A simple route to prepare zeolite Y nanosheets with hierarchical perfoliate pores

Daming Cui\textsuperscript{a}, Yi Wang\textsuperscript{b} and Meiqing Lou\textsuperscript{*a}

\textsuperscript{a}Department of Neurosurgery, Shanghai Tenth People’s Hospital, Tongji University School of Medicine, 301 Yangchang, Shanghai 200072, China

\textsuperscript{b}Center of Analysis and Measurement, Fudan University, 220 Handan, Shanghai 200433, China

\textit{E-mail:} 071105225@fudan.edu.cn

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\textbf{Abstract:} Using the high siliceous zeolite Y crystals (ZY-C) as precursor, zeolite Y nanosheets (ZY-N) with hierarchical perfoliate pores were successfully synthesized via a simple “top-down” approach. The ultrathin faujasite nanosheets with intact zeolite Y framework and hierarchical micro-meso-macropores were first observed in ZY-N by the characterization results. Contrary to the layer assembly process in growing zeolite Y crystals, the breakage and swelling of the energy-poor T-O-T bonds within double six membered rings (D6R) between the neighboring faujasite sheets were the possible principle for synthesis of ZY-N.

\textbf{Keywords:} Porous materials, multilayer structure, diffusion, crystal growth.

\section*{Introduction}

Zeolite crystals with diminished size and dimension have always been pursued by many researchers because these materials possess many extraordinary characteristics such as large surface area, high adsorption, fast diffusion and so on\textsuperscript{1–4}. Therefore, three-dimensional zeolite nanocrystals were first developed by regulating the speed of zeolite nucleation and growth\textsuperscript{5–7}. Then, two-dimensional ultrathin zeolite nanosheets were synthesized by swelling and exfoliating layered zeolites such as MCM-22 and AMH-3 because the interactions between their layers is the weak van der Waals force\textsuperscript{8–11}. However, for non-layered zeolites, it’s not easy to obtain their ultrathin nanosheets due to the high energy T-O-T bonds in the whole crystal. Encouragingly, recent report indicated that MFI nanosheets with single-unit-cell thick (2 nm) can be synthesized by using bifunctional surfactants as pillaring\textsuperscript{12}. Unfortunately, the “bottom-up” synthesis for the MFI nanosheets required complex bifunctional surfactants and strict operation conditions. Herein, we reported a novel and economical “top-down” approach to prepare zeolite Y nanosheets with hierarchical perfoliate pores. The process included the heterogeneous dissolution (OH\textsuperscript{−} ions attacking) of high siliceous zeolite Y crystals in alkaline hydrothermal solution, which was speculated as the reversal of layer assembly for growing zeolite Y crystals\textsuperscript{13}.

\section*{Experimental}

\textbf{Synthesis:}

0.88 g high siliceous zeolite Y (purchase from the Fushun Research Institute of Petroleum and Petrochemicals, SINOPEC) was added into the solution of sodium hydroxide (0.54 mol/L, analytical purity, First Chemical Co., Shanghai), and then stirring for 2.5 h. The gel was heated under static hydrothermal conditions at 100 °C in a stainless steel autoclave for 12 h. The precipitated product was filtered, washed with deionized water and dried in air at 80 °C overnight.

\textbf{Characterization:}

The X-ray powder diffraction (XRD) measurements of samples were carried out on a Rigaku D/MAX-RB X-ray powder diffractometer with Ni-filtered CuK\textsubscript{α} radiation at 40 kV and 100 mA. Scanning electron micrographs (SEM) were obtained from a Philips XL-30 scanning electron microscope. The samples were sputtered with a thin film of gold. The transmission electron mi-
croscopy (TEM) images and the selected area electron diffraction (SAED) were obtained on JEOL JEM-2010 instruments. For framework T-O-T bonds analysis, solid-state $^{29}$Si magic angle spinning nuclear magnetic resonance ($^{29}$Si-MAS NMR) spectra was employed. The resonance frequency is 59.63 MHz and the magnetic field is 7.0T. The nitrogen adsorption and desorption isotherms at the temperature of liquid nitrogen were measured using Tristar 3000 systems. The samples were outgassed for more than 5 h at 150 °C before measurements.

Results and discussion

The emergence of ZY-N was monitored by various characterization techniques. Figs. 1(a) and 2(a) displayed the SEM and TEM images of ZY-C, and showed well-defined morphology of irregular and massive polyhedral particle with size about 0.5–1.5 μm. HRTEM images (Figs. 2a, b) showed that ZY-C contain typical micropores and some mesopores. After subtly stacked by OH$^-$ in alkaline hydrothermal solution, SEM image in Fig. 1(b) showed that ZY-N was almost flat with silken edges and macropores (inset), indicating the formation of macroporous nanosheets. TEM images and SAED patterns (Fig. 2c) further clearly demonstrated that the ZY-N was stacked faujasite nanosheets. HRTEM images (inset in Fig. 2c) revealed that these nanosheets were ultrathin, may be single-unit-cell thick. Except that the multilayered ultrathin nanosheets could be observed clearly from Fig. 2d and Fig. S2, many macropores were also emerged in the nanosheets. Moreover, it could be found from TEM images (inset in Fig. 1b) that ZY-N richly contained many mesopores and macropores besides its own micropores, and most of these meso/macropores ran through the ZY-N. $N_2$ adsorption-desorption isotherm and the pore size distribution curve (Fig. S1 and Table S1) showed that the micropores, mesopores and macropores had the most probable pore sizes of 0.74 nm, 3.3 nm and 50 nm, respectively. The ZY-N showed BET area of 667 m$^2$/g and pore volume of 0.56 cm$^3$/g, while ZY-C exhibited 677 m$^2$/g and 0.49 cm$^3$/g, respectively. The XRD patterns of ZY-C (Fig. 1c) and ZY-N (Fig. 1d) showed, for comparison, that ZY-N still had well resolved zeolite Y framework after OH$^-$ attacking. It has been reported that some XRD reflections would disappear when the ultrathin zeolite nanosheets formed, because the framework thickness along these directions was extremely small. In our work, this phenomenon was not obvious since the ZY-N still kept strictly oriented stacking but not completely separated as observed from TEM images and ED patterns. Later, the ZY-N will try to be separated completely into monolayer.
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Fig. S1. N$_2$ adsorption-desorption isotherms and BJH pore size distribution curves (insets) of ZY-C (Left) and ZY-N (Right).

Fig. S2. TEM images of zeolite Y nanosheets abounded with hierarchical perfoliate pores.

| Samples | The framework Si/Al ratio | BET surface area (m$^2$ g$^{-1}$) | Micropore surface area (m$^2$ g$^{-1}$)$^a$ | Total pore volume (cm$^3$ g$^{-1}$)$^a$ | Micropore volume (cm$^3$ g$^{-1}$) | BJH pore diameter (D) (nm)$^b$ |
|---------|--------------------------|----------------------------------|--------------------------------|-------------------------------|-------------------------------|-----------------|
| ZY-C    | 6.7                      | 677                             | 593                           | 0.49                          | 0.27                          | 2.9, 32         |
| ZY-N    | 2.2                      | 667                             | 593                           | 0.56                          | 0.26                          | 3.3, 50         |

$^a$Calculated according to the "t-plot" method. $^b$Obtained from the BJH pore size distribution curves.

Structural changes and formation of nanosheets that occurred during the attacking process by OH$^-$ ions were also investigated using $^{29}$Si MAS NMR spectroscopic technique (Fig. 3). It has been known that the $^{29}$Si MAS NMR spectroscopy can provide structural information on the zeolite frameworks in terms of the connectivity of SiO$_4$ tetrahedra as well as the Si-O-Si (T=Si) bond angles$^{14-16}$. Three resonances in ZY-C at $\delta = -95.1$, -100.9 and -106.3 ppm were previously assigned to the Q$^2$, Q$^3$ and Q$^4$ (where Q$^0$ represents the Si-[OSi]$_n$[OH]$_{4-n}$) species, respectively, resulting in a Q$^4$/Q$^3$ ratio of 2 : 1$^9$.

Fig. 3. $^{29}$Si MAS NMR spectroscopy of the samples obtained at different stages of OH$^-$ attacking: (a) 0 h; (b) 2 h; (c) 4 h; (d) 8 h; (e) 12 h.
After gradually attacked by OH\(^-\) ions, the Q\(^4\) notably decreased while the Q\(^2\) and Q\(^3\) increased, even the Q\(^1\) and Q\(^0\) gradually emerged. In ZY-N, the Q\(^4\)/Q\(^3\) ratio was 1 : 4. These results confirmed that the Si-O-Si bonds were broken down since many silanols produced. Combining the characterized results above, it can be speculated that the breakage of Si-O-Si bonds mainly happened in D6R between the two adjacent faujasite sheets. It was also observed from \(^{29}\)Si MAS NMR spectroscopy that the chemical shifts of ZY-N were several ppm higher than those of ZY-C, thus implying much larger Si-O-Si angles in ZY-N structure\(^{14,16}\). The changes of Si-O-Si bond angles upon attacking indicated that new Q\(^2\) and Q\(^3\) species were produced by disconnection of Q\(^4\) species.

The reported AFM results revealed that crystallization of zeolite Y underwent a layer growth mechanism\(^{13}\). It has also been reported that zeolite Y crystals were constructed by the stacking of faujasite sheets\(^{17}\). The bond energy of the T-O-T atoms between the faujasite sheets was considered to be lower than the others, and it can be broken and swollen by designed ion attacking. Therefore, the possible principle for synthesis of ZY-N was suggested schematically in Fig. 4, which was reversal of layer assembly for growing zeolite Y crystals. As shown, every faujasite sheet was constructed by linking sodalite cages (truncated octahedra) through double six membered rings (D6R) and stacking of these sheets according to a given direction (ABCABC) results in the cubic phase of zeolite Y. In ZY-C, the stacking was solidified by closely connected T-O-T bonds of D6R, while the alkali treatment of ZY-C in condign conditions might break and swell the T-O-T bonds of D6R because they were much weaker than others. Once the breakage of the T-O-T bonds happened, ultrathin zeolite Y nanosheets would be observed. At the same time, dissolution of Si species in the Al-free zone produced the macropores in these nanosheets\(^{18,19}\). In this process some mesopores in high siliceous ZY-C were pivotal and benefit for the OH\(^-\) attacking\(^{20}\).

**Conclusion**

ZY-N with hierarchical perfoliate pores was successfully prepared, for the first time, by a top-down approach in alkaline hydrothermal solution. Emergence of the nanosheets was observed and verified by the characterized results. The prepared ZY-N was rich in hierarchical pores and most of them run-through each other. The mechanism of forming ZY-N could be explained as the selective broken of low energy Si-O-Si bonds of D6R between the neighboring faujasite sheets, while the Al-free zone sites were benefit for producing meso/macropores under the same hydrothermal treatment. Large surface area, pore volume as well as the hierarchical perfoliate pores in ZY-N will endow it with powerful mass transfer. This work provides a more simple method for the synthesis of ZY-N, which is economic in industry.

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