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Electronic Supplementary Information

Solvent-free synthesis of nanosized hierarchical sodalite zeolite with multi-hollow polycrystalline structure

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Experimental

Materials

$Na_2SiO_3 \cdot 9H_2O$ (SiO_2, ca.20 wt. %, Tianjin Guangfu Chemical Reagent Co., Ltd.), $NaAlO_2$ (Sinopharm Chemical Reagent Co. Shanghai, China), pseudoboehmite (Al_2O_3, ca.70 wt.%, H_2O, 30 wt.%, Liaoning hydratight science and technology development Co., Ltd.), Dimethyloctadecyl[3-(trimethoxysilyl)propyl]ammonium chloride ($[(CH_3O)_3\ SiC_3H_6N(CH_3)_2C_{18}H_{33}]Cl$, TPOAC, 72%) were purchased from Sigma-Aldrich, Diatomite (Tianjin Guangfu Chemical Reagent Co., Ltd.). All chemicals were used as received without further purification.

Synthesis

Solvent-free synthesis of hollow hierarchical sodalite.

For the synthesis of hierarchical sodalite zeolite, the organosilane surfactant TPOAC was used as mesopores template. In a typical synthesis, 1.52 g $Na_2SiO_3 \cdot 9H_2O$ was mixed with 0.6 g sodium aluminate. After grinding for 5 min, followed by adding of 0-0.5 g TPOAC (60 % in methanol) with a proportion of 0-10 mol % relative to sodium silicate. After grinding for another 5 min, the dry mixture was transferred to a autoclave and sealed, heating at 80 ^oC for 10-20h. The final product was recovered by repeated high-speed centrifugation and washing with deionized water and drying at 60 ^oC for 12h. The as-synthesized hollow hierarchical product prepared in a solvent-free route was designated as HS-SOD(n) (n=0, 3, 6, 10), where n was the mole proportion of organosilane TPOAC in regards to sodium silicate. The weight-loss detected by TG analysis was increased along with the TPOAC molar ratio increase, especially for HS-SOD(10), even 23% weight-loss was detected, as illustrated in Table 1.

Solvent-free synthesis of hollow hierarchical sodalite using diatomite as silicon source.

Considering inexpensive silicon source, diatomite was substituted for sodium silicate as silicon source and porous pseudoboehmite replaces sodium aluminate as aluminum sources respectively.[1] Additional experiments were conducted as follows. In a typical synthesis, 0.6 g diatomite , 0.34 g pseudoboehmite and 0.8 g NaOH were mixed together, after grinding for 5 min, followed by adding of 0.15 g TPOAC (60 % in methanol). After grinding for another 5 min, the dry mixture was transferred to a autoclave and sealed, heating at 80 ^{o}C for 10-20h. The synthesized sample was denoted HS-SOD-Dt(2).

Solvent-free synthesis of hollow sodalite using pseudoboehmite as aluminum source.

Another experiment was conducted using pseudoboehmite exclusively as aluminum source. Typically, 1.32 g $Na_2SiO_3 \cdot 9H_2O$ was mixed with 0.34 g pseudoboehmite. After grinding for 5 min, the solid mixture was transferred to a autoclave and sealed, heating at 80 ^{o}C for 10-20h. The as-synthesized sample denoted HS-SOD-AlOOH.

Characterization

X-ray diffraction (XRD) patterns were collected on a Rigaku D/MAX 2550 diffractometer with Cu Kα radiation (λ= 0.15418 nm). Scanning electron microscopy (SEM) images were obtained by JEOL electron microscopes (FE-JSM 6700, Japan). The nitrogen adsorption-desorption isotherms were measured at -196 °C using a Micromeritics ASAP 2020M system. Samples were outgassed for 10 h at 150 ^{o}C prior to analysis. The pore volume and pore-size distributions were derived from the adsorption branches of the isotherms using nonlocal density functional theory (NLDFT). TEM images were obtained on FEI Tecnai G2 F20 s-twin D573 field emission transmission electron microscope with an accelerating voltage of 200 kV. Thermogravimetric (TG) analysis was carried out on a Perkin-Elmer TGA 7 at a heating rate of 10 ^{o}C/min from room temperature to 800 ^{o}C in air. Deionized water was

all used in the synthesis. Fourier transform infrared (FT-IR) spectra were recorded using a Bruker 66V FTIR spectrometer.

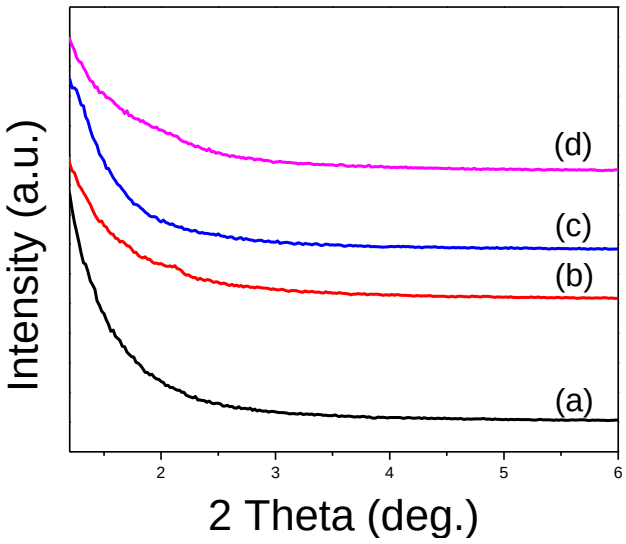

Fig. S1 XRD patterns (small-angle) of the as-synthesized sodalite samples prepared in a solvent-free route (a) HS-SOD(0), (b) HS-SOD(3), (c) HS-SOD(6), (d) HS-SOD(10).

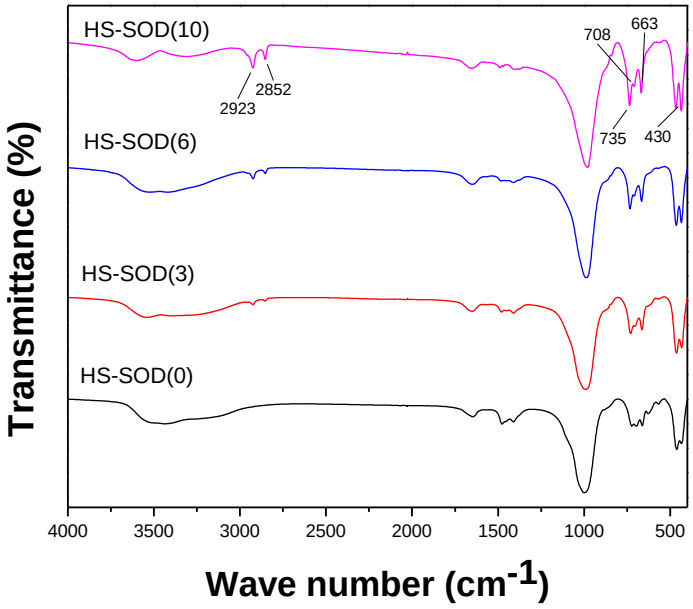

Fig. S2 The FT-IR spectra of as synthesized HS-SOD(n) (n=0, 3, 6, 10) samples.

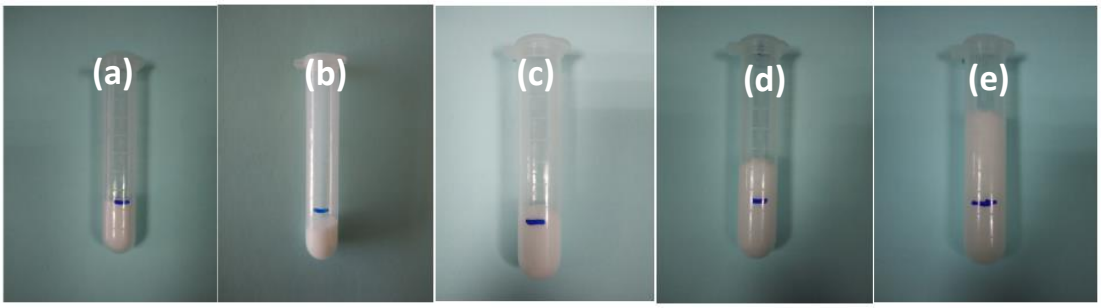

Fig. S3 Photographs of as-synthesized samples prepared in a solvent-free route, (a) prior of crystallization (b) HS-SOD(0) , (c) HS-SOD(3), (d) HS-SOD(6), (e) HS-SOD(10).

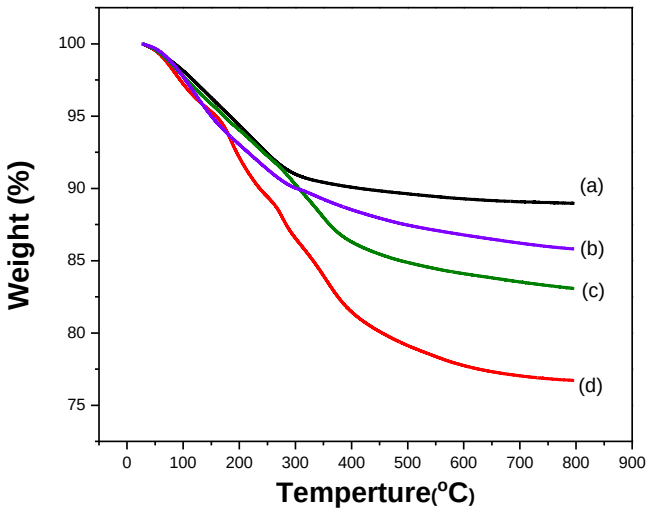

Fig. S4 TG curves of prepared sodalite samples with different organosilane amounts in a solvent-free route (a) HS-SOD(0) , (b) HS-SOD(3), (c) HS-SOD(6), (d) HS-SOD(10).

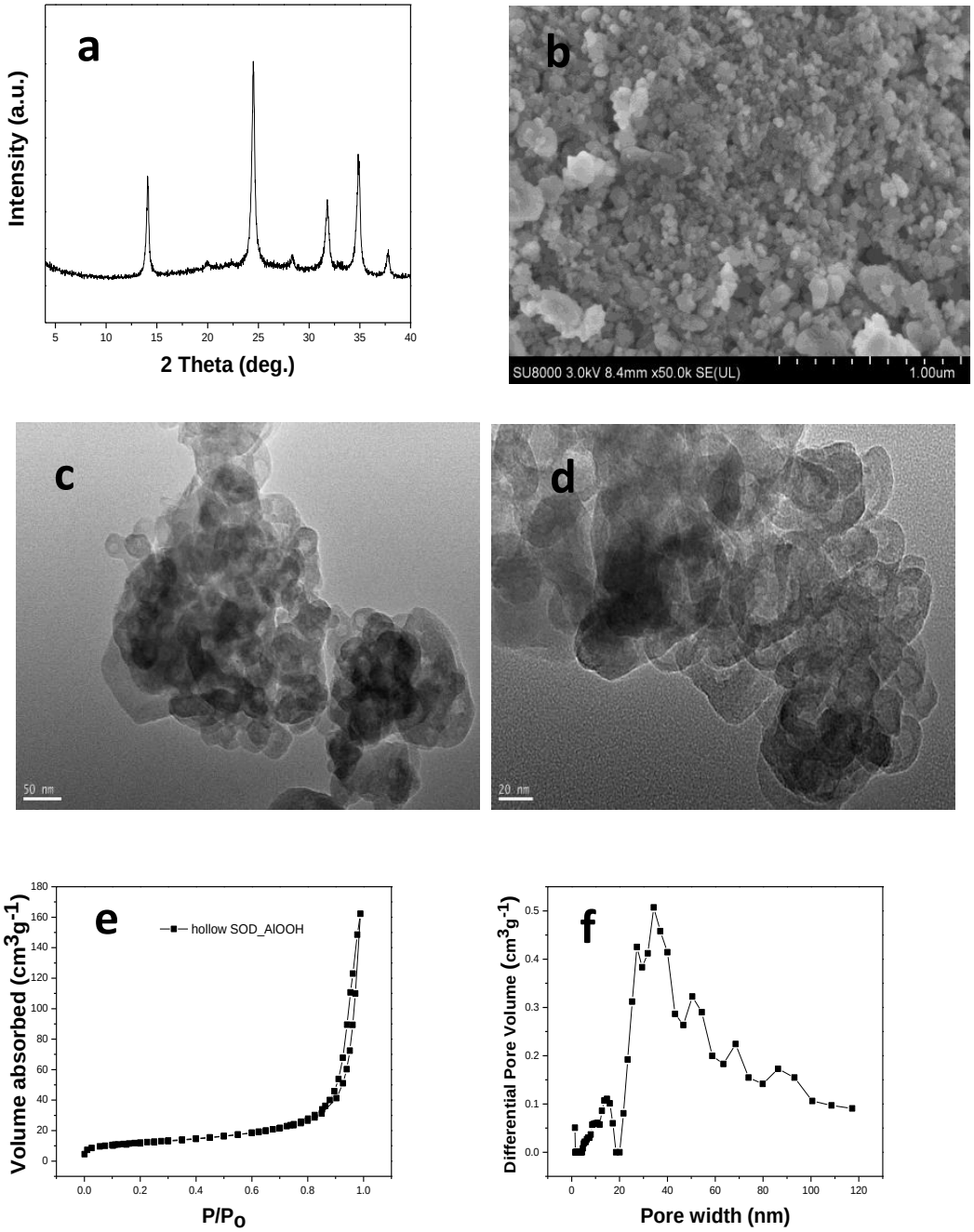

Fig. S5 Analytical data for as-synthesized HS-SOD-AlOOH. (a) XRD pattern, (b) SEM image, (c) TEM image (scale bar 50nm), (d) TEM image (scale bar 20 nm), (e) N_2 sorption isotherms, and (f) DFT pore size distribution.

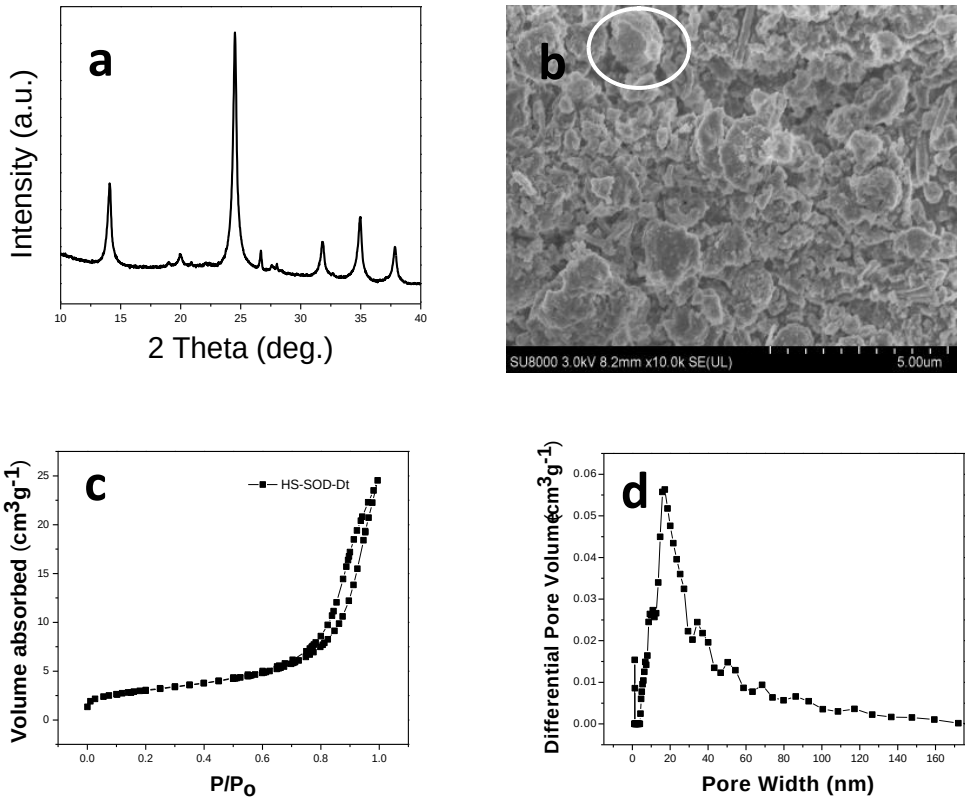

Fig. S6 (a) XRD pattern, (b) SEM image, (c) N_2 sorption isotherms, and (d) DFT pore size distribution of HS-SOD-Dt sample.

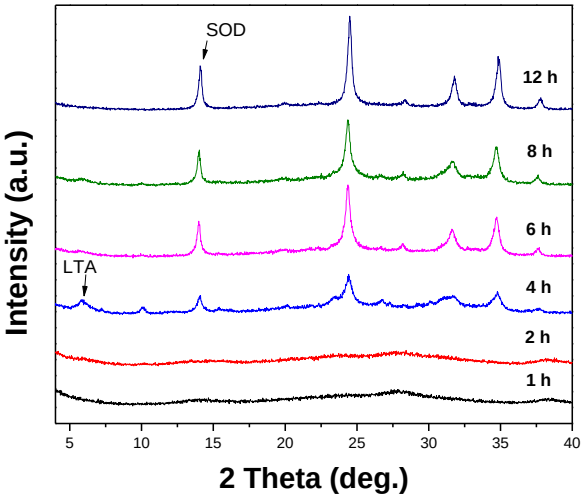

Fig. S7 XRD patterns of HS-SOD-AlOOH zeolite obtained from solid mixture for different reaction time. (pseudoboehmite was used as aluminum source)

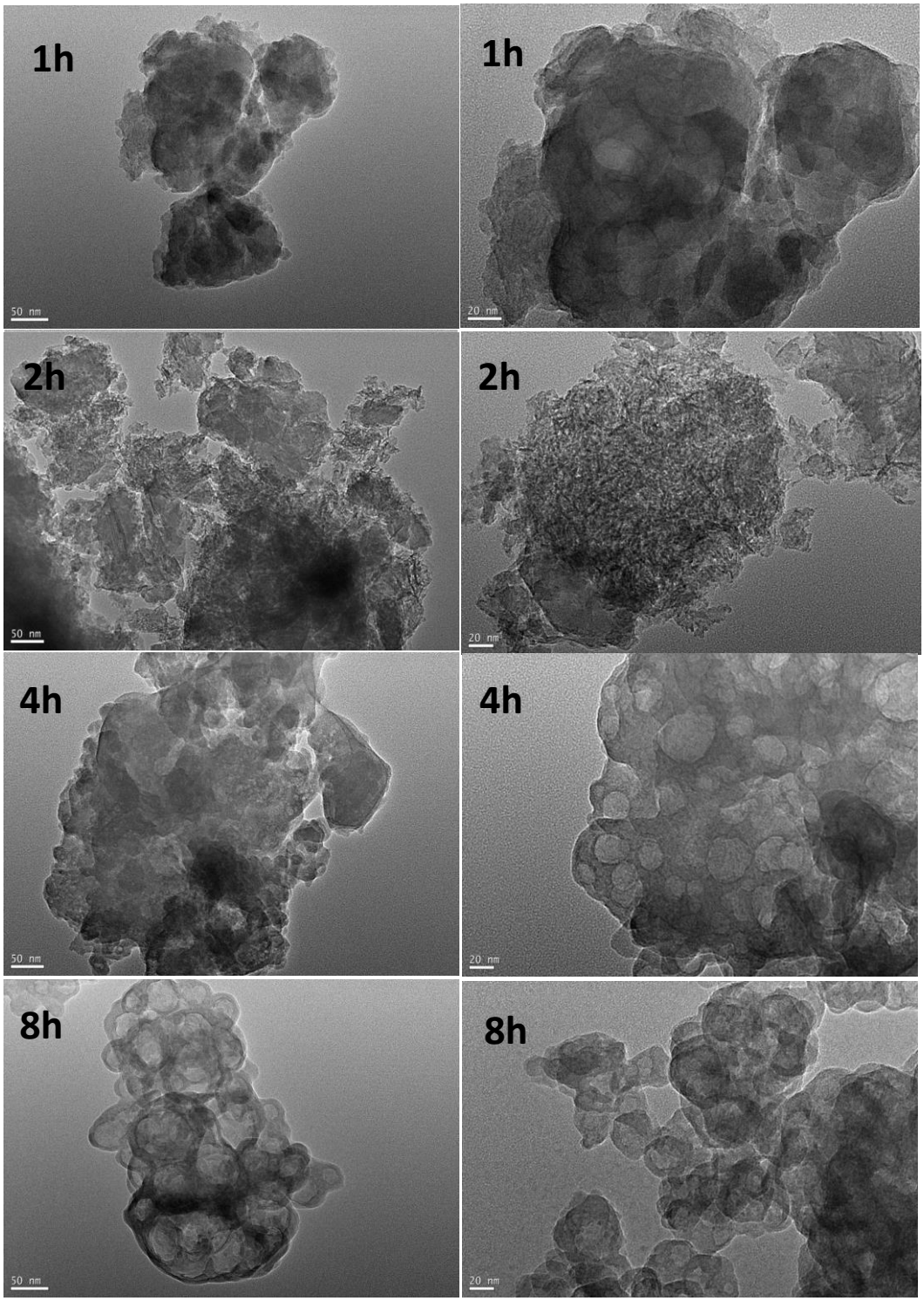

Fig. S8 TEM micrographs of HS-SOD-AlOOH(0) obtained at 80 ^{o}C at different time of thermal treatment.

Table S1 Crystallinity, weight loss and textural properties of the HS-SOD(n) zeolites

Sample	Crystallinity[a](%)	S_{BET}[b] /$m^2 g^{-1}$	S_{Ext}/$m^2 g^{-1}$	V_{total}[c] /$cm^3 g^{-1}$	Pore size[d]/nm	Weight loss(%)
HS-SOD(0)	100	35.7	25.9	0.24	13.6/27.2/50.3	11.0
HS-SOD(3)	117	54.7	51.5	0.07	4.6/27.2/50.3	14.2
HS-SOD(6)	94	62.7	61.4	0.09	4.6/27.2/50.3	17.0
HS-SOD(10)	131	52.5	49.9	0.08	4.6/27.2/50.3	23.3
HS-SOD-Dt(2)	n.d.	10.9	9.1	0.04	10.0/17.2/34.3	n.a
HS-SOD-AlOOH	133	42.9	33.1	0.25	14.7/34.3/50.3	n.a

a.The sodalie synthesized using sodium aluminate as aluminum source without template is taken to 100 % crystallinity.
b.Determined by multi-point BET.
c.Determined at $P/P_o = 0.99$.
d.Determined by NLDFT method.
n.d. Not determined.

Reference

1. Y. C. Du, S. L. Shi, H. X. Dai, *Particuology*, 2011, **9**, 174.