



## Preparation and applications of hierarchical porous carbons from direct coal liquefaction residue

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### HIGHLIGHTS

- ▶ Hierarchical porous carbons (HPCs) were prepared from coal liquefaction residue.
- ▶ The formed silicate during KOH activation by additive serves as template for HPCs.
- ▶ The HPCs have the ratio of mesoporosity to microporosity being close to 1:1.
- ▶ HPCs show better catalytic performance for catalytic methane decomposition.
- ▶ HPCs based electrodes show higher capacitance for supercapacitors.

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### ABSTRACT

Hierarchical porous carbons (HPCs) were prepared from direct coal liquefaction residue (CLR) by KOH activation with addition of silica or silicate. Based on the template role of the mineral salts formed during the KOH activation process, the obtained HPCs have both mesopores and micropores. Several series of samples with different preparation conditions, such as different silica sources, additive dosages, washing procedures after carbonization and additional KOH for the additive in the activation process, were prepared and characterized. The results show that the microporosity of the carbons can increase by more than 28% owing to the addition of silica or silicate, along with the ratio of mesoporosity to microporosity being close to 1:1. Compared with the CLR-based carbon from traditional KOH activation, HPCs with appropriate preparation conditions have improved catalytic performance for catalytic methane decomposition and higher capacitances for supercapacitors.

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### 1. Introduction

Porous carbons are of interest in many areas, such as adsorption and separation [1–4], high-energy capacitors [5–8] and catalysis applications [9–13]. Hard-template and soft-template approaches are two major methods for synthesis of porous carbons [14–16]. And the carbons are usually obtained with ordered and uniform pores by either of the methods. However, they are undesirable in some areas [17–19], such as heterogeneous catalysis and removal of pollutants with different sizes, where require carbon materials with hierarchical structures that contain mesopores (2–50 nm) and micropores (<2 nm) or macropores (>50 nm). Therefore, chemical and/or physical activations of the obtained carbons are additionally required to improve the porous networks [17–19]. But these strategies are complicated and time-consuming. In our

previous work [20,21], we reported that mesoporous carbons can be directly prepared from direct coal liquefaction residue (CLR) by KOH activation, using both the in situ mineral matter and its salts as templates. Here, based on the template roles of the mineral salts formed during KOH activation process, hierarchical porous carbons (HPCs) with both mesopores and micropores were directly prepared from CLR by KOH activation with addition of silica or silicate, simplifying the traditional process.

Various micro- or mesoporous carbon materials have been used as catalysts for catalytic methane decomposition (CMD) [10,12,13], but little work has been done for CMD on HPCs. Additionally, carbon-based supercapacitors can bridge the gap between batteries and conventional dielectric capacitors, and are promising for rapid storage and release of energy [5–8]. And HPCs with both micro- and mesopores can make the electrolyte ions diffuse faster than the micro- or mesoporous carbons, and shows higher performance for supercapacitors [5,6]. Herein, the catalytic performance for

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CMD and capacitive behaviors for supercapacitors of the resultant carbons were investigated.

## 2. Experimental

### 2.1. Preparation of HPCs

Shenhua CLR was used as the carbon precursor, which was crushed and sieved to particle size of 150–250  $\mu\text{m}$  before use. The CLR is rich in carbon content (about 87 wt.%, dry ash-free basis) and mineral matters (with the ash content up to about 22 wt.%, dry basis) according to its proximate and ultimate analyses [20]. KOH was used as the activating agent. Based on the fact that the mineral salts formed during KOH activation process can play a template role for the CLR-based porous carbon [20], additional silicate nanoparticles (or those formed by the additive and KOH) were employed to serve as space fillers of nanopores in the thermoplastic CLR for preparing HPCs. Commercial chemicals  $\text{SiO}_2$  [21], SBA-15 [21],  $\text{Na}_2\text{SiO}_3$  ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , Tianjin Bodi Chemical Agent Co.) and tetraethoxysilane (TEOS, Tianjin Damao Chemical Agent Co., with  $\text{SiO}_2$  content of 28.0%) were employed as the additive, respectively.

Preparation procedures of the carbon samples in present work were similar to the traditional KOH activation [20,21], involving mixing, carbonization and washing. In brief, 5 g CLR, 10 g KOH and certain amount of the additive were mixed in the solution containing 50 ml tetrahydrofuran (THF) and 10 ml deionized water, stirring for 24 h at ambient temperature. Then the mixture was evaporated in vacuum and dried at 120  $^\circ\text{C}$  overnight before carbonization and washing. And the methods for carbonization and washing have been detailed described elsewhere [20]. Several series of carbon samples with different preparation conditions, such as different silica sources, additive amounts, washing procedures after carbonization and additional KOH for the additive in the activation process, as shown in Table 1, were prepared. All the resultant carbon samples were crushed and sieved to be particle size of 150–250  $\mu\text{m}$  before use.

**Table 1**  
Preparation conditions of the carbon samples.

Sample	Additive		Washing agent <sup>e</sup>
	Type	Mass (g)	
SBA-RC	SBA-15	3	2 M HF, 2 M HCl, water
SiRC <sup>a</sup>	$\text{SiO}_2$	3	2 M HF, 2 M HCl, water
TEOS-RC	Tetraethoxysilane	3 <sup>d</sup>	2 M HF, 2 M HCl, water
$\text{Na}_2\text{SiO}_3$ -RC	$\text{Na}_2\text{SiO}_3$	3	2 M HF, 2 M HCl, water
RC	–	–	2 M HF, 2 M HCl, water
1SiRC	$\text{SiO}_2$	1	2 M HF, 2 M HCl, water
4SiRC	$\text{SiO}_2$	4	2 M HF, 2 M HCl, water
5SiRC	$\text{SiO}_2$	5	2 M HF, 2 M HCl, water
7SiRC	$\text{SiO}_2$	7	2 M HF, 2 M HCl, water
NW-SiRC	$\text{SiO}_2$	3	–
W-SiRC	$\text{SiO}_2$	3	Water
HCl-SiRC	$\text{SiO}_2$	3	2 M HCl, water
Si(FA-R) <sup>b</sup>	$\text{SiO}_2$	3	2 M HF, 2 M HCl, water
1SiRC + K <sup>c</sup>	$\text{SiO}_2$	1	2 M HF, 2 M HCl, water
2SiRC + K <sup>c</sup>	$\text{SiO}_2$	2	2 M HF, 2 M HCl, water
3SiRC + K <sup>c</sup>	$\text{SiO}_2$	3	2 M HF, 2 M HCl, water
4SiRC + K <sup>c</sup>	$\text{SiO}_2$	4	2 M HF, 2 M HCl, water

<sup>a</sup> Its another name is 3SiRC in this paper.

<sup>b</sup> With the mineral-free CLR as the precursor.

<sup>c</sup> The samples prepared with additional KOH for the additive according to stoichiometric coefficients of the reaction.

<sup>d</sup> Controlling the limits to the equivalent of 3 g  $\text{SiO}_2$ .

<sup>e</sup> Where “water” is deionized water. As for the washing order, for example, “2 M HF, 2 M HCl, water” means washing with 2 M HF, 2 M HCl and deionized water by sequence.

### 2.2. Characterization

$\text{N}_2$  adsorption/desorption isotherms of the carbons were measured at  $-196^\circ\text{C}$  in a physical adsorption apparatus (ASAP2420) and the information on pore structure was obtained by using BET and BJH methods. The micropore volume ( $V_{\text{mic}}$ ) was estimated by using the  $t$ -plot method, while mesopore volume was calculated from the difference of the total pore volume ( $V_t$ ) and  $V_{\text{mic}}$ . And the microporosity was determined by the ratio of  $V_{\text{mic}}/V_t$ . Ash contents of the samples were determined by burning the carbons at 900  $^\circ\text{C}$  under air flow of 60 ml/min in a thermogravimetric analyzer (Mettler Toledo TGA/SDTA851<sup>e</sup>). And the ash compositions of the carbons were obtained by X-ray fluorescence spectral analysis (SRS-3400, Germany). The carbon yield was calculated as a percentage of the product weight versus the initial CLR weight.

### 2.3. Catalytic methane decomposition

Isothermal CMD experiments were carried out in a fixed-bed reactor at 850  $^\circ\text{C}$  and atmospheric pressure. Pure methane (99.99 vol.%) with a total flow rate of 50 ml/min used as the feed gas, and 0.20 g of the carbon as the catalyst were employed along with the total volumetric hourly space velocity of 15,000 ml/(h g<sub>cat</sub>). The gas products were analyzed by an online gas chromatography. The detail information about the reaction process and setup has been described elsewhere [21]. Methane conversion and hydrogen selectivity were determined by the following equations:

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

$$S_{\text{H}_2} = 0.5F_{\text{H}_2,\text{out}} / (F_{\text{CH}_4,\text{in}} - F_{\text{CH}_4,\text{out}}) \times 100\% \quad (2)$$

where  $X$ ,  $S$  and  $F$  represent the conversion, selectivity and gas flow rate, respectively.

Because carbon black is considered to have the most stable catalytic activity for CMD among a lot of carbon catalysts [12,13,22,23], for comparison, the reaction test with a commercial carbon black BP2000 (CB, Carbot, US) was also conducted. It was pretreated in  $\text{N}_2$  at the reaction temperature and kept for 4 h before use.

### 2.4. Electrochemical measurements

HPCs were further crushed and sieved to fine powder ( $\sim 50 \mu\text{m}$ ) and mixed with certain polytetrafluoroethylene (PTFE) as the binder along with the weight ratio of HPC/PTFE up to 95:5. The mixture was pressed on a nickel foam current collector, with the ratio of the mass and the area at  $10 \pm 2 \text{ mg/cm}^2$ . And the mass of each electrode disc was kept at about 5 mg. A conventional three electrode system, with a platinum plate and saturated calomel electrode as the counter and reference electrode respectively, was used for cyclic voltammetry (CV) measurements. CV curves were recorded on an electrochemical workstation (BAS 100B/W) with a scan rate of 5 mV/s, by polarizing the working electrode between 0.0 and  $-1.0 \text{ V}$  versus chloridize argentine in a 6 M KOH aqueous solution. The specific capacitance ( $C$ , F/g) was determined by the following Eq. (3):

$$C = I\Delta t / U \quad (3)$$

where  $I$ ,  $\Delta t$  and  $U$  are the current based on the total mass of the carbon electrode (with the unit of mA/g), discharging time (s) and the potential range (V) from the end of charge to the end of discharge, respectively.

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