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Synthesis of Boron-containing CDS-1 Zeolite by Topotactic Dehydration–Condensation of [B]-PLS-1 Prepared from Layered Silicate H-LDS

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Boron-containing CDS-1 zeolite with CDO topology can be obtained from the layered borosilicate PLS-1 which was prepared from layered silicate H-LDS by dry-gel conversion. Pure crystals of [B]-PLS-1 can be formed in the range of Si/B ratio from ∞ to 280.

Microporous materials such as zeolites are inorganic materials which can be often used in many fields owing to their specific properties, e.g., a molecular sieve, an ion exchangeer and an adsorbent.[1] In particular, many efforts have been directed to apply solid acid catalysts in petroleum chemistry.[2] With increasing demands for a variety of zeolites, it is still a challenging and attractive task to explore novel zeolites with unique framework or character.

CDS-1 zeolite with CDO topology has been introduced as a microporous siliceous material with an eight-membered ring (8MR) with two-dimensional pore system (4.7 × 3.1 Å and 4.2 × 2.5 Å) developed by Ikeda et al., which can be prepared from a corresponding layered silicate PLS-1 via topotactic dehydration–condensation of a neighboring Q^3 silanol between each layer.[3] In a previous report, PLS-1 can be obtained from a mixture of amorphous silica, tetramethylammonium hydroxide (TMAOH) as a SDA, KOH, and 1,4-dioxane; however, it has recently reported that facile access to CDS-1 zeolite is possible by improving synthetic conditions as to use a layered silicate, H-kanemite, as a starting silica source.[4] Although CDS-1 zeolite shows high thermal stability, it cannot behave as a solid acid because the framework is only constructed of tetrahedral SiO_4 units. To overcome this issue, preparation of a CDS-1 zeolite bearing an acid site would be valuable task, and it can be expected to utilize as solid catalysts.

Recently, we have developed a novel potassium-cation-intercalated layered silicate K-LDS and the corresponding proton-type H-LDS and have been interested in potential applications of our layered silicates toward valuable chemical sources such as zeolites.[5,6]

Here, we report the synthesis of boron-containing PLS-1 ([B]-PLS-1) from layered silicate H-LDS and the preparation of microporous borosilicates with CDO topology.

Table 1 summarizes selected results of the synthesis of [B]-PLS-1 from H-LDS.[7] In the absence of boron, a pure crystal of PLS-1 was formed the same as a previous report (Run 1).[4] Addition of boron in Si/B ratio at 400, 300, and 200 successfully gave corresponding boron-incorporated PLS-1s (Runs 2 to 4); however, a mixture of [B]-PLS-1 and a small amount of RUT-type zeolite was unfortunately observed in >150 of Si/B ratios (Runs 5 and 6). It has been reported that RUB-10 zeolite (6-MR) with RUT topology is one of the microporous borosilicates prepared by TMAOH as a SDA.[8,9] In order to increase the incorporated boron atom in the framework of PLS-1, we examined the addition of 1,4-dioxane into the starting gel according to a previously reported synthetic procedure of PLS-1.[3] However, there was no improvement, affording a mixture of [B]-PLS-1 and RUT-type zeolite (Run 7). Addition of PLS-1 as a seed did not yield pure crystals of [B]-PLS-1 (Run 8). When H-kanemite was used as a starting silica source instead of H-LDS, pure [B]-PLS-1 was formed without any impurities (Run 9). Interestingly, it is worth noting that, although the framework resembles H-LDS and H-kanemite,[6] [B]-PLS-1 with Si/B ratio of 150 can be synthesized from H-kanemite.

Table 1. Synthesis of [B]-PLS-1 from H-LDS[a]

Run	Chemical content/molar ratio					Product
	Si	B	Na	TMAOH	H_2O	
1	1.0	—	—	0.30	5.0	PLS-1
2	1.0	0.0025	0.013	0.30	5.0	[B]-PLS-1
3	1.0	0.0033	0.165	0.30	5.0	[B]-PLS-1
4	1.0	0.0050	0.025	0.30	5.0	[B]-PLS-1
5	1.0	0.0067	0.033	0.30	5.0	[B]-PLS-1 and **RUT**
6	1.0	0.0100	0.050	0.30	5.0	[B]-PLS-1 and **RUT**
7[b]	1.0	0.0067	0.033	0.30	5.0	[B]-PLS-1 and **RUT**
8[c]	1.0	0.0067	0.033	0.30	5.0	[B]-PLS-1 and **RUT**
9[d]	1.0	0.0067	0.033	0.15	5.0	[B]-PLS-1

[a] Reactions were carried out in a Teflon-lined autoclave at 170 °C for 72 h under static conditions. [b] 1,4-Dioxane was used as an additive, the molar ratio of 1,4-dioxane/Si was 3.0. [c] PLS-1 was used as a seed, 5 wt %. [d] H-kanemite was used as a starting silica source.

Because CDS-1 zeolite is prepared by calcination under air flow via dehydration–condensation of a neighboring Q^3 silanol between each layer, the formation of fine CDS-1 zeolite should depend on temperature and heating rate. We then screened the calcination of [B]-PLS-1 ($Si/B = 200$) under different temperatures under air flow ($100\,\mathrm{mL\,min^{-1}}$) and evaluated surface areas by nitrogen adsorption. We found that the largest surface area ($271\,\mathrm{m^2\,g^{-1}}$) of [B]-CDS-1 zeolite was observed at 550 °C; however, at temperature above 600 °C and below 500 °C surface areas were decreased to $259\,\mathrm{m^2\,g^{-1}}$ at 480 °C and $63\,\mathrm{m^2\,g^{-1}}$ at 800 °C, respectively.

Elemental analysis by inductively coupled plasma (ICP) measurement revealed the actual Si/B ratio in the obtained [B]-CDS-1 zeolites in Table 2, and it was found that the incorporation of boron atom into the zeolite occurred to a 280 Si/B ratio. BET surface areas and pore volumes estimated from nitrogen adsorption show convincing values, considering a two-dimensional 8-MR pore system and a previous work.

Figure 1 shows the SEM images (left) and powder XRD patterns (right) of [B]-PLS-1 and [B]-CDS-1 zeolite ($Si/B =$

Table 2. Properties of [B]-CDS-1 zeolite

Run	Si/B ratio		N_2 adsorption	
	Input	Actual	Surface area/$m^2\,g^{-1}$	Pore volume/$mL\,g^{-1}$
1	∞	—	262	0.102
2	200	280	271	0.101
3	300	352	282	0.114
4	400	418	281	0.114

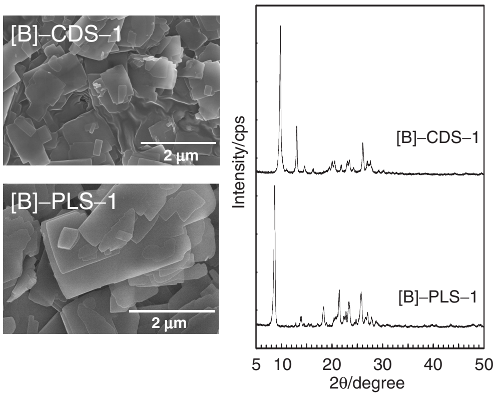

Figure 1. SEM images (left) and powder XRD patterns (right) of [B]-PLS-1 and [B]-CDS-1.

200), respectively. The morphologies of both samples were found to be an aggregate of thin layers like scales, those are the same as original PLS-1 and CDS-1, and there was no drastic change of the morphology after calcination. In XRD, characteristic peaks of CDO topology were observed at 9.7 and 13° corresponding to 200 and 101 reflections, respectively, and both peak patterns were also in good agreement with those of an original PLS-1 and CDS-1 zeolite. It is noted that broadened and lower intensities in XRD patterns resulted from particle sizes.

Figure 2 shows the spectra of solid-state ^{29}Si, ^{11}B, and ^{13}C NMR (Figures 2a, 2b, and 2c) of [B]-PLS-1 and ^{29}Si and ^{11}B NMR (Figures 2d and 2e) of [B]-CDS-1 zeolite (Si/B = 200), respectively. The N_2 adsorption isotherm of [B]-CDS-1 is also shown in Figure 2f.

The ^{29}Si CP/MAS NMR spectrum of [B]-PLS-1 shows two peaks of Q^4 ($Si(OSi)_4$) silicon at −110 and −112 ppm, and two distinct peaks of Q^3 ($Si(OSi)_3OH$) silicon at −99 and −103 ppm, respectively. Further, a small sharp peak at −106 ppm corresponding to tetrahedral silicon which coordinates at least one boron atom appeared in the spectrum, while only a broad peak at −111 ppm (Q^4) was detected in the ^{29}Si MAS NMR spectrum of [B]-CDS-1 zeolite. This clearly indicates that Q^3 sites of PLS-1 lost their terminal silanol groups upon the calcination to transform into CDS-1 zeolite.

In ^{11}B MAS NMR spectra, only one clear, sharp peak corresponding to the tetrahedral boron atom (BO_4) in the framework of PLS-1 was observed at −3.4 ppm in [B]-PLS-1, in good agreement with the known chemical shifts of boron-containing zeolites.[10,11] While in the spectrum of [B]-CDS-1 a clear peak at −3.4 ppm can be detected and two broad peaks with low intensity are observed at around 1.0 and 7.0 ppm, and those are assignable to an amorphous tetrahedral BO_4 coordinates and a trigonal BO_3 species, respectively. This evidently indicates that unfortunately boron atom in the framework of PLS-1 has come out during the calcination. Indeed, during ion-exchange treatment of [B]-CDS-1 by NH_4NO_3 solution, considerable leaching of boron occurred. NH_3-TPD analysis of ion-exchanged [B]-CDS-1 gave a negligible desorption peak of ammonia (figure not shown).

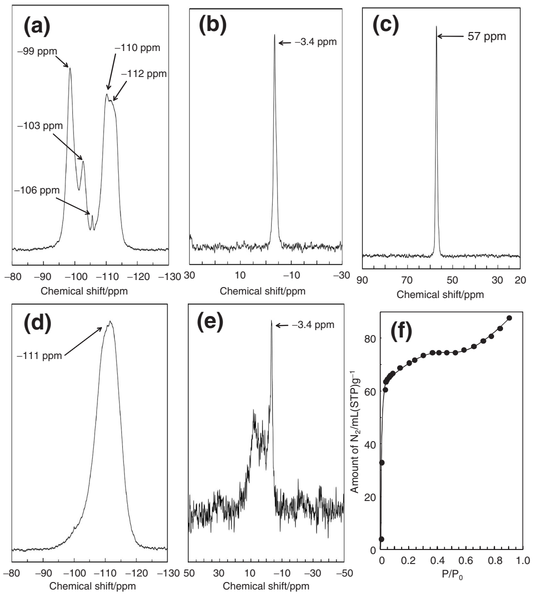

Figure 2. Solid-state NMR spectra and N_2 adsorption isotherm: (a) ^{29}Si CP/MAS NMR of [B]-PLS-1, (b) ^{11}B MAS NMR of [B]-PLS-1, (c) ^{13}C CP/MAS NMR of [B]-PLS-1, (d) ^{29}Si MAS NMR of [B]-CDS-1, (e) ^{11}B MAS NMR of [B]-CDS-1, and (f) N_2 adsorption isotherm of [B]-CDS-1.

In conclusion, this is the first report of the synthesis of boron-containing PLS-1 and [B]-CDS-1 zeolite. However, at this time, it is necessary to improve the limitation of boron concentration and to avoid leaching during the calcination. Research is now ongoing to obtain metallosilicates with CDO topology bearing an acceptable solid acid properties and to apply to solid catalysis.

References and Notes

1 *Introduction to zeolite science and practice*, ed. by H. van Bekkum, E. M. Flanigen, P. A. Jacobs, J. C. Jansen, Elsevier Science B. V., **2001**.

2 *Zeolite Microporous Solids: Synthesis, Structure, and Reactivity*, ed. by E. G. Derouane, F. Lemos, C. Naccache, F. R. Ribeiro, Kluwer Academic Publishers, Northerlands, **1992**, Part III, pp. 273–456.

3 T. Ikeda, Y. Akiyama, Y. Oumi, A. Kawai, F. Mizukami, *Angew. Chem., Int. Ed.* **2004**, *43*, 4892.

4 T. Ikeda, S. Kayamori, F. Mizukami, *J. Mater. Chem.* **2009**, *19*, 5518.

5 K. Komura, T. Ikeda, A. Kawai, F. Mizukami, Y. Sugi, *Chem. Lett.* **2007**, *36*, 1248.

6 T. Ikeda, M. Uenaka, K. Komura, Y. Sugi, *Chem. Lett.* **2010**, *39*, 747.

7 Supporting Information is available electronically on the CSJ-Journal Web site, http://www.csj.jp/journals/chem-lett/index.html.

8 H. Gies, J. Z. Rius, *Z. Kristallogr.* **1995**, *210*, 475.

9 G. Bellussi, R. Millini, A. Carati, G. Maddinelli, A. Gervasini, *Zeolites* **1990**, *10*, 642.

10 S. I. Zones, S.-J. Hwang, *Microporous Mesoporous Mater.* **2003**, *58*, 263.

11 J. B. Nagy, R. Aiello, G. Giordano, A. Katovic, F. Testa, Z. Komya, I. Kiricsi, in *Molecular Sieves Characterization II*, ed. by H. G. Karge, J. Weitkamp, Springer, **2007**, pp. 365–478.