

## Synthesis and Characterization of Novel Layered Lithium Sodium Silicate (Silinaite) and the Mesoporous Materials from Silinaite

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**Abstract:** Novel layered silinaite has been synthesized using an aqueous mixture of water glass, LiOH and NaOH under hydrothermal crystallization. Subsequently transformation of silinaite into mesoporous materials (SDM) was achieved at mild condition using cetyltrimethylammonium bromide as structure-directing agents. The resulting samples were characterized by XRD, SEM, FTIR nitrogen adsorption-desorption isotherms and catalytic performance in bulky molecular involved reaction. The results revealed that synthesized mesoporous materials derived from the silinaite exhibited an ordered hexagonal crystal structure with average pore diameter 2.7 nm and BET surface area 817m<sup>2</sup>/g. The SDM-supported ZnCl<sub>2</sub> catalyst, prepared by impregnation-evaporation method, retained the mesoporous structure and showed high selectivity in alkylation of benzene with benzyl chloride.

**Keywords:** Silinaite, mesoporous materials, layered solid, catalysts, characterization.

Layered compounds are of scientific and technological interest. They not only act as ion exchanger and fillers in detergents and nanocomposites<sup>1,2</sup>, but also act as hosts for intercalation of functional molecules or ions to yield hybrid materials<sup>3</sup>. Additionally, layered structures can be transformed into porous derivatives which are analogous to zeolites, showing great significance in the field of adsorption and catalysis<sup>4</sup>. So far there are two typical routes to the transformation of layered solids into porous materials. One route is to introduce bulky metal oxide clusters into the interlayers of layered solids followed by calcination, yielding pillared interlayered solids (PILS)<sup>5</sup>. The other is to introduce organic surfactants into the interlayer of layered solids, acting as supermolecular structure-directing agents (SDA) and the layers wind around the aggregated SDA micelles. After calcinations the porous materials called folded sheets mesoporous materials were obtained (FSM)<sup>6</sup>. In the latter route, the layered solid must be with flexible layers. The synthesis of novel layers solid with flexible layers has received widespread interest because of their potential application for production of mesoporous materials. Many layered silicates minerals have been investigated and synthesized for decades. The silinaite with flexible framework of [SiO<sub>4</sub>] tetrahedron have not been found until 1995<sup>7</sup>. Silinaite (NaLiSi<sub>2</sub>O<sub>5</sub>·2H<sub>2</sub>O) is a monophyllosilicate

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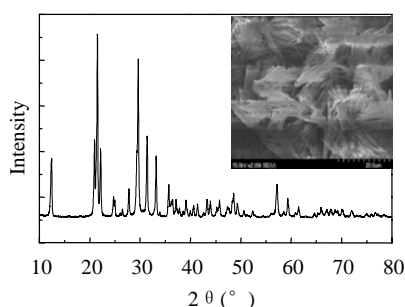
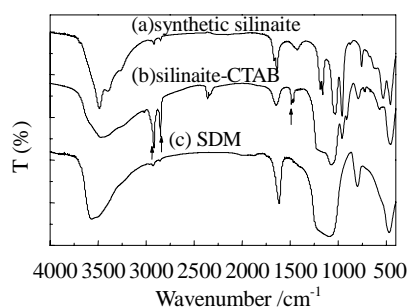
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consisting of layers of  $[\text{SiO}_4]$  tetrahedrons. The  $\text{Li}^+$  as exchangeable ion are held in tetrahedral ordination by the four oxygen ions of four  $[\text{SiO}_4]$  tetrahedrons and pull the layers together. The natural silinaite minerals are very few, so the development of its synthetic techniques is of great importance for further scientific research and industrial application. We have synthesized silinaite by hydrothermal method with water glass as silica source and transformed silinaite into mesoporous materials, which were used as solid catalyst supports.

Silinaite and its mesoporous derivatives were synthesized by following procedures. An aqueous mixture of water glass (Hangzhou Chunyi,  $\text{SiO}_2/\text{Na}_2\text{O}=3.4$ ),  $\text{LiOH}$  and  $\text{NaOH}$  with a molar ratio of  $\text{LiOH}/\text{SiO}_2=0.5$ ,  $\text{NaOH}/\text{SiO}_2=0.5$  and  $\text{H}_2\text{O}/\text{SiO}_2=10$  was vigorously stirred for 6 h at room temperature. Then the gel was transferred into a teflon-lined stainless steel autoclave and crystallized at  $130^\circ\text{C}$  for 96 h. The solid was filtered, washed with distilled water and dried in air to give silinaite sample. The synthesized silinaite was added to an aqueous solution of cetyltrimethylammonium bromide (CTAB) and the mixture was heated with stirring at  $70^\circ\text{C}$  for 3 h. The pH value of the suspension was adjusted to 8.5 using 2 mol/L of hydrochloric acid and the stirring was kept at  $70^\circ\text{C}$  for 3 h. Then the solid was filtrated and calcined at  $500^\circ\text{C}$  for 4 h. The product was silinaite-derived mesoporous materials (SDM). The powder X-ray diffraction (PXRD) were taken with Thermo ARL SCINTAG X'TRA diffractometer using monochromatic  $\text{Cu K}\alpha$  radiation. FTIR spectra were recorded on a Nicolet Avatar 370 spectrometer by KBr wafer technique. The BET specific area and nitrogen adsorption-desorption experiments were carried at 77K on Micromeritics ASAP2010C. Scanning electron microscopy (SEM) was recorded on Hitachi S-4700 field-emitting scanning electron microscopy. The  $\text{ZnCl}_2$  supported SDM catalysts with 4 mmol/g of  $\text{ZnCl}_2$  loading were prepared according to our previous method and calcined at  $150^\circ\text{C}$  prior to use<sup>8</sup>.

PXRD pattern of synthesized silinaite sample is shown in **Figure 1**. Reflection peaks in the range of  $10\text{--}70^\circ$  are well-resolved with the d-spacing values and intensity of (d(A), (I)): 7.16(24), 4.24(40), 4.13(94), 4.01(35), 3.59(12), 3.58(9), 3.37(4), 3.21(17), 3.02(100), 2.84(53), 2.71(42), 2.52(22), 2.46(12), 2.42(13), respectively. The PXRD pattern was in good agreement with that of the natural silinaite. The diagram showed no impurity such as silica and lithium salt. The synthesized silinaite exhibited good crystallinity. The SEM images revealed that the crystals are in lath-like shape with few microns in size.

**Figure 2** is the FTIR spectra of synthetic silinaite and its derivatives. As shown in **Figure 2a**, absorption bands at 3490, 3399, 3490, 1634, 1036, 954, 755, 528, 456 and  $456\text{ cm}^{-1}$  are characteristics of  $-\text{OH}$ , Si-O and Li-O stretching and bending vibrations, respectively, in silinaite structure. After the reaction with CTAB, the IR spectra changed (**Figure 2b** and **c**). Strong absorption bands at 2964, 2924,  $1482\text{ cm}^{-1}$  are attributed to stretching vibrations of  $-\text{CH}_3$ ,  $-\text{CH}_2$ , C-N groups of CTAB chains, respectively. Thus the formation of CTAB-silinaite hybrid was confirmed. After calcination, the characteristic absorbance bands of organic groups disappeared. The bands in the region of  $-\text{OH}$  stretching vibration shifted from  $3446\text{ cm}^{-1}$  to  $3540\text{ cm}^{-1}$ , indicating that there were dehydroxylation and condensation processes during calcination.

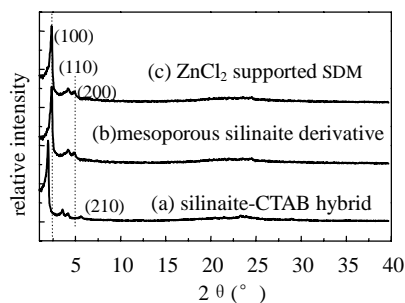
**Figure 1** PXRD spectra of synthetic silinaite (inset. SEM image)**Figure 2** FTIR spectra of synthetic silinaite and its organic-inorganic derivatives

The formation of SDM was further verified by PXRD investigation (**Figure 3**). The PXRD patterns of silinaite-derivatives differed strongly from that of original silinaite. Interaction between inorganic and organic species occurred. As shown in **Figure 3**, after reaction with CTAB, the resulting sample presented typical reflection characteristics with a very strong peak at a lower angle ( $d_{100}$  reflection line) and weaker peaks at higher angles that can be indexed to structure of hexagonal unit cell. These reflections belong to a typical mesoporous structure derived from the layered precursors<sup>6</sup>. After calcination to burn off the occluded CTAB, the hexagonal structure still retained, thus, inorganic solid with empty void was obtained (**Figure 3b**). But after calcination, the angles of PXRD reflection peaks shifted to higher field. The reflection indexed to (100), (110), (200) and (210) lattice planes all appeared in sharper shape compared with those from CTAB-exchanged samples. These phenomena indicated that the stacking of pore wall become more ordered after calcinations, arising from the condensation of silanol Si-OH during the process of calcination. Removal of organic species from the structure could be further confirmed by FTIR spectra as shown in **Figure 2b**. The band around 1036  $\text{cm}^{-1}$ , characterized Si-O, shifted after calcination, indicating the condensation of silanol Si-OH. The PXRD results are in well agreement with FTIR spectra.

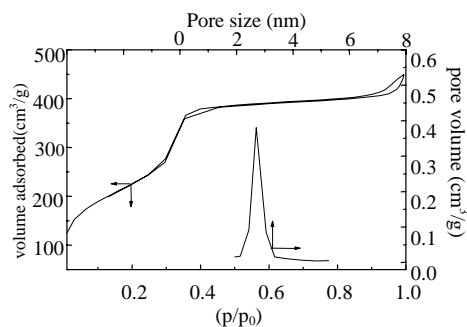
Furthermore, the pore structure of SDM was explored by nitrogen adsorption-desorption isotherms (**Figure 4**). The shapes of nitrogen adsorption-desorption isotherms of synthesized SDM were in typical mesoporous structure. The isotherms showed the sharp step at intermediate relative pressure, which belong to a type-IV isotherms with a noticeable hysteresis loop<sup>9</sup>. Nitrogen adsorption-desorption isotherms also confirmed the existence of uniform mesopores with a BJH (Barrett-Joyner-Halenda) pore diameter 2.7 nm and BET (Brunauer-Emmett-Teller) surface area 817  $\text{m}^2/\text{g}$ , respectively. The results confirmed that the SDM has a highly ordered hexagonal mesoscopic structure.

We also investigated the catalytic activities of the pure silinaite catalysts and  $\text{ZnCl}_2$  supported silinaite-derived mesoporous catalysts, using probe reaction of benzene alkylation with benzyl chloride to yield bulky diphenylmethane (DPM). The  $\text{ZnCl}_2$  loading did not change the pore structure (**Figure 3c**), revealing high conversion of benzyl chloride (BC, 63.2%) over SDM-supported  $\text{ZnCl}_2$  catalyst. The selectivity to DPM was 82.4%. For the pure silinaite the BC conversion was 0% and for  $\text{ZnCl}_2$  supported catalyst the BC conversion was 35.4% and DPM selectivity was 22.2%. Consequently, silinaite-derived materials (SDM) with mesoporous structure showed a great

**Figure 3** PXRD patterns of silinaite-derived hybrid and mesoporous material (a) silinaite-CTAB hybrid, (b) SDM, (c) ZnCl<sub>2</sub> supported SDM catalyst



**Figure 4** N<sub>2</sub> adsorption-desorption isotherm of silinaite-derived mesoporous materials (inset: pore size distribution.)



potential application using as catalysts or supports.

In conclusion, silinaite crystals can be synthesized using water glass as silica source by hydrothermal method. The crystals exhibit lath-like shape with a few micrometers in size. It was proposed that the layers of silinaite consists of soft [SiO<sub>4</sub>] tetrahedron which are foldable, the layers were pulled together to form a novel mesoporous phase under the induction of pre-assembled organic CTAB. After removal of occluded organic species by calcination, the pore structure was not fragile. From preliminary characterization, it was clearly revealed that the synthesized mesoporous materials derived from silinaite exhibited hexagonal crystal structure with average pore diameter 2.7 nm and BET surface area 817 m<sup>2</sup>/g. The structure of ZnCl<sub>2</sub> supported SDM catalyst was stable, showing mesoporous catalytic feature. Silinaite with layered structure is suitable for foldable assemblies, yielding a permanent mesoporous structure. It is of great scientific and industrial significance for bulky molecular catalysis and adsorption.

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### References

1. H. H. Murray, *Appl. Clay Sci.*, **2000**, 17(5-6), 207.
2. C. H. Zhou, Z. H. Ge, X. N. Li, H. Q. Guo, J. Sun, *Chin. Chem. Lett.*, **2003**, 14(12), 1285.
3. C. L. B. Peter, Z. Wang, T. J. Pinnavaia, *Appl. Clay Sci.*, **1999**, 15 (1-2), 11.
4. Gil, M. L. Gandia, M. A. Vicente, *Catal. Rev. Sci. Eng.*, **2000**, 42, 145.
5. C. H. Zhou, Q. W. Li, Z. H. Ge, X. N. Li, Z. M. Ni, *Chem. J. Chin. Univ. (Gaodeng Xuexiao Huaxue Xuebao (in Chinese))*, **2003**, 24(12), 1351.
6. T. Yamamoto, T. Tanaka, T. Funabiki, S. Yoshida, *J. Phys. Chem. B*, **1998**, 102, 5830.
7. K. Beneke, P. Thiesen, G. Lagaly, *Inorg. Chem.*, **1995**, 34, 900.
8. C. H. Zhou, X. Luo, Z. H. Ge, *et al.*, *Cuihua Xuebao (Chin. J. Catal., in Chinese)*, **2003**, 24 (8), 579.
9. J. R. Anderson, K. C. Pratt, *Introduction to Characterization and Testing of Catalysis*. Academic Press, Australia, **1985**, p113.

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