesoporous carbide-derived carbon DUT-19. The results showed that DUT-19 with higher surface area and higher pore volume catalytically outperforms CMK-3 in methane decomposition. However, the poor activities of traditional carbon catalysts and the expensive template of ordered mesoporous carbons leave much to be desired.

In our previous work, Zhang et al. [23–26] reported a simple and effective method for preparing hierarchical porous carbon (HPC) from direct coal liquefaction residue (CLR) by KOH activation with addition of some silica, silicate or aluminum oxide. It was considered that the additional mineral salts or those formed by the reaction of the additive and KOH could serve as space fillers of nanopores in the thermoplastic CLR. HPCs can be formed by washing off the mineral matters that occupied the inner space of the carbonized sample.

$Ca(NO_3)_2$, as a mineral salt, can turn into CaO and release NO_x under inert atmosphere and high temperature. Both CaO, which showed a positive effect on reactivity of coal pyrolysis [27–29] and increased gas product yield [30,31], and NO_x are beneficial to form and enlarge pores of resultant carbons during the preparation process, thus improves the surface chemistry, texture properties and catalytic performance of the resultant AC in methane decomposition to hydrogen. However, few literatures were reported about the effect of calcium addition in coal on the surface chemistry and texture properties of the resultant ACs.

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In this work, we aimed to prepare activated carbon by directly adding $Ca(NO_3)_2$ as the calcium source to coal as carbon precursor via KOH activation. The effect of calcium addition amount in coal on the surface chemistry and texture properties of the resultant ACs and their catalytic performances in CMD were investigated.

2. Experimental

2.1. Materials

Shenmu coal (SM), a subbituminous coal from Shaanxi, China, as the carbon precursor, was crushed and sieved to a size below 150 μm before use. $Ca(NO_3)_2{\cdot}4H_2O$ and KOH (Shantou Xilong Chemical Technology Co., China) were used as the calcium source and the activating agent, respectively.

2.2. Catalyst preparation

About 10 g coal was mixed with certain amount of $Ca(NO_3)_2{\cdot}4H_2O$ in a mixture solvent containing 100 mL deionized water and 20 mL ethanol, and stirred in a sealed beaker for 6 h at 60 °C. The mixture was then evaporated and dried at 100 °C to remove the solvent, and the resultant mixture containing coal and $Ca(NO_3)_2$ was named as *x*Ca-SM, here *x* is the mass percentage of calcium added in the coal before carbonization (x = mass ratio of Ca/coal × 100). Thereafter, 5 g mixture containing coal and $Ca(NO_3)_2$ was physically mixed with the desired amount of KOH so as to keep the mass ratio of KOH/coal being 2/1, and carbonized/activated in a horizontal furnace with a N_2 flow rate of 110 mL/min according to the temperature program shown in Fig. 1. After cooling down, the samples were washed with 2 M HCl to remove the residual KOH and part of minerals. The resultant catalyst was expressed as *x*Ca-AC, corresponding to the carbon precursor *x*Ca-SM.

2.3. Characterization

The textural properties of the AC 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 Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (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). Thermogravimetric (TG) analyses of the samples were 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 coal and the mixture. The oxygen containing functional groups on the carbons were investigated by Fourier-transform infrared (FTIR) spectroscopy on an EQUINOX55 FTIR spectrometer. Raman spectra of ACs were obtained by using a laser Raman spectrometer DXR Microscope. Scanning electron microscopy (SEM, QUANTA 450) was applied to record the morphology of ACs before and after CMD reaction.

2.4. Methane decomposition reaction

CMD was conducted in a vertical fixed-bed reactor at 850 °C and atmospheric pressure. The reactor charged with 0.2 g catalyst was first heated to 850 °C under N_2 (99.999 vol%) with a flow rate of 40 mL/min, and then the mixture gas of 10 mL/min methane and 40 mL/min nitrogen instead of pure N_2 was introduced into the reactor. The total volumetric hourly space velocity was set at 15,000 mL/(h·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) and a flame ionization detector (GDX502 packed column). Methane conversion was calculated by the following formula:

$$X_{CH_4} = (F_{CH_4,in} - F_{CH_4,out})/F_{CH_4,in} \times 100\% \tag{1}$$

where, X and F represent the CH_4 conversion and gas flow rate.

3. Results and discussion

3.1. Texture properties of ACs from coal with addition of $Ca(NO_3)_2$

As shown in Fig. 2, the coals added with $Ca(NO_3)_2$ show very different weight loss curves, indicating that the pyrolysis characteristic of coal was changed by the addition of $Ca(NO_3)_2$. The raw coal has two main peaks of weight loss rate, one at about 455 °C is ascribed to pyrolysis of coal and another at about 690 °C is caused by the secondary thermal cracking or/and decomposition of mineral. After the coal was added with $Ca(NO_3)_2$, another peak around 380 °C appears besides two peaks, which is ascribed to the decomposition of $Ca(NO_3)_2$ because it is absent for the raw coal. Additionally, the corresponding temperatures of the peaks are also changed. The peak ascribed to coal pyrolysis shifts to higher temperature with increasing the addition amount of calcium, indicating that the coal pyrolysis could be delayed by added $Ca(NO_3)_2$. And the maximum weight loss rate at 400–600 °C also increases with the addition amount of calcium, which may be caused by the decomposition of $Ca(NO_3)_2$. Especially, a sharp peak appears at about 520 °C when the addition amount of calcium is up to 15 wt%, which is attributed to the rapid decomposition of large amount of $Ca(NO_3)_2$. In addition, the weight loss at about 690 °C increases as the addition amount of calcium, which may be because of the CaO promoting the secondary thermal cracking of coal to release more gas products.

The texture properties of the resultant ACs from the calcium added coal are listed in Table 1. The specific surface area and pore volume of ACs increase from 1535 m^2/g to 1864 m^2/g and 0.76 cm^3/g to 0.97 cm^3/g after the addition of calcium, respectively. SM-AC from raw coal has the least surface area and pore volume among ACs. When the addition amount of calcium in coal is less than 7.5 wt%, the surface area and pore volume remarkably increase, especially the microporous surface area (S_{mic}), and 7.5Ca-AC has the largest S_{mic} among all the prepared ACs, while the external or mesoporous surface area increases a little compared with SM-AC. With increasing the addition amount of calcium from 7.5 to 15 wt%, especially when the addition amount is up to 12.5 wt%, the microporous surface area decreases gradually while the external surface area increase to more than 1000 m^2/g, indicating that the large addition amount of calcium benefits the development of mesoporous. It is concluded that when the addition amount of calcium is less than 7.5 wt%, both the microporous and mesoporous surface area, but mainly the former, of the resultant ACs increase. However, when the addition amount of calcium is more than 10 wt%, more mesoporous are produced. According to the results from TG analyses of raw coal and mixed coals with $Ca(NO_3)_2$, $Ca(NO_3)_2$ affects coal pyrolysis and promotes the release of gas produced in the process, which will benefit the formation and enlarging of pore during the carbonization/activation process. The NO_x produced from the decomposition of $Ca(NO_3)_2$ also promotes the formation and enlarging of pore. As the increase of calcium addition amount, more gases are produced in carbonization process, thus more and larger pores are formed in the resultant ACs.

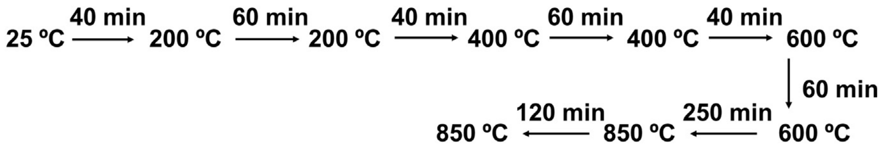

Fig. 1. Carbonization/activation temperature program during the preparation of ACs.