

Carbon Nanotube Templated Preparation of Mesoporous NaA Zeolite

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The mesoporous NaA zeolite, by multiwall carbon nanotubes covered with organic group (*e.g.*, -OH or -COOH) or treated with silane coupling agent templating, has been synthesized with hydro-thermal method. The formation of mesoporous NaA zeolite was investigated by X-ray diffraction, N₂ absorption-desorption and scanning electron microscope illuminates that the mesoporous NaA zeolite could be synthesized with higher BET surface area of 24.3 m² g⁻¹ than microporous NaA zeolite (*ca.* 3.4 m² g⁻¹).

Key Words: Carbon nanotubes, Mesoporous zeolite, Silane coupling agent.

INTRODUCTION

Zeolites have attracted much attention for their well physico-chemical properties¹. In many areas, the only micropores for zeolites embarrass their application with slower reaction rate. Many attempts^{2,3} have been made to prepare zeolitic crystals with a mesoporous system in the past. From the discovery of carbon nanotube in 1991, researchers have reviewed several applications of them⁴⁻⁶. Specifically, they are used as template agents for preparing nanostructure material similar to their morphology, such as mesoporous zeolite^{7,8} crystal, zeolite nanowire⁹ and nanosize zeolite crystal¹⁰. As a general rule, the carbon nanotubes should be purified by refluxing with concentrated hydrochloric acid⁸ or the other strong oxidizers¹⁰ like H₂O₂, HNO₃ or acidic potassium permanganate before using, so that the surface of multiwall carbon nanotubes is covered by organic groups (-OH or -COOH, for instance). These organic groups can enhance the interaction force between silicate oligomer and carbon nanotubes.

There are several advantages of using carbon nanotubes as template. That makes it possible to prepare zeolite crystal with a tuneable mesoporous system. Moreover, the carbon nanotubes can be burning off^{7,8} easily. After removing the matrix from the large single crystals, mesoporous are created. In this paper, we report the preparation of mesoporous NaA zeolite by functionalized multiwall carbon nanotubes templating. At the same time, the silane coupling agent is grafted onto the surface of carbon nanotubes, so that the interaction between carbon nanotubes and silicate oligomer can be improved. In comparison with microporous NaA zeolite, it is pointed how it is possible to prepare mesoporous NaA zeolite

using multiwall carbon nanotubes as mesoporous-forming agents, just like the Fig. 1 showing.

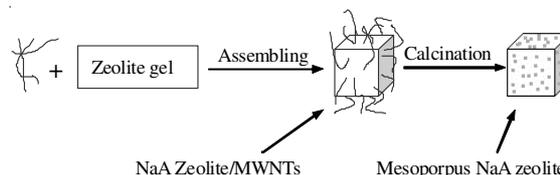


Fig. 1. Schematic diagram of the synthesis principle for mesoporous NaA zeolite

EXPERIMENTAL

Multiwall carbon nanotubes with an average outer diameter less than 8 nm and lengths between 0.5 and 2.0 μm were supplied by Chengdu Organic Chemicals Co. Ltd., Chinese Academy of Sciences. The multiwall carbon nanotubes involve three kinds: the surface were covered with nothing, covered with -COOH and covered with -OH, naming M1, M2 and M3, respectively. γ-(2,3-Epoxypropoxy) propyltrimethoxysilane (KH-560, min 97 %) and 3-methyldimethoxysilylpropylamine (KH-660, min 97 %) were supplied by Trustchem Silanes Ltd. Both sodium metasilicate (Na₂SiO₃·9H₂O) and sodium aluminate (NaAlO₂) were analytical reagent grade.

Characterization: The XRD patterns were carried out with a Japanese RigakuD/max-2500 diffractometer, using CuK_α radiation and operating at 40 kV and 30 mA. Scanning electron microscopy (SEM) was characterized using German ZEISS scanning electron microscope at a voltage of 15 kV. BET surface areas were measured at liquid-nitrogen temperature (-196 °C) by American Quantachrome NOVA 2000e

automated surface area and pore size analyzer. All samples were outgassed under vacuum at 300 °C for 3 h. The total surface areas were calculated according to the BET method. Mesoporous volumes were determined by the BJH method from the desorption branch of the isotherms.

Preparation of M4 (Scheme-I): 0.2 g M3 was steeped in the KH-560 aqueous solution (5 wt. %) for 1 h with agitating, then, the M3 was filtrated with 100 mL deionized water and dried at 100 °C for 10 min.

Preparation of graft copolymer (Scheme-I): The oxyhydyl from KH-660 was joined to the surface of silicate oligomer precursor. Then, the graft copolymer was gained by the reaction among M4, KH-660 and silicate oligomer under alkaline conditions.

Synthesis of mesoporous NaA zeolite: The zeolite gel precursor with the following oxides molar composition, $1\text{Al}_2\text{O}_3:1.17\text{SiO}_2:4.34\text{Na}_2\text{O}:200\text{H}_2\text{O}:x\text{MWCNTs}$, was prepared by dissolving 0.75 g $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ in 5 g H_2O , then, a certain amount of MWCNTs was added into the former solution. At the same time, 0.37 g NaAlO_2 was dispersed into 3 g H_2O . The obtained admixture of MWCNTs and $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ was transferred into the sodium aluminate aqueous solution under vigorous stirring. 0.1 g KH-660 should be added into the sodium metasilicate aqueous solution before M4 was put in. Then, the resulting gel was transferred into stainless steel autoclave having teflon lining and heated at 100 °C for 15 h. Then, the composite was filtered several times by suction filtration with deionized water in order to remove the unreacted soluble fraction and dried at 100 °C, subsequently. The carbon nanotubes were completely removed by calcining in air in a muffle furnace at 550 °C for 15 h.

RESULTS AND DISCUSSION

Powder XRD analysis: The XRD patterns of samples agree well with that of standard NaA zeolite (Fig. 2) indicating that the as-synthesized samples are LTA phase and the adding of multiwall carbon nanotubes or silane coupling agent have little effect on the crystallization of NaA zeolite.

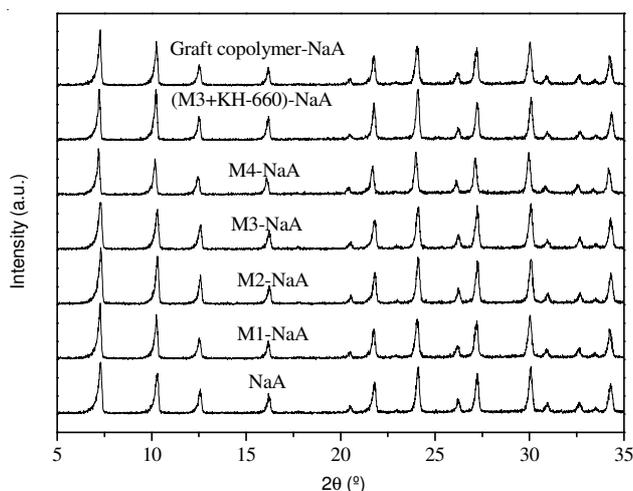


Fig. 2. XRD patterns of NaA zeolites

SEM analysis: The Fig. 3 reveals that SEM image of the sample by M3 templating is similar to that of microporous

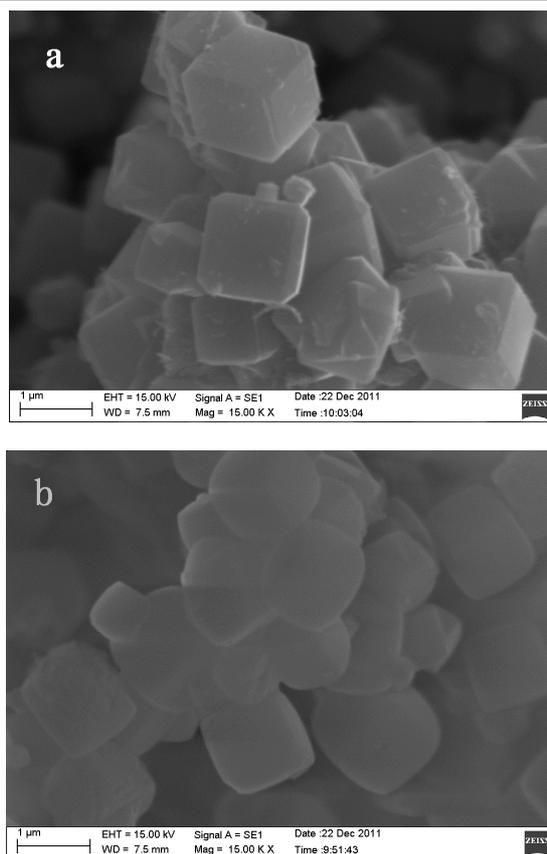
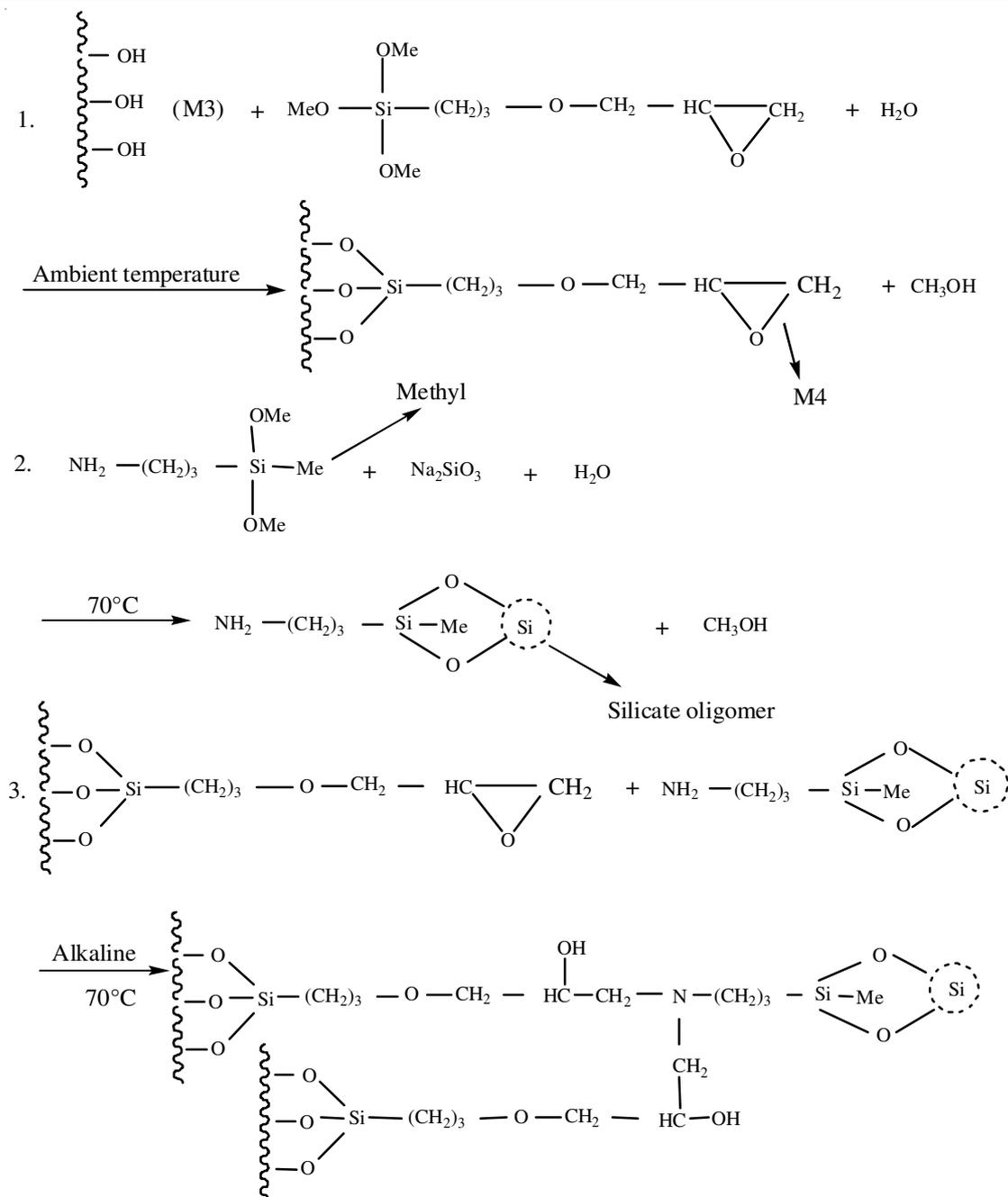


Fig. 3. SEM images of mesoporous NaA zeolite by M3 and graft copolymer templating: a-M3, b-graft copolymer

NaA zeolite¹¹. The crystal sizes measured on the SEM image range from 1-2 μm. But the sample by graft copolymer templating having smooth arrises gives the fact that the silane coupling agents have slight effect on the crystallization of NaA zeolite, which can be proved by the XRD patterns with unchanged peak heights.

N₂ adsorption-desorption measurements: In Fig. 4, it shows a tendency towards higher nitrogen adsorption quantity for the samples with difference templates. The pore size distribution ranging from 10-30 nm are broader than that of MWCNTs (max 8 nm). This is because the MWCNTs will reunite of themselves, which causes the MWCNTs couldn't disperse well and results in the pore size of mesoporous pores becoming larger than the diameter of MWCNTs. However, the sample by M2 templating has a close BET surface area to that by M3 templating, that reveals the interaction strength between M2 and silicate oligomer is similar with that between M3 and silicate oligomer and the latter is a bit stronger than the former.

That is to say, the M3 can be encapsulated into the NaA zeolite crystal easier than M2. The BET surface areas of samples by M2 and M3 templating are larger than that by M1 templating (Table-1). We know that the M2 and M3 are carboxyl-functionalized and oxyhydyl-functionalized, respectively, while M1 is not. It exactly proves that the functionalized MWCNTs can upgrade the bonding force with silicate oligomer, so that the MWCNTs can be encapsulated in the NaA zeolite crystal more easily. However, the surface hydroxyl group of M3¹²⁻¹⁴ is so little that the BET surface areas are still small. The sample by M4 templating has an even more small BET



Scheme-I: Reaction mechanism of M3, KH-560, KH-660 and the silicate oligomer

surface area than by M3 templating for the weaker activity of epoxy group of KH-560. Table-1 and Fig. 4 evince the adding of KH-660 does not impact the BET surface area of sample by M3 templating. But comparing to the samples by M3, M4 or the mixture of M3 and KH-660 templating, the sample by graft copolymer templating has a maximum BET surface area (*ca.* 24.3 m² g⁻¹) among these samples. The BET surface area is small yet for the reason that only a small quantity of KH-560 is grafted onto the M3 surface (**Scheme-I**) for small amounts of hydroxyl group on M3. Nevertheless, the activity of graft copolymer is still the highest one of all samples. So it is convinced that the BET surface area of mesoporous NaA zeolite by MWCNTs templating will grow with the increase of the activity of MWCNTs.

Conclusion

The reactivity order of these templates is as follows: M1 < M4 < M2 ≈ M3 < graft copolymer. No matter which template was added, the crystalline of samples have not changed obviously. However, the N₂ adsorption/desorption measurements illustrate that the functionalized MWCNTs are beneficial to the construction of mesoporous in NaA zeolite. Moreover, the higher activity of groups on the surface of MWCNTs is, the higher BET surface areas of samples will be. Among these templates, the sample by graft copolymer templating has the maximum BET surface area. For the purpose of heightening BET surface area, we can improve the reactivity of groups on the surface of MWCNTs by selecting suitable silane coupling agent or increasing the hydroxyl group amount on the MWCNTs

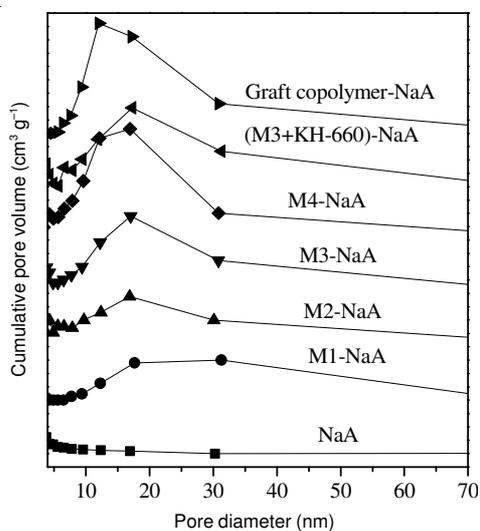
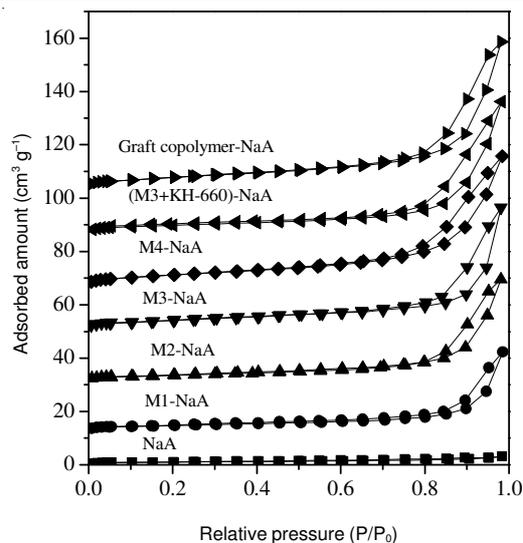


Fig. 4. N_2 adsorption-desorption isotherms and pore size distribution of samples of NaA zeolite

surface, so that the reaction between MWCNTs and silicate oligomer will be more vigorous.

TABLE I
BET SURFACE AREA, PORE VOLUMES AND
PORE SIZE OF SAMPLES AFTER COMBUSTION

Samples	S_{BET} ($m^2 g^{-1}$)	Pore volume ($cm^3 g^{-1}$)	Pore size (nm)
NaA	3.4	0.005	2.2
M1-NaA	10.1	0.047	12.5
M2-NaA	16.5	0.053	12.9
M3-NaA	17.8	0.067	15.0
M4-NaA	13.4	0.056	17.8
(M3+KH-660)-NaA	16.9	0.071	17.4
Graft copolymer -NaA	24.3	0.078	14.1

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