

## Rapidly reversible adsorption of methane with a high storage capacity on the zeolite templated carbons with glucose as carbon precursors



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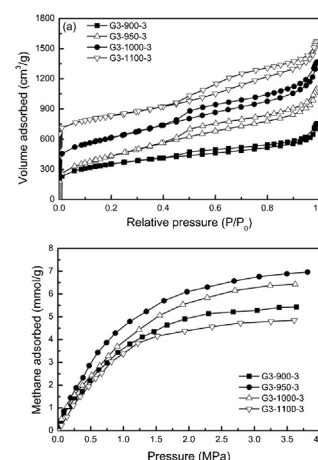
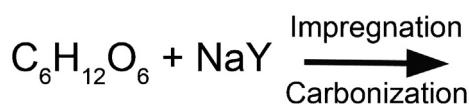
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### HIGHLIGHTS

- ZTC is synthesized with glucose as carbon precursor via impregnation method.
- Carbonization conditions have significant influences on carbon properties.
- High surface area of 1562 m<sup>2</sup>/g and pore volume of 1.67 cm<sup>3</sup>/g are achieved.
- Methane adsorption amount at 300 K and 3.5 MPa is 9.9 wt.%.

### GRAPHICAL ABSTRACT



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### ABSTRACT

Microporous carbon material with a high surface area of 1562 m<sup>2</sup>/g is prepared via an impregnation method with NaY zeolite as hard template. The results indicate that glucose, an environmental friendly material, could be used as the carbon precursor of zeolite templated carbons, in comparison with the toxicity of furfuryl alcohol and lower surface area of carbons generated from sucrose. Effects of reactant molar ratios and carbonization conditions on the textural properties are addressed. Although higher carbonization temperature favors more complete carbonization reactions, it also causes the collapse of small pores and the formation of large pores at the same time. Further characterizations of the obtained carbon materials with XRD, SEM and N<sub>2</sub> adsorption–desorption measurements are presented. Methane adsorption tests on carbon materials are investigated with the static volumetric method at 300 K. The higher adsorption amount of 9.9 wt.% was achieved at 3.5 MPa on sample with a higher micropore volume, indicating that micropores were playing a crucial role for the methane storage process.

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### 1. Introduction

Porous materials including carbonaceous adsorbents and silica have high surface area and large pore volume, high thermal and chemical stability, and low manufacturing cost [1]. Com-

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**Table 1**  
Reactant molar ratios of different samples.

Sample	NaY (g)	Glucose (g)	H <sub>2</sub> O (ml)	H <sub>2</sub> SO <sub>4</sub> (g)
G1	0	2	5	0.2
G2	1	2	5	0.2
G3	2	2	5	0.2
G4	3	2	5	0.2
G5	4	2	5	0.2
G6	2	2	5	0
G7	2	2	5	0.1
G8	2	2	5	0.3

pared with porous carbons, silica has superior biocompatibility [2] and shows outstanding stability under oxidative conditions, but it is not conductive and is susceptible to the corrosion of certain chemicals such as hydrofluoric acid and sodium hydroxide [3]. It is not easy to prepare stable silica with the specific surface area higher than 1500 m<sup>2</sup>/g, particularly in the case of the mesoporous silica [4,5]. Different types of carbon materials including activated carbons [6,7], carbon nanotubes [8,9], templated carbons [10] and graphenes [11] have been widely investigated as gas storage materials. Zeolite templated carbons (ZTCs) are obtained by carbonization of carbon precursor in the pore channels of zeolite and the subsequent removal of zeolite framework [10,12], which offers the possibility of precise manipulation of the porous structure. Although ZTC materials have been investigated as the storage media of hydrogen [12–16], their storage of methane has been relatively less reported [10].

ZTCs are usually prepared via impregnation method [12] or chemical vapor deposition (CVD) [14,15] or a combination of both [10,16]. In the impregnation method, the most frequently used carbon precursor is furfuryl alcohol (FA), which has been known to be toxic [17]. Furthermore, in order to introduce FA into the pore channels of zeolite, a very lengthy mixing process is usually demanded [16]. Konwar et al. reported synthesis of ZTC with FA as the precursor and NH<sub>4</sub>Y zeolite as the template [12]. FA and NH<sub>4</sub>Y zeolite were mixed at room temperature for 72 h to guarantee the dispersion of FA, after a complex stepwise heat treatment ZTC with a high BET surface area of 1886 m<sup>2</sup>/g was obtained. On the other hand, in the CVD method different carbon-containing gases such as acetonitrile [14], ethylene [18], propylene [19], ethanol [20] are employed as carbon source. For instance Xia et al. obtained carbons with Y zeolite as template after CVD of acetonitrile, the BET surface area value was 1912 m<sup>2</sup>/g [15], where the process is difficult to scale up because of its productivity and a potential danger of explosion at high temperature.

Ryoo et al. have used glucose as a green chemical to prepare mesoporous carbons with surface area up to 1380 m<sup>2</sup>/g [21]. In this paper, ZTC with a higher specific surface area of 1562 m<sup>2</sup>/g is obtained with glucose as a carbon precursor templated with NaY zeolite. Several synthesis parameters on the properties of ZTCs are studied, and then methane storage performances on these ZTCs materials are also investigated.

## 2. Materials and methods

### 2.1. Synthesis

The templated carbons were synthesized by carbonization of glucose at high temperature after its impregnation of NaY zeolite. Glucose (AR grade), sucrose (AR grade), sulfuric acid (98 wt.%) and hydrofluoric acid (40 wt.%) were purchased from Sinopharm Chemical Reagent Co., Ltd., NaY zeolite with a Si/Al ratio of 5.3 was supplied by The Catalyst Plant of Nankai University. All chemicals were used as received. Samples with different reactant molar ratios were prepared, as listed in Table 1. In a typical synthesis, 2.0 g of

glucose was dissolved in 5.0 ml of water containing 0.2 g of H<sub>2</sub>SO<sub>4</sub> at room temperature, then 2.0 g of NaY zeolite was added to this clear solution. The white mixture was kept stirring for about 90 min at 70 °C to evaporate the solvent, and was then dried at 100 °C for 3 h, followed by treatment at 160 °C for 6 h. The obtained brown solid product was ground into a fine powder, and then subjected to high temperature carbonization process in a tube furnace in nitrogen with a flow rate of 50 ml/min. The sample was calcined at a heating rate of 3 °C/min to a fixed temperature and then remained constant for different times. After being cooled to the room temperature in nitrogen stream, the black carbon/zeolite composite was washed with 40 wt.% HF solution at room temperature for 24 h to remove NaY zeolite. The resultant carbon material was filtered and washed with deionized water repeatedly, and dried in an oven at 110 °C for 3 h. The carbon/zeolite composites and the obtained carbon samples were denoted as Gn-C-T-t and Gn-T-t, respectively: Gn was the corresponding reactant molar ratio in Table 1, C represented carbon/zeolite composite, T was the carbonization temperature (°C) and t was the carbonization time (h). The heat treatment conditions were denoted as °C/h, for instance 950 °C/3 h meant that sample was treated at 950 °C for 3 h.

### 2.2. Characterization and methane adsorption tests

Power XRD analysis was performed using a Rigaku D/MAX-2500/PC. The morphology of the samples was examined by a scanning electron microscope (SEM, Hitachi S-4800). Nitrogen adsorption-desorption isotherms were measured at 77 K on a Micromeritics ASAP 2020 analyzer. Samples were degassed at 250 °C for 6 h under vacuum prior to the determination of isotherms. Specific surface area was calculated with the Brunauer-Emmett-Teller (BET) method based on adsorption data in the relative pressure ( $P/P_0$ ) range of 0.05–0.25. Total pore volume ( $V_t$ ) was determined from the amount of nitrogen adsorbed at  $P/P_0 = ca. 0.99$ . Micropore volume ( $V_{micro}$ ) was obtained with Dubinin-Radushkevich (DR) equation, while mesopore volume ( $V_{meso}$ ) was calculated by subtracting  $V_{micro}$  from  $V_t$ . Pore size distribution (PSD) was determined with the density functional theory (DFT) method. Methane adsorption isotherms of ZTCs were measured at room temperature (300 K) with the static volumetric method on a Sievert-type equipment with pressure up to 3.5 MPa. All samples were heated at 250 °C under vacuum for 3 h to remove adsorbed water and other contaminants before methane adsorption measurements.

## 3. Results and discussion

### 3.1. Effects of different synthesis parameters

Fig. 1 depicts the optimization of reactant molar ratios and effects of carbonization conditions on BET surface area of obtained ZTCs, the amount of glucose is kept constant for all samples. Fig. 1(a) shows the significant influence of carbon source/template ratio on the surface areas. Among these samples G3-900-3 with 2 g of NaY zeolite addition shows the highest surface area of 1222 m<sup>2</sup>/g; while after the direct pyrolysis of glucose at high temperature with no template involved (G1-900-3), the carbon sample gives a much lower surface area of 389 m<sup>2</sup>/g, indicating that the formation of the pores in the final product is mainly due to the templating effects within the pores of NaY zeolite. Fig. 1 also shows that medium amount of NaY zeolite is more favorable for high surface area products, which possibly results from the demands of efficient filling of the zeolite template pores and meanwhile minimizing carbonization processes outside the template pores. If the zeolite template pores are not sufficiently filled by glucose, the linkages

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