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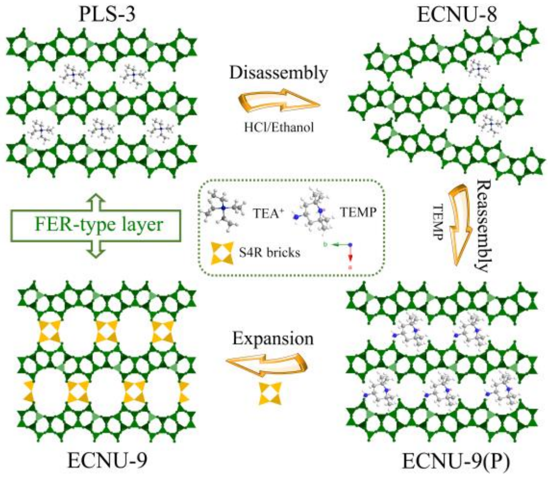
Lego Chemistry-Inspired Synthesis of Extra-large Pore Zeolite ECNU-9 with Intersecting 14*12-Ring Channels

Boting Yang[+§‡], Jin-Gang Jiang[+§,] Hao Xu*[§], Haihong Wu[§], Mingyuan He[§], and Peng Wu*[§]

Abstract: Highly crystalline and (hydro)thermally stable zeolites with extra-large pores (≥14-ring) are highly desirable in term of catalytic viewpoint of processing bulky molecules. A novel zeolite ECNU-9 with an intersecting 14*12-ring (R) channel system was rationally designed and post-synthesized from a layered precursor of PLS-3 silicate through a LEGO chemistry strategy, in which the interlayer expansion of two-dimensional silicate structure was realized by combining together organic amine-assisted layer-stacking reorganization and subsequent silylation with a square-shaped single 4-ring (S4R) silane, 1,3,5,7-tetramethylcyclotetrasiloxane (TMCS). The PLS-3 precursor, consisting of the ferrierite (FER)-type nanosheets, was disassembled to LEGO bricks by partially breaking interlayer hydrogen bondings, and then intercalated with flexible and removable organic amine pillars to offer enough interlayer spacing for accommodating guest TMCS silane molecules, which condensed with the silanol groups on up-down layer sheets. The additionally introduced structural building blocks interconnected the neighbouring layers to construct new 14-R and 12-R pores along [001] and [010] directions, respectively. The resulting ECNU-9 zeolite possessed a well-ordered structure with a novel topology never obtained by direct synthesis or other approaches. The corresponding titanosilicate Ti-ECNU-9 with tetrahedral Ti ions in framework showed superior catalytic performances in the liquid-phase selective epoxidation of bulky alkenes with hydrogen peroxide.

Microporous zeolites are widely used in catalysis, ion-exchange, adsorption and separation.[1] However, the narrow pores of conventional zeolites have restricted their applications to processing the substrates with relatively small sizes. Design synthesis of novel porous materials in particular with extra-large pores of 14-R or more is highly demanded, which would definitely expand the practical applications of zeolites.[2] Employing large-size organic structural-directing agents (OSDA)[3] and/or Ge atoms[4] in the hydrothermal synthetic gels are useful strategies for developing novel zeolites with open pore systems. Nevertheless, the complexity involved in synthetic process as well as the high cost of the OSDAs and Ge sources cannot be ignored. The structural instability of extra-large pore germanosilicates is also a concerned issue in real applications, although various post-treatments have been reported to enhance their (hydro)thermal stability.[5] As a special family of zeolitic materials, layered silicates, with relatively weak interlayer hydrogen bondings, are endowed with modifiable and flexible structure properties.[6] Several structural modification routes, including swelling,[7] delamination,[8] pillaring,[9] and silylation,[10] have been reported to enlarge the external surface area or pore sizes, which releases effectively the diffusion constrains of large-size substrates. Among these, silylation induces an accurate interlayer structural expansion, normally achieved via reacting with monomer silane agents in acidic aqueous, although metal-linker has also been reported.[10] Larger silane agents, like dimeric silane and 1,4-*bis*(triethoxysilyl)benzene, have also been applied to expand interlayer pores with the ring number increased by 4 or even to build interlayer mesopores.[11] The interlayer insertion of large silane molecules required the pre-swelling process in alkaline media, which may cause an extensive desilication to the silicate framework.[7] The enlargement of interlayer space can also be achieved by intercalation with larger-size guest molecules.[12] Since the nanosheets are loosely packed in layered zeolite, it would be marvelous to disassemble them into LEGO-bricks and then insert new structural component to construct novel frameworks through a so called “bottom-up” strategy. In present study, a LEGO-inspired method was employed to synthesize novel ECNU-9 zeolite with intersection 14*12-R pore channels by interlayer expansion of layered FER silicate PLS-3 with a S4R-shaped silane. As shown in Scheme 1, the layered PLS-3 precursor was firstly disassembled into LEGO bricks, that is, a sub-zeolite ECNU-8 composed of FER-type nanosheets,[13] in HCl/Ethanol solution by extracting some of the OSDA tetraethylammonium (TEA^+) cations after partially breaking the interlayer hydrogen bonding linkage. These LEGO bricks subsequently were reassembled or reorganized with the help of 4-amion-2,2,6,6-tetramentylniperidine (TEMP) intercalation, a classical OSDA for the synthesis of PREFER silicate.[14] With enough expanded interlayer space between these LEGO bricks, the TMCS silane molecules are possibly introduced as linkers to interconnect the up-down layers, creating new 14-R and 12-R pores.



Scheme 1. LEGO-inspired synthesis of extra-large pore ECNU-9 via structural expansion of PLS-3 silicate with 4R building units.

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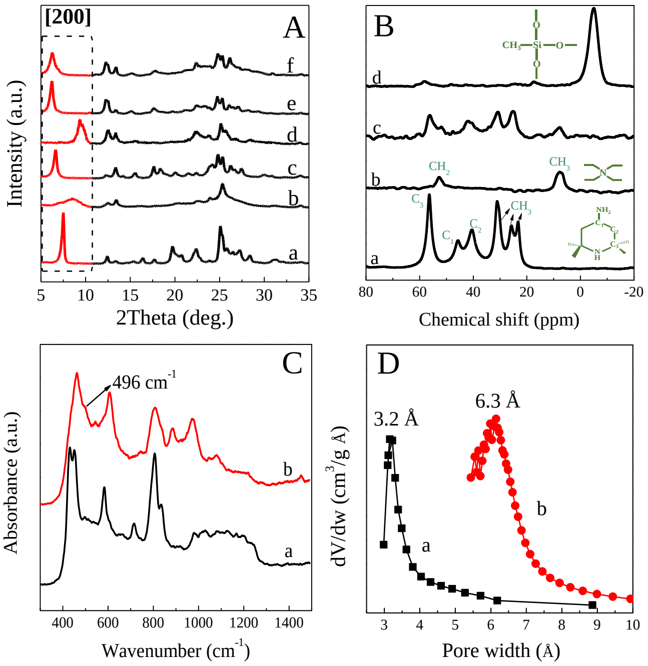

Figure 1. (A) XRD patterns of PLS-3 (a), ECNU-8 (b), ECNU-9(P) (c), ECNU-9(P)-cal823 (d), ECNU-9 (e), and ECNU-9-cal823 (f). (B) ^{13}C MAS NMR spectra of conventional PREFER (a), PLS-3 (b), ECNU-9(P) (c) and ECNU-9 (d). (C) UV-Raman spectra and (D) pore size distribution of PLS-3 (a) and ECNU-9 (b) both after calcination at 823 K.

The PLS-3 precursor exhibited a characteristic diffraction at 2θ = 7.6º (Figure 1Aa), assigned to the [200] plane of the layered structure that was composed of the FER nanosheets and the TEA^+ cations alternatively interlaced along *a* axis.[15] Any diffraction broadness should be mainly due to the fact that PLS-3 was of nanosized crystals (Figure S2a). The HCl/Ethanol treatment for 40 min disassembled the PLS-3 precursor to a sub-zeolite ECNU-8 lacking long-range ordered structure (Figure 1Ab). The layer-related [200] diffraction was broadened and shifted to higher angle, meanwhile the (*hkl*) diffractions with $h \neq 0$, such as [200], [220], [400], [202] and [600] planes, were severely weakened in intensity corresponding to its partially collapsed structure along *a* axis.[13] Then the LEGO bricks of FER-type nanosheets were rapidly reorganized in TEMP solution within 15 min (Figure S1). The resultants showed shaper and more intensive reflections and the layer-related [200] one moved to a lower angle (2θ = 6.6º) than that of PLS-3 (2θ = 7.5º), indicative of re-ordering of the layer stacking and simultaneous expansion of the interlayer spacing. The intensity levelled-off when the treatment time reached 16 h (Figure S1f), implying completion of reassembling process. With the TEMP molecules, the classical OSDA for PREFER synthesis, were intercalated into ECNU-8 sub-zeolite, a layered precursor ECNU-9(P) with structural analogy to PREFER was obtained (Figure 1Ac). Its [200]-related diffraction moved to higher angle (2θ = 9.4º) upon calcination and a conventional 3D FER structure was constructed (Figure 1Ad), indicating the removable organic pillars only changed the interlayer spacing. Although the TEMP aqueous solution is alkaline, the dissolving of zeolite framework and nanocrystals was not observed from the SEM images (Figure S2). This could be attributed to the recognition or matching between FER nanosheet structure and TEMP molecule configuration, very similar to the observed interlayer reinsertion when treating 3D MWW zeolite with piperidine.[16] By immersing the ECNU-9(P) precursor in HCl/Ethanol solution with the S4R-shaped TMCS silane, the [200] diffraction moved to even lower 2θ angle of 6.3º as a result of further interlayer expansion (Figure 1Ae). This interlayer expanded structure kept intact upon calcination up to 773 K, while it suffered minor degradation at higher temperature of 823 K (Figure S3). As a control experiment, an identical silylation process with TMCS silane was carried out directly on the PLS-3 precursor (Figure S4). However, the resultant structure is identical to that expanded by monomeric silane,[17] because of the limited interlayer spacing of PLS-3. To realize an interlayer silylation with S4R silane with a relatively large molecular dimension, it is critical to make the entrance match the size of guest molecules, which could be realized by present strategy of interlayer dissembling and reorganization.

The organic-inorganic interaction played an important role in the expansion of PLS-3 lamellar silicate with S4R silane. According to TG analysis, PLS-3 precursor contained *ca*. 20.1 wt% of TEA^+ species, while the HCl/Ethanol treatment removed them by 80% (Table S1, No. 2), disturbing extensively the original ordered layer stacking (Figure 1Ab). The TEMP treatment on ECNU-8 increased the content of organic species from 4 to 21.8 wt% at 20 h (Table S1, No. 6), indicative of the intercalation of TEMP molecules and responsible for the [200] reflection shifting to lower angle (Figure 1Ac). Consistent with this, the resonance bands attributed to TEMP appeared in the ^{13}C NMR spectrum of ECNU-9(P) after the intercalation (Figure 1Bc), which is very similar to that of PREFER directly synthesized with TEMP as OSDA (Figure 1Ba). Meanwhile, the relatively weak resonances attributed to TEA^+ around 7.8 and 52.4 ppm were still observed after intercalation due to the incomplete extraction in the former HCl/Ethanol treatment. Upon silylation with TMCS silane, these resonances attributed to TEA^+ and TEMP disappeared and a new one around -5.2 ppm was developed (Figure 1Bd), which is attributed to the $CH_3Si(OSi)_3$ groups,[10c] suggesting the insertion of organic silane into the inorganic framework. During the hydrothermal process in acid solution, the four hydrogen atoms in TMCS silane were oxidized and hydrolyzed into four hydroxyl groups. They then interacted and condensed with the silanol groups on up-down layers to make the silane ring fixed between the nanosheets, while keeping the four inert methyl groups intact.

The pure TMCS silane exhibited three IR vibration bands at 1260, 836 and 770 cm⁻¹, attributed to the C-H deformation, C-H rocking and Si-C stretching mode of $-CH_3$ groups, respectively (Figure S5a). Neither PLS-3 nor ECNU-9(P) showed such vibration bands (Figure S5b and c). Upon TMCS silylation, the vibration bands at 1278 and 775 cm⁻¹ together with the relatively weak and board one around 841 cm⁻¹ emerged in the IR spectrum of ECNU-9 (Figure S5d), indicating the existence of Si-CH_3 moiety.[18] These bands became weaker with the calcination temperature increasing and totally disappeared at 823 K (Figure S5, e-g), indicating the complete removal of $–CH_3$ groups *via* calcination. Figure 1C shows the UV-Raman spectra of PLS-3 and ECNU-9 both in their calcined form. In comparison to calcined PLS-3, ECNU-9-cal823 showed an extra band around 496 cm^{-1}, corresponding to the S4R structure units,[19] also indicated the insertion of S4R silane. The silylation process also changed the coordination state of silicon as evidenced by ^{29}Si MAS NMR spectra (Figure S6). ECNU-9(P) possessed 23% $(OH)Si(SiO)_3$ (Q^3) species and 77% $Si(OSi)_4$ groups (Q^4) (Figure S6a and Table S2). After the silylation with TMCS, the resonance attributed to Q^3 groups decreased by 80% (Figure S6b and Table S2) and a new one was developed at -65.9 ppm, attributed to the $(CH_3)Si(OSi)_3$ groups (T^3).[10a] This qualitatively verified that the incorporation of silane molecules into the structure was realized by reacting with the silanol groups on the PLS-3 layer surface. After calcination at 773 K for 6 h, the T^3 resonance band became extremely weaker while the Q^3 one was intensified (Figure S6c), because the -CH_3 groups attached to silicon were replaced by -OH groups. The T^3 band disappeared by increasing the temperature to 823 K (Figure S6d), as a result of completed decomposition of -CH_3 groups. Nevertheless, the resonance attributed to $(OH)_2Si(SiO)_2$ species (Q^2) around -91 ppm also appeared upon calcination, probably due to a partial ring-opening of the inserted S4R units at higher calcination temperatures.

N_2 and Ar adsorptions were performed to characterize the porosity of PLS-3-derived zeolites. The surface area and the total pore volume are given in Table S3. With partial collapsed structure, ECNU-8 exhibited the lowest surface area and pore volume (Figure S7 and Table S3, No. 2). Despite exhibiting identical framework type of FER, the calcined ECNU-9(P) showed slightly lower surface area and pore volume than PLS-3 (Figure S7 and Table S3, No. 1 and 3), because the larger interlayer distance in ECNU-9(P) caused a partial irregular condensation upon calcination.[20] With an interlayer expanded structure, the ECNU-9 samples calcined at different temperatures showed higher surface area (Figure S7 and Table S3, Nos. 4-6). The total pore volume increased with the calcination temperature by removing the pore blocking –CH_3 groups. However, ECNU-9-cal823 possessed a comparable pore volume to calcined PLS-3, because higher temperature caused partial structural degradation, as evidence by XRD patterns (Figure S3). The pore size distribution was centred at 3.2 Å and 6.3 Å for PLS-3 and ECNU-9, respectively (Figure 1D). The enlarged 3.1 Å is almost twice the length of Si-O bond (1.6 Å), in good agreement with insertion of two Si-O bonds along [100] direction. More direct and strong proofs were given by TEM images (Figure S8). Under the same magnification, the interlayer distance of the calcined ECNU-9 sample was obviously larger than PLS-3 by 2.9 Å along [100] direction, meaning the successful insertion of S4R units.

Considering the above characterization, a structure model was built for ECNU-9 with the collection of FER sheets expanded by S4R cyclosiloxane units (Figure 2, inset), which possessed intersecting 14*12-R channels. The S4R linker across the interlayer space was obviously observed in the electron density map. Then, the structural refinement was performed (Figure 2), giving the space group of *IMM2* and the unit cell composition of $Si_{44}O_{84}C_8H_{24}$. ECNU-9 possessed the lattice parameters of a = 27.5048 Å, b = 13.7513 Å and c = 7.2637 Å (Table S4). Its b and c parameters were very comparable to those of PLS-3 (a = 18.721 Å, b = 13.987 Å, c = 7.415 Å), but its parameter a was enlarged by 8.8 Å, simply because the structural expansion occurred dominantly along [100] direction. The orientation of the methyl groups attached to the Si atoms in inserted S4R units was considered. Among all the possible structural models, the one with the four methyl groups sit on the same side of S4R units exhibited highest symmetry and minimum energy (Figure S9). ECNU-9-cal823 was also refined, exhibiting well-matched simulated and experimental data (Figure S10).

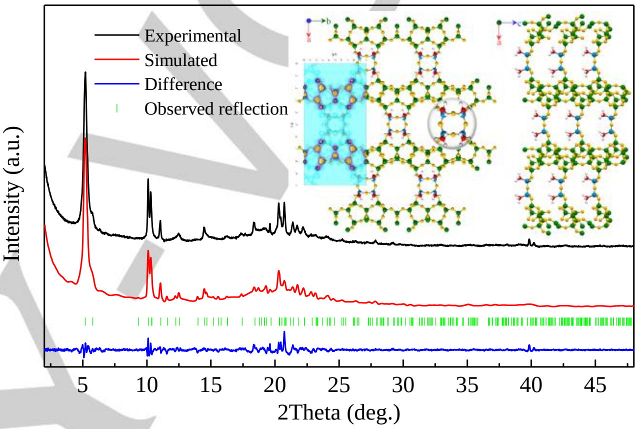

Figure 2. Rietveld refinement of X-ray powder pattern of as-made ECNU-9. Experimental (black) and calculated (red) XRD patterns as well as the difference profile are shown (blue). The short tick marks (green) below the patterns give the position of the Bragg reflections (A). Structure of ECNU-9 along [001] and [010] directions (inset). Projection of the experimental electron density map along [001] was shown on top of the structure model.

Ti ions were isomorphously incorporated into ECNU-9 framework via the treatment in H_2TiF_6 aqueous solution. The XRD pattern of Ti-ECNU-9 was similar to that of ECNU-9, indicating the structure was well-preserved after the H_2TiF_6 treatment (Figure S11). Ti-ECNU-9 showed a sharp band around 215 nm in the UV-vis spectrum (Figure S12), disclosing that the Ti ions were tetrahedrally coordinated in the framework and excluded the existence of extraframework Ti species as well as anatase.[21] Table S6 compared the catalytic performance of Ti-ECNU-9 with other traditional titanosilicates in the epoxidation of 1-hexene. Ti-MWW exhibited the highest conversion while Ti-ECNU-9 gave the highest turnover number (TON) value per Ti site. Within the family of three FER-related titanosilicates, the specific catalytic activity took an order of ECNU-9 (14*12-R) >> Ti-IEZ-PLS-3 (12*10-R) > Ti-PLS-3 (FER-type 10*8-R), corresponding to their pore sizes. For larger substrate of cyclohexene, Ti-ECNU-9 showed a much higher activity than the representative titanosilicates like Ti-MWW, TS-1, Ti-Beta and Ti-MOR and other FER-type zeolites, providing an extremely high TON value of ~300 at 2 h (Figure 3 and Table S7). The extra-large 14*12-R pore system of Ti-ECNU-9 would release efficiently the diffusion constrains of bulky molecules and then contribute to the superior catalytic performance for processing bulky molecules.

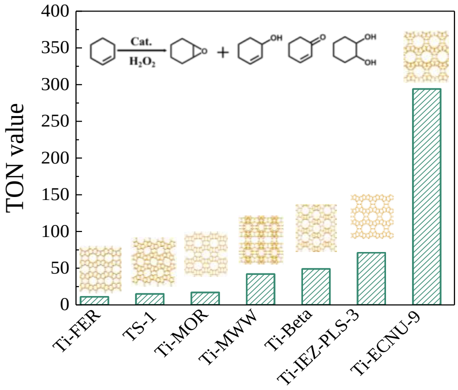

Figure 3. The turnover number (TON in mol (mol-Ti)$^{-1}$) for the epoxidation of cyclohexene with hydrogen peroxide over various titanosilicates. Reaction conditions: see Table S6.

In conclusion, a novel extra-large pore zeolite ECNU-9 was synthesized by LEGO-inspired interlayer expansion of layered PLS-3 silicate with S4R-shaped silane molecules which linked the neighboring layers, forming new structural units and constructing intersecting 14*12-R pores. With open pore system and less diffusion constrains, Ti-incorporated ECNU-9 showed superior catalytic performance for bulky substrates. This LEGO-inspired method is potentially expanded to other layered precursors for developing novel zeolitic catalysts.

Experimental Section

The layered silicate PLS-3 was synthesized through a solid-state conversion of protonated kanemite using TEAOH as the structure-directing agent (SDA).[16] Then, ECNU-8 sub-zeolite was obtained by treating PLS-3 zeolite in HCl/Ethanol solution at 443 K for 40 min. By immersing ECNU-8 zeolite in TEMP solution for 20 h, an analogy of PREFER was prepared and named as ECNU-9(P). Finally, ECNU-9 zeolite was synthesized by the structural expansion of ECNU-9(P) with TMCS silane in HCl/Ethanol. For experimental details, please see supporting information.

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Keywords: layered zeolite • LEGO-inspired • extra-large pore • interlayer expansion • titanosilicate

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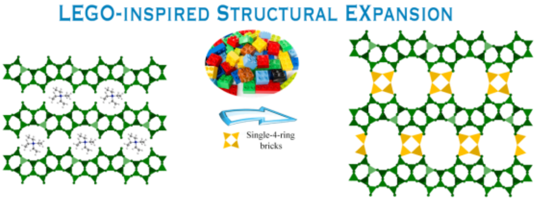

A novel extra-large pore zeolite of ECNU-9 was synthesized via a LEGO-inspired structural expansion of layered PLS-3 silicate with S4R-shaped silane.

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