

## Supplementary Information

### Atom-Economical Synthesis of High Silica CHA Zeolite from a Solvent-Free Route

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### Experimental Section

#### *Chemicals*

The chemicals used in this work include aluminum sulfate ( $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , AR, 99%, Sinopharm Chemical Reagent Co., Ltd.), sodium metasilicate nonahydrate ( $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , AR,  $\text{SiO}_2$  of 20 wt.%, Aladdin Chemistry Co., Ltd.), solid silica gel (Qingdao Haiyang Chemical Reagent Co, Ltd.), ammonium nitrate ( $\text{NH}_4\text{NO}_3$ , AR, 99%, Beijing Chemical Reagent Co., Ltd.), N,N-dimethylcyclohexylamine (AR, 98%, Aladdin Chemistry Co., Ltd.), bromoethane (AR, 98%, Aladdin Chemistry Co., Ltd.), acetone (AR, 99.5%, Aladdin Chemistry Co., Ltd.), ethanol (AR, 99.7%, Shanghai Lingfeng Chemical Reagent Co, Ltd.), and N,N,N-trimethyl-1-1-adamantammonium hydroxide (TMAdaOH, 25%, Sichuan Zhongbang Co., Ltd.).

### *Synthesis of S-CHA zeolite*

Solvent-free synthesis of high silica CHA zeolite was performed by grinding the solid raw materials followed by heating at 180°C. As a typical run for synthesis of high silica CHA zeolite, 1.41 g of  $\text{Na}_2\text{SiO}_3 \cdot 9\text{H}_2\text{O}$ , 0.65 g of  $\text{Al}_2(\text{SO}_4)_3 \cdot 18\text{H}_2\text{O}$ , 1.37 g solid silica gel, and 0.8 g of DMCHABr were added. After grinding for 10-20 min, the mixture was transferred to an autoclave. After heating at 180°C for 5 days, the sample was completely crystallized. The products were finally obtained by filtration at room temperature and calcination at 550°C for 5 h. This sample was designated as S-CHA. The H-form of the S-CHA was prepared by triple ion-exchange with 1 M  $\text{NH}_4\text{NO}_3$  solution at 80°C for 2 h, followed by calcination at 500°C for 4 h.

### *Synthesis of N,N,N-dimethylethylcyclohexylammonium bromide (DMCHABr)*

45 g of ethylbromide was added to a mixture of 50 g of N,N-dimethylcyclohexylamine and 100 g of ethanol. After reaction for overnight at 50°C, the product was finally obtained by washing with acetone and drying under vacuum condition.<sup>1</sup>

### *Synthesis of conventional high silica CHA zeolite (C-CHA)*

Conventional high silica CHA was synthesized according to a published literature.<sup>2</sup> As a typical run, 2 g of 1 M NaOH solution, 2 g of N,N,N-trimethyl-1-adamantanammonium hydroxide solution (TMAOH, 25 wt.%) and 2.0 g of deionized water were mixed, followed by addition of 0.05 g of aluminum hydroxide (Sigma Aldrich) and 0.6 g of fumed silica (Shenyang Chemical Reagent Co., Ltd) under stirring. Until the formation of homogeneous gel, the gel was transferred into a Teflon-lined autoclave, heating in oven at 160°C for 5 days. After the filtration at room temperature and calcination at 550°C for 5 h in air, the product was finally obtained. This sample was designated as C-CHA. The H-form of the zeolite was obtained by triple ion-exchange of the calcined zeolite with 1 M  $\text{NH}_4\text{NO}_3$  at 80°C for 2 h and calcination at 500°C for 4 h in air.

### *Characterization:*

X-ray powder diffraction (XRD) patterns were measured with a Rigaku Ultimate VI X-ray diffractometer (40 kV, 40 mA) using  $\text{Cu}_{K\alpha}$  ( $\lambda=1.5406 \text{ \AA}$ ) radiation. The argon sorption isotherms at the temperature of liquid nitrogen were measured using Micromeritics ASAP 2020M and Tristar system. The sample composition was determined by inductively coupled plasma (ICP) with a Perkin-Elmer 3300DV emission spectrometer. Scanning electron microscopy (SEM) experiments were performed on Hitachi SU-1510 electron microscopes.  $^{27}\text{Al}$ ,  $^{29}\text{Si}$ , and  $^{13}\text{C}$  solid MAS NMR spectra were recorded on a Varian Infinity Plus 400 spectrometer.  $^{13}\text{C}$  liquid NMR spectrum was recorded on a Bruker Avance 500 spectrometer using a 5 mm QNP probe equipped with z-gradient coil. The acidity of the catalysts was measured by the temperature-programmed-desorption of ammonia ( $\text{NH}_3$ -TPD). The catalyst (0.2 g, 40-60 mesh) was pretreated at  $500^\circ\text{C}$  in a  $\text{N}_2$  flow for 60 min, followed by the adsorption of  $\text{NH}_3$  at  $100^\circ\text{C}$  for 30 min. After saturation, the catalyst was purged by  $\text{N}_2$  flow for 30 min to remove the physically adsorbed ammonia on the sample. Then, desorption of  $\text{NH}_3$  was carried out from 100 to  $600^\circ\text{C}$  with a heating rate of  $10^\circ\text{C}/\text{min}$ .

### *Catalytic tests*

The methanol-to-olefin (MTO) reaction was carried out with a fixed-bed tubular steel reactor with an inner diameter of 8 mm and a length of 30 cm at atmospheric pressure. 0.50 g of catalyst (40-60 mesh) was loaded in between two layers of quartz wool. The sample was pretreated in flowing nitrogen at  $500^\circ\text{C}$  for 2 h and then cooled to  $350^\circ\text{C}$ , followed by the introduction of gaseous methanol mixed with  $\text{N}_2$  into the reactor (methanol partial pressure of  $9.3 \times 10^3 \text{ Pa}$ ). The weighted hourly space velocity (WHSV) was  $0.8 \text{ h}^{-1}$ . Effluent gas from the reactor was analyzed on-line by an Agilent 6890 gas chromatograph equipped with a FID detector and a HP-PONA methyl siloxane capillary column. The product selectivities were expressed as mass percentages of each product among all the detected products except dimethyl ether.

The SCR activity measurements were carried out in a fixed-bed quartz reactor with the reactant gas mixture containing 500 ppm NO, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, and N<sub>2</sub> balance. The gas hourly space velocity (GHSV) was 80000 h<sup>-1</sup>. Cu-S-CHA and Cu-C-CHA were prepared *via* ion-exchanged method with (CH<sub>3</sub>COO)<sub>2</sub>Cu aqueous solution, and the copper loading of the samples was about 2 wt %.

### **Supplementary References**

1. G. Cao, M. M. Mertens, A. S. Guram, H. Li, J. C. Yoder, U. S. Patent 7,754,187, 2010.
2. S. I. Zones, U. S. Patent 4,544,538, 1985.

## Supporting Figure Captions

**Fig. S1** TG-DTA curve of the as-synthesized S-CHA synthesized at 180°C.

**Fig. S2** Investigation on S-CHA crystallization. (A) Photographs, (B) XRD patterns, (C) SEM images of the samples crystallized at (a) 0, (b) 1, (c) 1.5, (d) 2, (e) 3, (f) 4, and (g) 5 days for synthesizing S-CHA zeolite.

**Fig. S3** The dependence of the S-CHA crystallinity on the crystallization time.

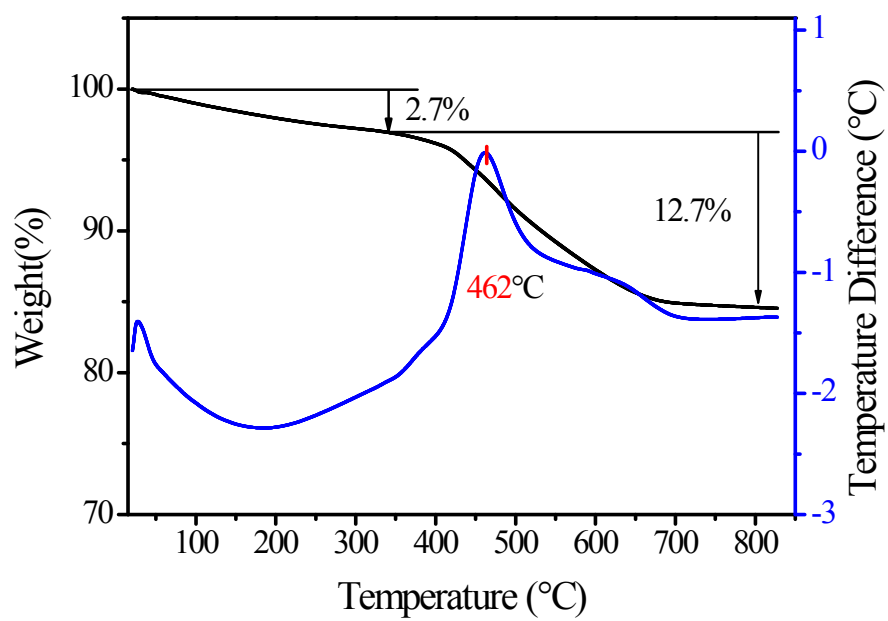
**Fig. S4** NH<sub>3</sub>-TPD curve of the H-form of S-CHA synthesized at 180°C.

**Fig. S5** NH<sub>3</sub>-TPD curve of the H-form of CHA hydrothermally synthesized at 160°C.

**Fig. S6** XRD pattern and SEM image of C-CHA synthesized at 160°C

**Fig. S7** Dependence of NO conversion on reaction temperature in NH<sub>3</sub>-SCR over Cu-C-CHA catalyst synthesized from conventional hydrothermal route. Reaction conditions: 500 ppm NO, 500 ppm NH<sub>3</sub>, 10% O<sub>2</sub>, and N<sub>2</sub> balance; GHSV: 80000 h<sup>-1</sup>.

**Fig. S8** Conversion and product selectivities in MTO at 350°C (◇C<sub>1</sub>; △C<sub>2</sub>; ▲C<sub>2</sub><sup>+</sup>; ◇C<sub>3</sub>; ◆C<sub>3</sub><sup>+</sup>; ●C<sub>4</sub><sup>+</sup>; ●C<sub>4-6</sub>; ■Conv. ) over C-CHA zeolite synthesized from conventional hydrothermal route.



**Fig. S1**

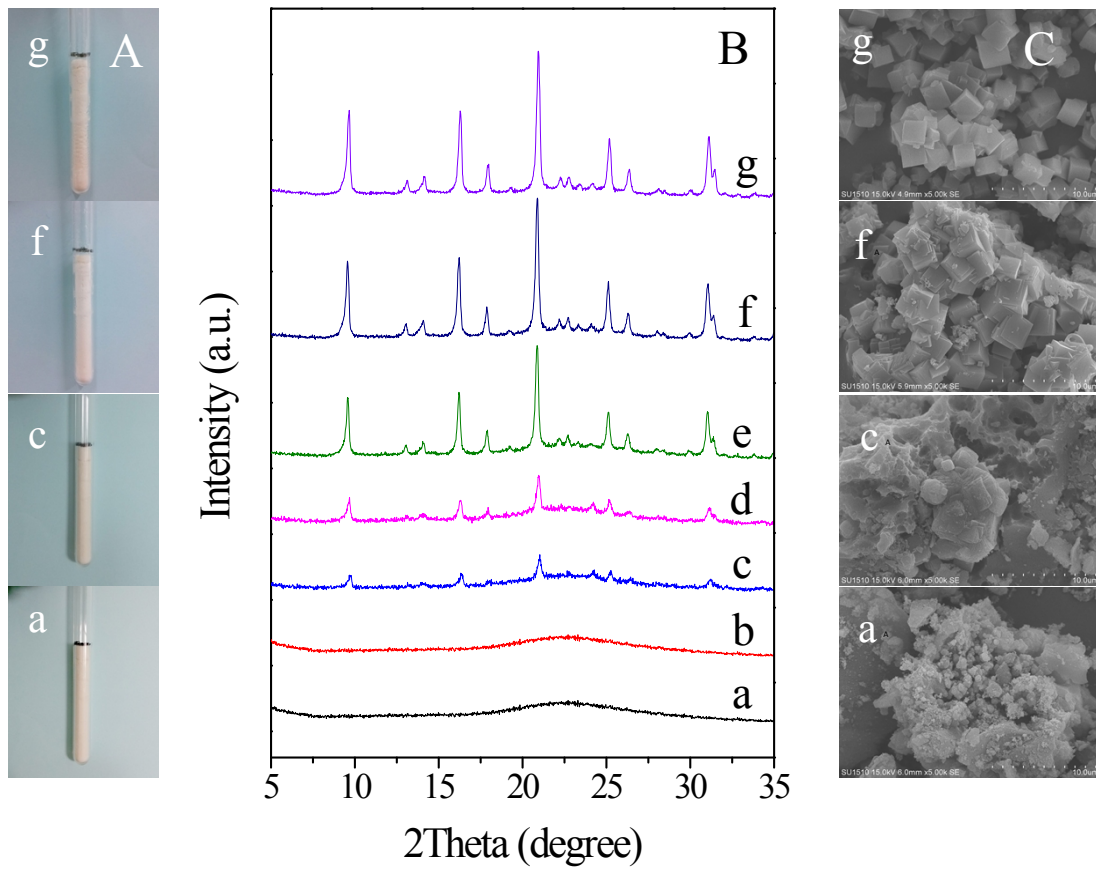
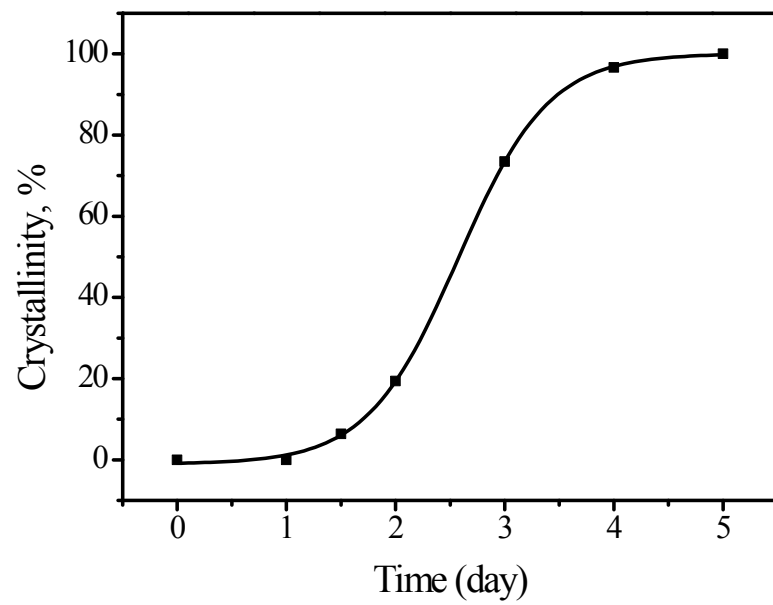
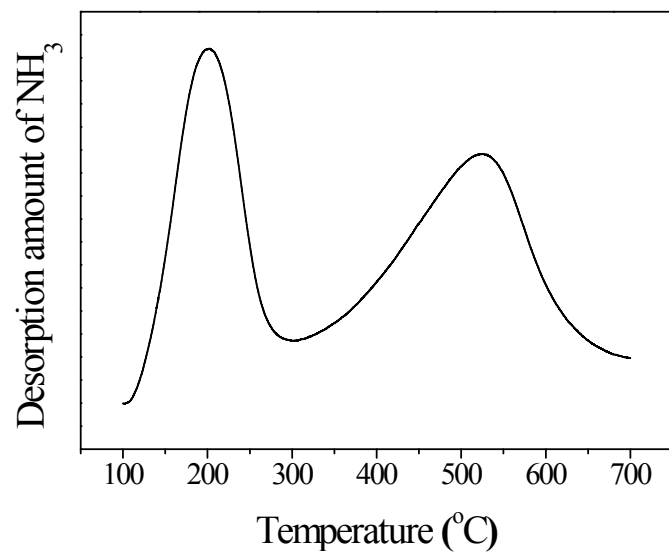


Fig. S2

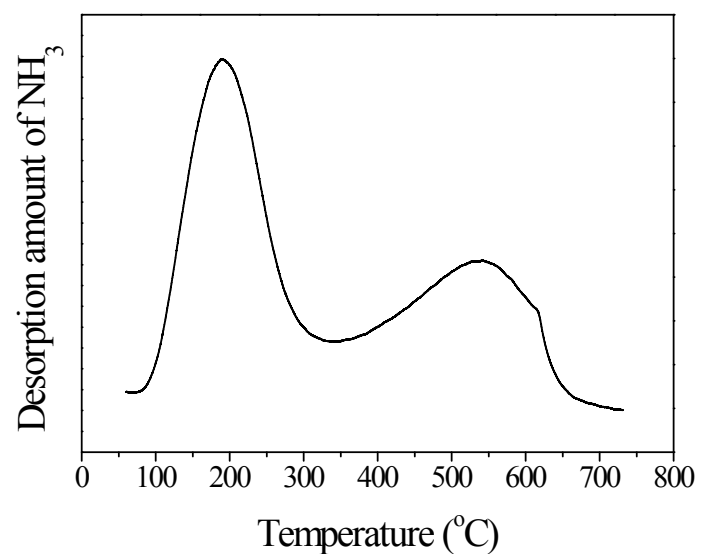


**Fig. S3**

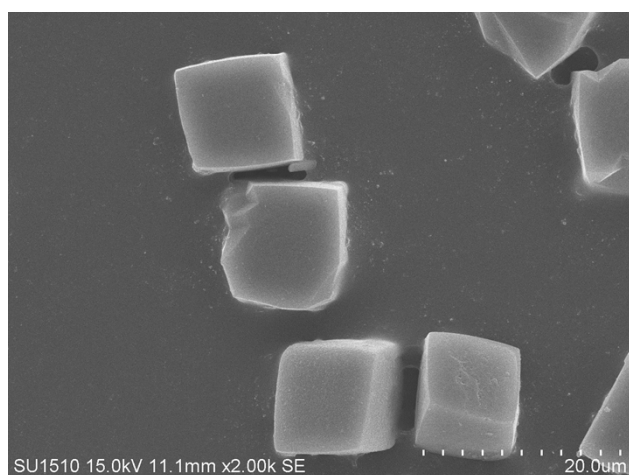
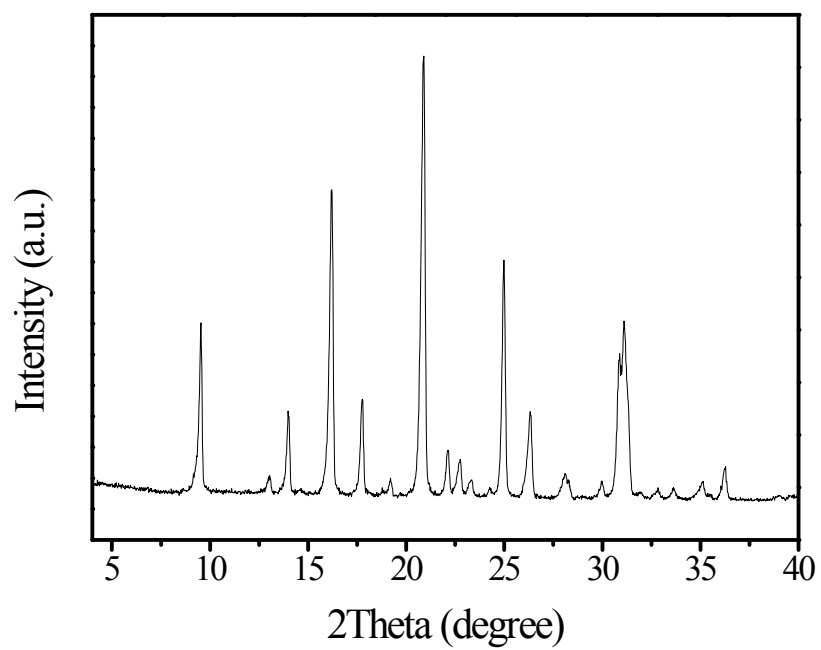




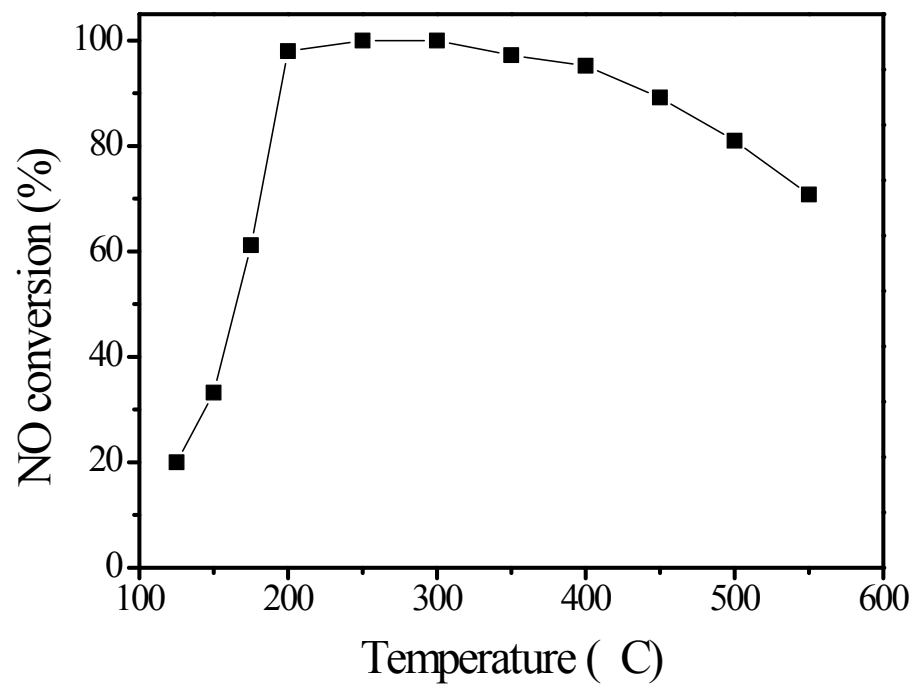
**Fig. S4**



**Fig. S5**



**Fig. S6**



**Fig. S7**

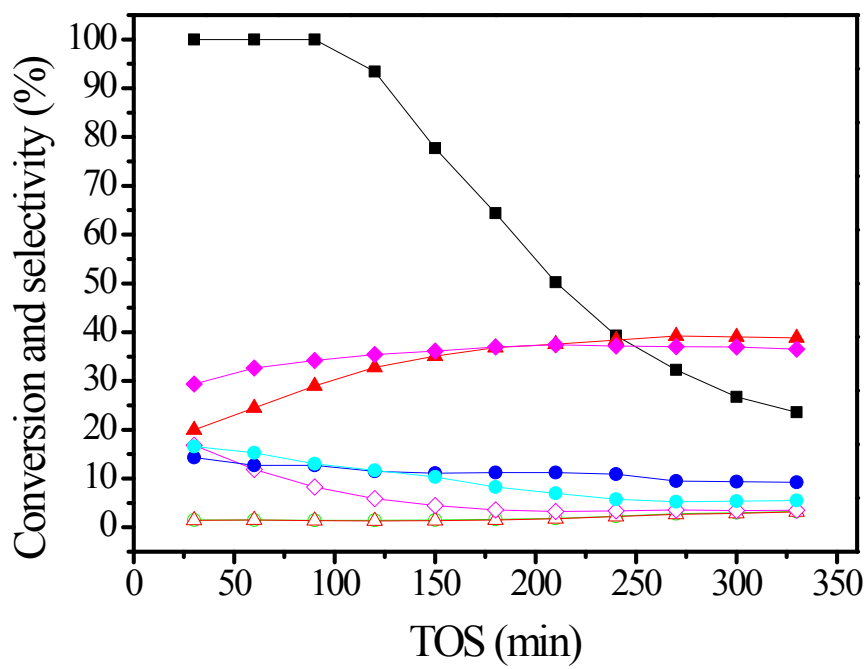


Fig. S8