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# **Supporting Information**

## For

## Facile Synthesis of ECNU-20 (IWR) Hollow Sphere Zeolite

### **Composed of Aggregated Nanosheets**

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#### Synthesis of ECNU-20 zeolites

ECNU-20 was synthesized using 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) as structure-directing agent (SDA) from the gels with the molar compositions of  $1.0SiO_2$ : *x*GeO<sub>2</sub>: *y*DBU: 7H<sub>2</sub>O, where x = 0.2-0.5 and y = 0.5-1.5. In a typical synthesis, appropriate water was firstly added into DBU (purchased from J&K Chemical, 98%) followed by the dissolving of GeO<sub>2</sub> (Sinopharm Chemical Reagent Co., Ltd, 99.9%) in the mixture. Fumed silica (Aerosil 200) was then added into the pellucid solution and the mixture was stirred gently to get a homogeneous gel, which was crystallized at 443K in a PTFE-lined stainless steel under static station. The product was obtained by filtration, washed with water and then dried at 353 K for 12 h.

ITQ-24<sup>1</sup> and ECNU-3<sup>2</sup> zeolite were synthesized with hexamethonium dihydroxide and dimethyl-hexamethyleneimine as SDA, respectively, according to the literatures.

#### **Characterization**

The X-ray powder diffraction (XRD) patterns were measured on a Riguku Ultima IV X-Ray diffractometer (35 kV and 25 mA) using Cu-K $\alpha$  radiation ( $\lambda$ =1.5405 Å). The Scanning electron microscopy (SEM) images were measured on a Hitachi S-4800 microscope. The transmission electron microscopy (TEM) images were collected with a FEI G2F30 with an accelerating voltage of 300 kV. Nitrogen gas adsorption measurements were carried out at 77 K on a BEL-MAX gas/vapor adsorption instrument. The zeolite was evacuated at 573 K for at least 6 h before adsorption. <sup>13</sup>C solid-state MAS NMR spectra was performed on a Varian model

VNMRS-400WB spectrometer under one pulse condition. The liquid-state <sup>13</sup>C NMR spectrum for the analyses of the organic amines was recorded on a Brucker Avance 500 spectrometer at ambient temperature. The thermogravimetric and derivative thermogravity (TG-DTG) analyses were carried out on a Mettler-Toledo Model TGA/SDTA851e apparatus from room temperature to 1063 K at a heating rater of 10 K min<sup>-1</sup> in air.

#### High-resolution XRD experiment, profile fitting and structure simulation

The high-resolution powder X-ray diffraction (PXRD) data for ECNU-20 was collected on synchrotron beam line 14B at Shanghai Synchrotron Radiation Facility (SSRF) with the X-ray wave length of 1.2438 Å. The preferred orientation of the samples was improved by using 0.5 mm glass capillary as sample holders. The data was obtained in the 2θ angle range of 5-48° at an effective X-ray energy of 10 keV. The profile fitting of ECNU-20 was performed using TOPAS 5.0. The coordinates of the conventional IWR zeolite tetrahedral network was used as starting parameters for DIFFFax simulation.

Si/Ge	SDA/Si Time (d)	<b>T:</b> (1)	Crystal morphology			
		hollow	nanosheet	sphere		
	0.5	9				
2	1.0	7	$\checkmark$	$\checkmark$	$\checkmark$	
	1.5	7	$\checkmark$	$\checkmark$	$\checkmark$	
3	0.5	9				
	1.0	7	$\checkmark$	$\checkmark$	$\checkmark$	
	1.5	7	$\checkmark$	$\checkmark$	$\checkmark$	
4	0.5	14				
	1.0	9		$\checkmark$	$\checkmark$	
	1.5	7		$\checkmark$	$\checkmark$	
5	0.5	14				
	1.0	14		$\checkmark$	$\checkmark$	
	1.5	9		$\checkmark$	$\checkmark$	

**Table S1** List of synthesis conditions and the corresponding morphologies of ECNU 

 20 zeolite.<sup>a</sup>

<sup>a</sup> Crystallization conditions: H<sub>2</sub>O/SiO<sub>2</sub>=7; temp., 443 K.



**Figure S1.** The organic structure directing agents used in the synthesis of the ECNU-20 zeolite (a), ECNU-3 zeolite (b) and ITQ-24 zeolite (c).



**Figure S2.** N<sub>2</sub> adsorption/desorption isotherms of calcined ECNU-20 zeolite (Si/Ge=3, SDA/Si=1) (a), calcined ECNU-3 zeolite (b).

<b>Table 52</b> . Thysical properties of Lerio-20 Zeonic and Lerio-5 Zeonic
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	SSAa	<b>S</b> b	V.c	V.b	V d
	SSA	Sext	v total	v micro	v meso
	$m^2 g^{-1}$	$m^2 g^{-1}$	$cm^3 g^{-1}$	$cm^3 g^{-1}$	$cm^3 g^{-1}$
ECNU-3	573.4	68.2	0.27	0.16	0.11
ECNU-20	625.1	146.0	0.49	0.14	0.35

 $^{\rm a}$  Specific surface area (SSA) determined by  $N_2$  adsorption isotherms at 77 K using Langmuir method.

<sup>b</sup> Calculated by *t*-plot.

<sup>c</sup> Given by the adsorption capacity at relative pressure of  $P/P_0=0.99$ .

<sup>d</sup> V<sub>meso</sub>=V<sub>total</sub>-V<sub>micro</sub>

As shown in Table S2, ECNU-20 with interparticle mesopores from the aggregation of nanosheets exhibited higher external surface area and mesoporous volume than column-like ECNU-3 zeolite.



**Figure S3.** Liquid-phase <sup>13</sup>C NMR of DBU molecules (a) and solid-state <sup>13</sup>C NMR of as-synthesized ECNU-20 zeolite (b).

The DBU species occluded in as-synthesized ECNU-20 showed a less resolved spectrum, yet it resembled that of free DBU molecules, which implies that the DBU molecules were not decomposed during zeolite crystallization process.



Figure S4. TG-DTG curves of as-synthesized ECNU-20 zeolite.

The first step in TG curve indicated a weight loss of 4.3 wt %, attributed to adsorbed water molecules. The weight loss between 300°C and 800°C was 15.1 wt % due to the decomposition of OSDA molecules.



**Figure S5.** Observed (black), calculated (red) and difference (blue) profiles for the profile fitting of ECNU-20. The short-tick marks (green) below the patterns indicate the Bragg reflection positions.

Orthorhombic		
<i>Cmmm</i> (No. 65)		
a = 21.3204 Å		
b = 13.4621 Å		
c = 12.6837  Å		
3640.44 Å <sup>3</sup>		
PANalytical X'-Pert Pro		
298(2) K		
Cu Ka <i>l</i>		
1.540596Å		
3.000-80.00°		
665		
5864		
Pseudo-Voigt		
TOPAS 5.0		
0.0123		
0.0164		
0.0099		
1.6479		

**Table S3**. Crystallographic data, experimental conditions for powder X-ray data collection and results of the Pawley fitting of as-synthesized ECNU-20.



**Figure S6.** XRD patterns of IWR-type zeolites simulated with a different crystal thickness of 100 nm (a), 50 nm (b) and 10 nm (c) along c axis.

With decreasing the crystal thickness along c axis from 100 to 10 nm, the c-related reflections were broadened and weakened in intensify greatly.



**Figure S7.** SEM images of ECNU-20 zeolite (SDA/Si=1) synthesized at different Si/Ge ratio of 2 (a), 4 (b), 5 (c); SEM images of ECNU-20 zeolite (Si/Ge=3) synthesized at different SDA/Si ratio of 1.5 (d), 0.5 (e); SEM image of ECNU-20 zeolite (Si/Ge=3, SDA/Si=0.5) crystallized for 1 day (f).

#### Theoretical methods and models.

For modeling the interaction between the surface of zeolites and SDA molecules, one important question that must be addressed first, is how to get the unequivocal surface structure for porous materials. As demonstrated in a separate study<sup>3</sup>, a jointly use of SIESTA<sup>4</sup> and VASP<sup>5,6</sup> packages is an effective and efficient approach to explore the surface structures of zeolite. Simply put, the SIESTA package is used for structure relaxation of system with thousands of atoms, and then the electronic energy was refined by a single-point energy calculation with the VASP package.

The geometry relaxation was performed by using the SIESTA package with the Perdew-Burke-Ernzerhof (PBE) functional<sup>7,8</sup>, wherein a linear-scaling density-functional methods<sup>9</sup> was implemented for efficient calculation of large system. This package utilizes periodic boundary conditions, norm-conserving pseudopotentials<sup>10</sup> and a localized numerical basis set to describe the valence electrons. A double- $\zeta$  basis set with polarization functions was used for all atoms. The Brillouin zone was sampled at the  $\Gamma$  point with a mesh cutoff of 300 Ry. The split gauss basis set were used for all atoms. In geometry optimization, the convergence criterion for the electronic self-consistency was 10<sup>-4</sup> eV, and that for the ionic relaxation was set to 10<sup>-3</sup> eV.

Once the structure obtained, the single point energy calculation was followed by using VASP with the DFT-D3 scheme<sup>11,12</sup> as implemented in to account for the weak interaction between the surface of zeolite and SDA molecules. The exchangecorrelation energy was described by the PBE functional. The Brillouin-zone sampling was restricted to the  $\Gamma$  point. The electron-ion interaction was solved by the projector augmented wave (PAW)<sup>13,14</sup> method, and the iterative solutions of Kohn-Sham equations was done using a plane-wave basis set with a cutoff energy of 500 eV. The convergence criterion for the electronic self-consistency cycle was set to 10<sup>-5</sup> eV for final single-point energy calculation.

Considering Si and Ge are both tetrahedral elements, here we use pure Si framework as the model system for simplification in following studies. Surface slabs were created along 7 low-index directions, and stable termination of external surface was constructed to reduce surface hydroxyls density. The calculated surface free energies ( $\gamma$ ) were listed in Table S4. Each of surface terminations would expose unsaturated Si or O atoms in the slab model that contains no more than 900 atoms. The vacuum gap in the slab is kept large enough (~15Å) to prevent unphysical interactions between the top and the bottom of the surface. The surface slabs were thick enough for the convergence of surface free energy. The surface free energy was calculated using the following expression:

$$\gamma = \frac{G_{surf} - G_{bulk} - n\mu_{H_2O}(T)}{A_{hkl}}$$
$$= \frac{E_{0K}(surf_{hkl}) - E_{0K}(bulk) - n\mu_{H_2O,l}(T)}{A_{hkl}} \qquad (1)$$

The smaller the surface free energy, the more stable is the corresponding surface structure. Here, we use the 420 K as the circumstance temperature of water molecular for getting as possible as close to the actual condition of reaction.

The cell vectors and the middle region in the slab model representing the bulk

phase were fixed during geometry relaxation of the surface structures. In order to investigate the influence of SDAs on the morphology of zeolite, the adsorption energies of SDAs on each surface of zeolite were calculated first. Then, the surface free energy of a bare surface structure was corrected according to the following expression. The corrected surface free energy  $\gamma_{cor}^{15}$  is given by:

$$\gamma_{cor} = \frac{E_{0K}(surf_{hkl}) - E_{0K}(bulk) - n\mu_{H_2O,l}(T) - E_{ad}(SDAs)}{A_{hkl}}$$
$$= \gamma_{hkl} - \Delta\gamma$$
(2)

The more negative the adsorption energy, the stronger of the interaction between each surface and SDAs is, accordingly reducing the surface free energy to a larger extent. To compare the effect of different SDAs on the external surface of zeolites, we assumed that each half-open cage on the external surface accommodates only one SDA molecule duo to the size of SDAs molecules.

For efficiently comparing the interactions of SDAs on each external surface, we adopted slab models with less atoms (as shown in Figure S9) while retaining the half-open cages on the surface structure as simulated above. The two layers in the bottom of slabs were fixed in order to maintain the framework of zeolite surface and the other atoms was fully relaxed to estimate the interaction between SDAs and external surface of zeolites. The adsorption energy of SDAs on the external surface was defined as the energy difference between the SDAs-surface complex ( $E_{slab-sda}$ ) and the isolated form of the surface slab ( $E_{slab}$ ) and SDAs ( $E_{sda}$ ):

$$\Delta E_{ads,D3} = E_{slab-sda} - E_{sda} - E_{slab} \qquad (3)$$

To fairly compare the interaction of each SDA with half-open cage on different surfaces, we only considered the adsorption of the single half-open cage on different surfaces. The interaction between SDAs and external surfaces was described by the adsorption energy Eads as listed in Table S5. The stable configurations between SDAs and these half-open cages were confirmed by comparing different orientations of SDAs among the half-open cages, we find that the interaction between DMHMI and external half-open cages is not sensitive to the orientation of DMHMI molecule, while the amino group of DBU molecule is more prone to the surface silanol due to the forming of H-bonds (Figure 5c). The most stable orientation was carefully determined among possible configurations as shown in Figure S9. The adsorption energy and the corrected surface free energy due to the adsorbed SDAs are listed in Table S5.

Terminals*	$\gamma_{surf}~(mJ~m^{-2})$
(001) <sup>a</sup>	233
(001) <sup>b</sup>	231
(001) <sup>c</sup>	191
(010)	238
(100) <sup>a</sup>	283
(100) <sup>b</sup>	309
(100) <sup>c</sup>	305
(110)	205
(130)	246
(201)	392
(510) <sup>a</sup>	392
(510) <sup>b</sup>	293

**Table S4** The surface free energies of surface termination along 7 directions.

\*The superscript means the least density of surface hydroxyls along certain direction is not unique.



**Figure S8.** The structures of stable terminations of (110) surface (a), (100) surface (b), (001) surface(c) and (010) surface (d) predicted by DFT calculations.

**Table S5** The adsorption energy  $E_{ads}$  (eV) of SDA1 and SDA2 on the external surfaces of IWR zeolite, the surface free energy  $\gamma$  (mJ m<sup>-2</sup>) the corrected surface free energy  $\gamma_{cor}$  (mJ m<sup>-2</sup>).  $D_{cage}$  (10<sup>16</sup>/m<sup>2</sup>) means the density of half-cages on the external surfaces.

Surfaces	$D_{cage} (10^{16}/m^2)$	Eads	Δγ	γ	$\gamma_{cor}$
001 <sup>SDA1</sup>	7.1	-0.70	-78	191	113
$001^{SDA2}$	7.1	-1.56	-177	191	14
010 <sup>SDA1</sup>	3.7	-0.78	-48	226	178
$010^{SDA2}$	3.7	-1.39	-84	226	141
$100^{SDA1}$	5.9	-0.85	-81	270	189
$100^{SDA2}$	5.9	-1.68	-159	270	111
110 <sup>SDA1</sup>	6.3	-0.64	-63	196	133
110 <sup>SDA2</sup>	6.3	-1.20	-116	196	80



**Figure S9.** The geometry of the DMHMI molecule located in the half-cage structure of the external surface. The DMHMI molecules has a non-planar 7-ring (7R) structure, which get more close toward the framework of the half-open cage after optimization, indicating the Van der Waals forces between them. In comparison, DBU mole additionally interacts with the surface silanols located on the half-open cages as shown in Figure 5c.

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