



# Functioned carbon nanotube templated hierarchical Silicate-1 synthesis: On the existence of super-micropore



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## ABSTRACT

In present study, the functioned carbon nanotube was used as secondary template for hierarchical Silicate-1 synthesis. Special attentions were paid to the existence of super-micropore (1–2 nm) and additional hysteresis loop between 0.1 and 0.2 in nitrogen adsorption isotherms of the synthesized samples. The main findings of present study are: (1) Silicate-1 with additional mesoporosity can be synthesized with functioned carbon nanotube as secondary template through impregnation or direct hydrothermal synthesis method. The functional group in carbon nanotube doesn't influence the crystallization process with impregnation method but have large influence in direct hydrothermal synthesis method; (2) With typical subsequently impregnation method, no hysteresis loop between 0.1 and 0.2 was found in the nitrogen adsorption isotherms of samples. And the single wall carbon nanotube penetrated the zeolite crystal as a bundle other than separate nanotube with size range in 1–2 nm, (3) In zeolite samples synthesized with direct hydrothermal method, additional hysteresis loop was found in several samples. However, SEM and crystallization process analysis indicated that the hysteresis loop was more likely due to the large crystal size other than the existence of any real pores.

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## 1. Introduction

Zeolites are widely used as catalysts, especially in oil refinery because of their excellent shape selectivity and high acidity [1,2]. In recent years, the pore structure of zeolitic materials has expanded from solely microporous materials to hierarchical materials with either inter-crystalline or intra-crystalline mesopore/macropore channels [3–5]. The synthesis, characterization and catalytic application of the hierarchical zeolite are the hottest topics in past decades in the area of catalytic materials [6–10]. Methods including crystallization in the presence of secondary template (e.g. nanoporous materials, amphiphilic organosilane), post modification (dealumination or desilication) or combination of both were developed for hierarchical zeolite synthesis [11,12].

Despite a lot of successes have been achieved, the successful synthesis of zeolite with additional super-micropore (pore size being 1–2 nm) has not yet been widely accepted. Yang et al. [13,14] have reported the successful synthesis of ZSM-5 with additional super-micropore with the hysteresis loop of nitrogen partial

pressure between 0.1 and 0.2 as the main evidence. However, this conclusion was suspected by other researchers that the hysteresis loop between 0.1 and 0.2 doesn't indicate the presence of real pore but only physical properties of nitrogen under specific condition [15]. Our previous experiment on MFI structure materials synthesis with CMK-3 as secondary template indicated the formation of zeolite nanocrystal aggregate. Neither hysteresis loop between 0.1 and 0.2 in nitrogen adsorption isotherm nor super-micropore in SEM investigation was found [16].

In previous research, the presence of hysteresis loop between 0.1 and 0.2 had drawn a lot of studies since the unique feature of nitrogen isotherms was first reported by Carrott and Sing [17]. In situ  $^{15}\text{N}$  NMR spectroscopy indicated this hysteresis loop was due to the phase transformation of nitrogen inside zeolite. Energetic and structural studies by means of Tian-Calvet isothermal microcalorimetry and neutron diffraction techniques also revealed that the low-pressure hysteresis and associated energy changes were due to phase transition of adsorbate [18–20]. Kyriakou et al. [21] further made a systematic study of the nature of the low-pressure hysteresis loop observed in the nitrogen adsorption isotherms of some MFI zeolites and obtained evidence from diffuse reflectance infrared Fourier-transform spectroscopy (DRIFTS) spectra. Their

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results indicated that above mentioned unique hysteresis loop was linked to the energetically homogeneous pore surface other than the existence of real mesopore system.

It is thus interesting to study the nitrogen adsorption behavior of zeolite with real super-micropore system. For this purpose, a zeolite with additional pore channels with size being 1–2 nm should be confirmed clearly by other characterization methods such as TEM and STEM study. Until now, using carbon nanomaterials as secondary template is still the most successful method for hierarchical zeolite synthesis. The properties of carbon nanomaterials such as nanoparticle size, pore structure (size and interconnectivity), surface functional group and morphology have large influence when used as secondary template for hierarchical zeolite synthesis [22]. In some cases, replication of the structure order of template in nanoscale was proven. For example, our group has successfully synthesized zeolite with controllable mesoporous channels with carbon aerogel as secondary template [23]. Successful replication of the nanostructure of carbon aerogel to hierarchical zeolite has proven. Based on this, the carbon nanomaterials template method was used for the synthesis of zeolite with super-micropore system.

In this study, functionalized carbon nanotube was selected as the secondary template for zeolite with super-micropore synthesis for following reasons: (1) single wall carbon nanotube is conceptually the most promising secondary template which outer wall is 1–2 nm, (2) carbon nanotube is now commercially available under acceptable price, and (3) different functional groups can be introduced into the carbon nanotube. Hence in the paper, both multi-walled carbon nanotube with different functional groups and single wall carbon nanotubes were used as secondary template for hierarchical zeolite synthesis. Two different synthesis methods with different mixture manner between carbon nanotube template and zeolite synthesis sol were used. Some interesting results regarding the existence of super-micropore in Silicate-1 crystal were obtained and discussed.

## 2. Experimental

### 2.1. Materials

Tetrapropylammonium hydroxide (TPAOH, 25 wt.% in water) was from Zhejiang Kente Chemical co. Ltd,  $\text{NH}_3 \cdot \text{H}_2\text{O}$  ( $\text{NH}_3$  25–28 wt.%) was from Beijing Chemical co. Ltd, tetraethyl orthosilicate (TEOS, 98 wt.% in water), non-functionalized hydroxylate/carboxyl/amino graphitized multi-walled carbon nanotubes (MWCNT, MWCNT-COOH, MWCNT-OH) and graphitized single-walled carbon nanotubes (SWCNT) from Xianfeng Nano, INC, MWCNT-NH<sub>2</sub> from Beijing Boyu Gaoke Nano, Advanced Material Corporation were used without further purification and detail characters are shown in Table 1. Deionized water was used for all reactions.

**Table 1**  
Characters of carbon nanotubes.

Characters	MWCNT	MWCNT-COOH	MWCNT-OH	MWCNT-NH <sub>2</sub>	SWCNT
Outer diameter (nm)	8–15	8–15	8–15	8–15	1–2
Length ( $\mu\text{m}$ )	~50	~50	~50	~50	5–30
Ash (wt.%)	<0.1	<0.1	<0.1	<1.5	<1.5
Surface area ( $\text{m}^2/\text{g}$ )	>117	>117	>117	>233	>380
Conductivity (s/cm)	>100	>100	>100	>100	>100
Purity (wt.%)	>99.9	>99.9	>99.9	>95	>90
Function (wt.%)		>1.28	>1.85	>0.45	>2.73

### 2.2. Synthesis of Silicate-1 samples by typical impregnation method

Silicate-1 zeolite was synthesized by using a procedure similar to that described in the literature [24]. Carbon nanotubes were firstly impregnated to incipient wetness with TEOS and digested in a saturator with ammonia at room temperature for 10 h. This process was repeated twice. The digesting step was carried out in a closed saturator in which an ammonia solution (30 wt.%) was kept in an open beaker, and the sample was kept in another beaker. Then the carbon/silica mixture was further impregnated to incipient wetness with TPAOH. The mixture with a molar ratio of  $\text{SiO}_2$  to TPAOH being 1:0.2 was transferred into a PTFE cup, introduced into a stainless steel autoclave with enough water filled in the bottom of autoclave to ensure a saturated steam atmosphere, then they were heated in an oven at 170 °C for 48 h for zeolite crystallization. The carbon nanotubes as well as organic template was removed by burning in a muffle furnace at 550 °C for 5 h. The zeolite samples are denoted as S-1-Ix, wherein x indicates the kind of nanotubes. Reference S-1 sample was synthesized without carbon nanotube template under identical condition.

### 2.3. Synthesis of Silicate-1 samples by direct hydrothermal method

Silicate-1 zeolite was hydrothermally synthesized by using carbon nanotubes as template by direct mix the carbon nanotubes in the zeolite synthesis mixture. The zeolite synthesis gel composition was  $\text{SiO}_2/0.2\text{TPAOH}/238\text{H}_2\text{O}$ . In a typical synthesis procedure, 0.5 g of carbon nanotube was firstly dissolved in 50 g of  $\text{H}_2\text{O}$ , and 2.5 g of TEOS and 1.9 g of TPAOH were added to the resultant solution under vigorous stirring. The final mixture was further stirred for 2 h at room temperature. The mixture was transferred into a PTFE lined autoclave, then it was heated in an oven at 170 °C for 48 h for zeolite crystallization. The carbon nanotubes as well as any organics were removed by burning in a muffle furnace at 550 °C for 5 h. The zeolite samples are denoted as S-1-Hx, wherein x indicates the kind of nanotubes. Reference S-1 sample by direct hydrothermal method was also synthesized without carbon nanotube template under identical conditions.

### 2.4. Materials characterization

X-ray diffraction (XRD) measurements were carried out using a Bruker diffractometer with Cu radiation (40 kV, 120 mA), data were recorded in the  $2\theta$  range of 5°–50° with an angular step size of 0.05° and a counting time of 8 s per step.

Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) analyses were carried out using a HITACHI S-4800 and an FEI Tecnai G<sup>2</sup> 30 S Twin microscope, respectively. The samples were prepared according to the typical sample preparing procedure. High resolution STEM image was also obtained with HAADF detector in dark mode during TEM investigation.

Nitrogen adsorption–desorption measurements were performed on a Micromeritics ASAP 2020 HD 88 surface area and

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