

Synthesis and Characterization of a Boron-Aluminum Oxochloride

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A novel microporous crystalline boron-aluminum oxochloride with a cationic framework, designated BAC(3), has been synthesized hydrothermally in the system $B_2O_3-Al_2O_3-Na_2O-H_2O$ and characterized using ICP, ion chromatograph, X-ray diffraction (XRD), magic-angle spinning nuclear magnetic resonance spectroscopy (MAS NMR), infrared spectroscopy (IR), thermal analysis, and adsorption measurement. Some factors, such as temperature, pH value, and anions have important effects on the crystallization. Chemical analysis shows that the as-synthesized solid has the molar composition $0.2B_2O_3 \cdot 1.0 Al_2O_3 \cdot 0.6HCl \cdot 5.7H_2O$. XRD analysis shows that the crystal has a unique framework structure. The crystal is indexable on an orthorhombic unit cell with $a = 22.55$, $b = 14.42$, and $c = 8.75$ Å. The three-dimensional framework is built up from triangular BO_3 and tetrahedral BO_4 units with BO_3/BO_4 of 2.6, as well as octahedrally coordinated Al. XRD, IR, and DTA-TG studies demonstrated that the microporous crystal is unstable to thermal treatment above 300°C, with the decomposition of structural H_2O and HCl confirmed by mass spectroscopy analysis. On calcination above 800°C, this microporous crystal is converted via an amorphous phase to a known crystalline $Al_{18}B_4O_{33}$. The measurement of adsorption of water indicates that it possesses characteristic micropore adsorption properties. Ion-exchange analysis shows that the Cl^- anions in BAC(3) can be partially exchanged by Br^- anions, suggesting that this novel microporous crystal has a cationic framework. © 1996

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INTRODUCTION

Since the first discovery of microporous aluminophosphates in 1982 (1, 2), a great deal of effort has been devoted to the synthesis of other novel compounds with open-framework structures containing elements other than Si or Al. Notable examples are $M(III)X(V)O_4$ families (3–6), the GeO_2 family (7), and metal sulfides (8). The chemistry of microporous materials has been following a "Periodic Table Strategy" (9). So far, approximately a quarter of the

elements of the periodic table can be incorporated into the framework structure of microporous compounds.

Recently, a series of novel crystalline boron-aluminum oxochlorides has been hydrothermally synthesized successfully in our laboratory (10, 11). These materials have a unique three-dimensional framework structure built up from triangular boron, tetrahedral boron, and octahedral Al units. It is interesting to find that one of them, a novel microporous crystalline boron-aluminum oxochloride [denoted BAC(10)], with the molar composition $0.5B_2O_3 \cdot 1.0Al_2O_3 \cdot 0.4HCl \cdot 3.0H_2O$, has a cationic framework structure. It is unlike microporous aluminosilicates and aluminophosphates which have a negatively charged or neutral framework. Here, we report the synthesis and characterization of another microporous boron-aluminum oxochloride, denoted BAC(3).

EXPERIMENTAL

Synthesis

Boron acid [analytical reagent (A.R.), Kaiyuan Chemical, China] was used as the boron source and aluminum trichloride (A.R., Beijing Chemical, China) was used as the Al source.

Boric acid was first dissolved in distilled water with stirring and heating to form a solution, and then aluminum trichloride was added slowly to the solution. NaOH was added to the mixture. The pH of the mixture thus formed was kept at 1.8–3.0 by using HCl or triethylamine Et_3N . The mixture was stirred thoroughly for 0.5 h, followed by crystallization in a Teflon-lined stainless steel autoclave at 180°C for 8–10 days under autogenous pressure. The product was filtered, washed with distilled water, and dried at 100°C.

Characterization

A scanning electron micrograph (SEM) was taken with a Hitachi X-650B electron microscope.

X-ray powder diffraction patterns of the sample were

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recorded on a Rigaku 3DX diffractometer with $\text{CuK}\alpha$ radiation.

Inductive coupled plasma analysis (ICP) was carried out on a JARRELL-ASH 800 Mark-II ICP instrument.

^{27}Al and ^{11}B magic-angle spinning nuclear magnetic resonance spectra (MAS NMR) were recorded on a Bruker 400 spectrometer with a magnetic-field strength of 4.77 T. The spinning rates were ca. 6KHz. ^{27}Al and ^{11}B spectra were obtained at 52.1 and 64.2 MHz and chemical shifts were relative to external standards of $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$ and KBF_4 , respectively.

Infrared (IR) spectra were recorded on a Nicolet 5DX FTIR instrument with KBr pellet.

Differential thermal analysis (DTA) and thermogravimetric analysis (TGA) were performed on a Perkin-Elmer DTA1700 and TGA7, respectively. The rate of temperature increase was $10^\circ\text{C}/\text{min}^{-1}$. Desorption species were detected using a mass spectrometer.

Adsorption measurements were carried on a CAHN 2000 vacuum electronbalance at 20°C .

Ion chromatograph analysis was carried out on a Soda LC-601 ion chromatograph analyzer. Prior to analysis, the solid sample was melted with NaOH and then dissolved in distilled water. The ion exchange capacity of BAC(3) was obtained by stirring the powder sample in a 0.1 N NH_4Br -water solution at 60°C for 2 hr.

RESULTS AND DISCUSSION

Crystallization

Pure microporous crystalline boron-aluminum oxo-chloride BAC(3) samples were synthesized from the typical batch molar composition $3.25\text{B}_2\text{O}_3 : 1.0\text{Al}_2\text{O}_3 : 0.75\text{Na}_2\text{O} : 100\text{H}_2\text{O}$ at 180°C for 9 days.

The crystallization field formed in the B_2O_3 - Al_2O_3 - Na_2O - H_2O system with an H_2O content of 90 mol, pH 2.5, $T = 180^\circ\text{C}$ is shown in Fig. 1. BAC(3) can be formed within a lower B/Al molar ratio range.

As found in the synthesis of B-C(1) and BAC(10) reported before (10, 11), temperature and pH value are important factors affecting the products. Table 1 shows the effect of temperature and pH value on BAC(3). It is seen that BAC(3) can be crystallized within the temperature range of 160 – 180°C . It is interesting to note that in some reactant mixture, even the reactant composition and temperature are kept the same as that for the crystallization of BAC(3), but with a different pH value, B-C(1) or microporous BAC(10) can be formed.

Microporous BAC(3) can also be easily formed in the presence of CaO with a typical batch composition of $2.25\text{B}_2\text{O}_3 : 2.5\text{Al}_2\text{O}_3 : 1.5\text{CaO} : 200\text{H}_2\text{O}$. However, ICP analysis shows that there were no any cations such as Na^+ or Ca^{2+} in the as-synthesized microporous phase. Further, it is found that BAC(3) can also be synthesized in the

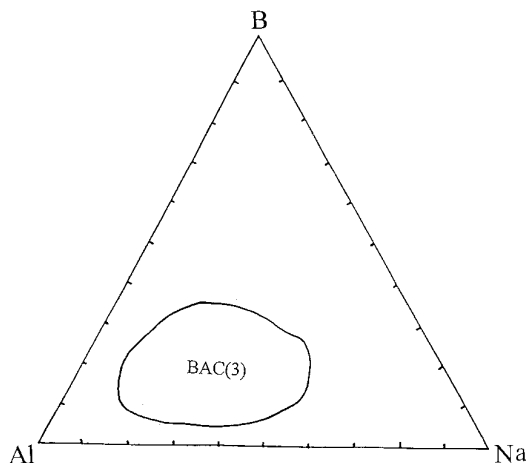


FIG. 1. Crystallization field of BAC(3) at 180°C .

presence of $\text{NH}_3 \cdot \text{H}_2\text{O}$ instead of Na_2O or CaO ; the typical batch composition is $0.25\text{B}_2\text{O}_3 : 2.25\text{Al}_2\text{O}_3 : 4.0\text{NH}_3 \cdot \text{H}_2\text{O} : 200\text{H}_2\text{O}$. Thus, it is concluded that the main role of $M_x\text{O}$ is to adjust the pH value of the reaction mixture. The suitable pH value range for the formation of BAC(3) is 1.8–3.0.

The selection of Al source is very important for the formation of BAC(3). Only aluminum trichloride can be used as Al source. When $\text{Al}(\text{OH})_3$, $\text{Al}(\text{NO}_3)_3$, $\text{Al}_2(\text{SO}_4)_3$, or AlPO_4 instead of AlCl_3 are used, BAC(3) cannot be synthesized. Ion chromatograph analysis shows the existence of a certain amount of Cl anions in BAC(3) product, suggesting that Cl is the essential component of BAC(3) product.

ICP analysis gives rise a B/Al molar ratio of about 0.2 for all BAC(3) products which can be synthesized in different reaction mixtures with various B/Al molar ratios. The molar composition of BAC(3) is $0.2\text{B}_2\text{O}_3 \cdot 1.0\text{Al}_2\text{O}_3 \cdot 0.6\text{HCl} \cdot 5.7\text{H}_2\text{O}$.

TABLE 1
The Effect of pH and Temperature on the BAC(3) Products

Gel composition in molar ratio	Temperature		Product
	pH	($^\circ\text{C}$)	
$1.5\text{B}_2\text{O}_3 : 2.25\text{Al}_2\text{O}_3 : 2.5\text{CaO} : 200\text{H}_2\text{O}$	2.5	160	BAC(3)
	2.5	180	BAC(3)
	3.5	160	BAC(10)
	2.5	200	B-C(1)
	3.5	200	B-C(1)
$1.0\text{B}_2\text{O}_3 : 3.0\text{Al}_2\text{O}_3 : 1.0\text{CaO} : 200\text{H}_2\text{O}$	1.8	160	BAC(3)
	1.8	180	BAC(3)
	2.5	160	B-C(1)
	3.5	160	B-C(1)



FIG. 2. Electron micrograph of BAC(3).

Characterization

Figure 2 shows the electron micrograph of the as-synthesized crystal. It is seen from the photograph that the crystals are homogeneous with good shape, indicating the as-synthesized solid is pure phase. The average particle sized is about $0.3 \mu\text{m}$.

Figure 3 shows the X-ray powder diffraction pattern of BAC(3). The crystalline product shows novel phase with excellent crystallinity. The X-ray powder diffraction data and indexing results obtained with the TREOR Program

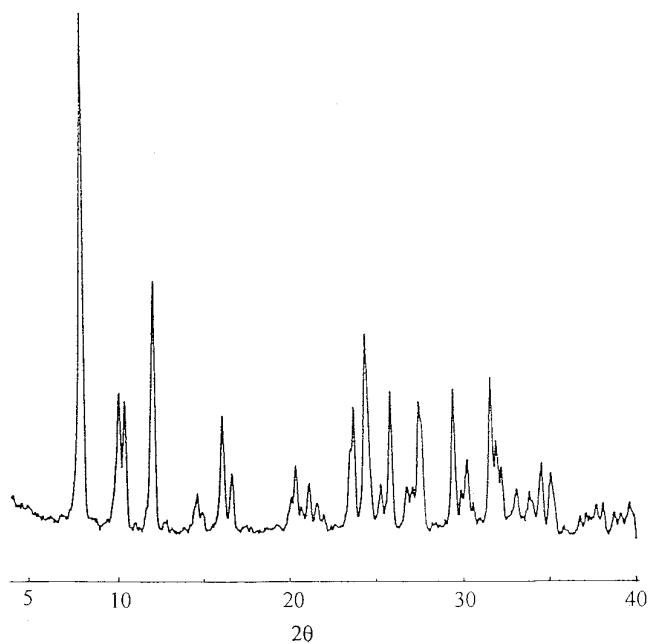


FIG. 3. X-ray powder diffraction pattern of BAC(3).

TABLE 2
Observed and Calculated X-Ray Powder Diffraction Data for BAC(3)

$d_{\text{obs.}} (\text{\AA})$	$d_{\text{calc.}} (\text{\AA})$	h	k	l	$d_{\text{obs.}} (\text{\AA})$	$d_{\text{calc.}} (\text{\AA})$	h	k	l
10.8531	10.8524	2	0	0	3.2224	3.2228	-2	3	2
8.6745	8.6858	2	1	0	3.0235	3.0172	-4	3	2
8.4197	8.4189	0	0	1	2.9781	2.9798	3	2	2
7.2371	7.2349	3	0	0	2.9398	2.9370	-6	3	1
6.8538	6.8441	1	2	0	2.9173	2.9159	-2	0	3
6.0131	6.0066	2	2	0	2.8066	2.8063	0	0	3
5.9015	5.9180	2	0	1	2.6995	2.7029	4	4	1
5.4804	5.4771	0	2	1	2.6302	2.6292	-8	0	2
5.2793	5.2798	-2	2	1	2.5918	2.5931	2	5	1
4.3968	4.3959	2	3	0	2.5503	2.5504	2	4	2
4.3373	4.3360	4	2	0	2.3805	2.3796	0	5	2
4.1797	4.1751	0	3	1	2.3547	2.3561	4	5	1
4.0884	4.0857	-2	3	1	2.2963	2.2962	-2	6	1
4.0406	4.0409	0	1	2	2.2609	2.2606	-7	4	2
3.7294	3.7312	-1	2	2	2.2266	2.2276	2	6	2
3.6304	3.6355	0	2	2	2.1642	2.1639	3	5	2
3.5011	3.4999	2	1	2	2.0999	2.1002	-6	4	3
3.4269	3.4221	2	4	0	2.0413	2.0416	4	3	3
3.2997	3.2988	-6	2	1	2.0180	2.0184	6	4	2
3.2759	3.2721	3	0	2	1.9271	1.9277	-10	2	3

(12) are listed in Table 2. BAC(3) is indexable on the orthorhombic unit cell with $a = 22.55$, $b = 14.42$, and $c = 8.75 \text{\AA}$, $\beta = 105^\circ$.

The ^{11}B spectrum (see Fig. 4) exhibits two resonance signals appearing at 2.0 and 15.0 ppm, respectively. The asymmetric peak on the high-field side (2.0 ppm) is attributed to tetrahedrally coordinated boron, whereas the low-field signals exhibiting evident quadrupolar interaction is assigned to triangular coordinated boron (13). A powder program is used to simulate the ^{11}B NMR experimental spectra, and the simulation parameters of component are listed Table 3. It is noted from Table 3 that the percentages of trigonal boron and tetrahedral boron in the crystalline

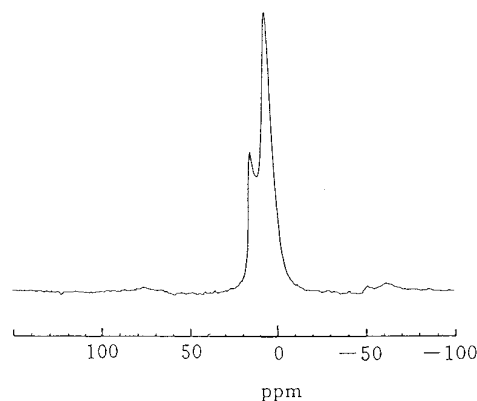


FIG. 4. ^{11}B MASNMR spectrum of BAC(3).

TABLE 3
The Simulation Parameters of the Components

Quadru: (powder pattern)	Component No. 1
Quadrupole coupling constant [Mhz]	2.9
Dipolar broadening [Hz]	500.0
Asymmetry parameter	0.0
Relative intensity [%]	72.0
Chemical shift [ppm]	20.0
Quadru: (Gaussian/Lorentzian Curve)	Component No. 2
Gaussian/Lorentzian ratio	0.5
Linewidth [Hz]	600.0
Relative intensity [%]	28.0
Chemical shift [ppm]	2.0

product are 72 and 28%, respectively. Therefore, the trigonal to tetrahedral boron ratio B_3/B_4 is of 2.6. It has been found that in the microporous BAC(10), there are also two boron coordination states with trigonal to tetrahedral B_3/B_4 of 2.3 (14). It seems that trigonal borons occupy the majority of these two microporous boron-aluminum oxochlorides.

Figure 5 shows the ^{27}Al NMR spectrum. There is a peak appearing at 3.8 ppm, characteristic of octahedrally coordinated Al in the framework (15). The fact that the signal of ^{27}Al is broad may be caused by Cl ($I = 3/2$) and B ($I = 3/2$), probably existing in the environment of the six-coordinated Al of the crystalline framework.

Figure 6 gives the X-ray powder patterns of the as-synthesized and calcined BAC(3) at various temperatures. It is noted that BAC(3) retains its structure after calcination at 200°C. It collapses to an amorphous form at above 300°C. When the temperature reaches 800°C, another crystalline phase $\text{Al}_{18}\text{B}_4\text{O}_{33}$ (16) starts to form, and the crystallinity becomes higher at 1000°C.

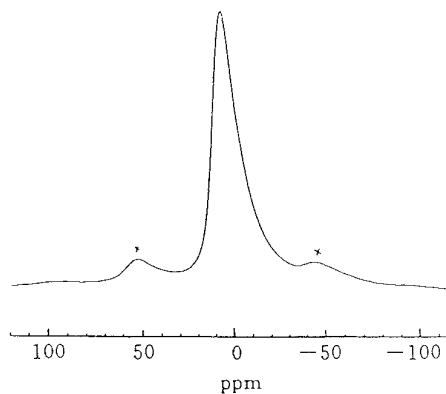


FIG. 5. ^{27}Al MASNMR spectrum of BAC(3).

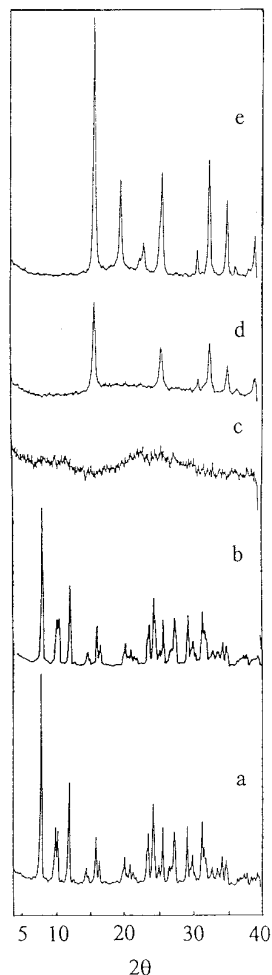


FIG. 6. X-ray powder diffraction patterns of BAC(3): (a) as-synthesized, and calcined at (b) 200, (c) 300, (d) 800, and (e) 1000°C.

Figure 7 shows the IR spectra of the as-synthesized sample and those treated at 200, 300, 800, and 1000°C, respectively. It can be seen that the IR absorption bands at 1385, 1336, 1232 cm^{-1} [associated with BO_3 vibration (11)] and 1129, 1077, 1024 cm^{-1} [associated with BO_4 vibration (11)] remain more or less unchanged as the sample is heated from room temperature to 200°C. However, at 300°C, the change in the absorption is remarkable. Those bands characteristic of BO_3 and BO_4 groups in the framework disappear completely, consistent with the XRD results. After the sample is treated at 800°C, an obvious broad band at maximum 1302 cm^{-1} and a band at 1060 cm^{-1} are observed, suggesting the existence of BO_3 and BO_4 groups, and at 1000°C, those bands at 1385, 1329, 1129, and 1019 cm^{-1} become stronger, indicating that a new crystalline framework structure has been built up. This is in good agreement with the XRD result that at 800–1000°C, the as-synthesized BAC(3) has transformed to crystalline $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

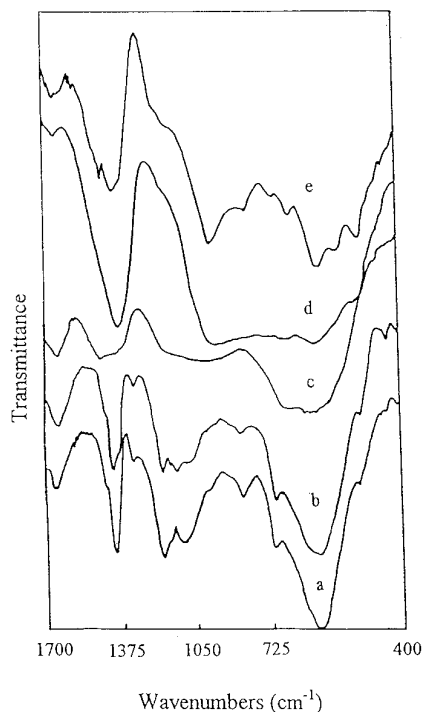


FIG. 7. IR spectra of BAC(3): (a) as-synthesized, and calcined at (b) 200, (c) 300, (d) 800, and (e) 1000°C.

DTA-TG analyses give a proper explanation of thermal stability of BAC(3) (see Fig. 8). The DTA curve has two distinct thermal effects at about 304 and 880°C. The first endothermic effect is attributable to the decomposition of HCl and H₂O in the BAC(3) crystal confirmed by mass analysis, its corresponding weight loss reflected by TG curve is 43.8%, close to the sum of the calculated HCl and H₂O (44%) in BAC(3). This suggests that the thermal transition of BAC(3) at ca. 300°C to an amorphous state

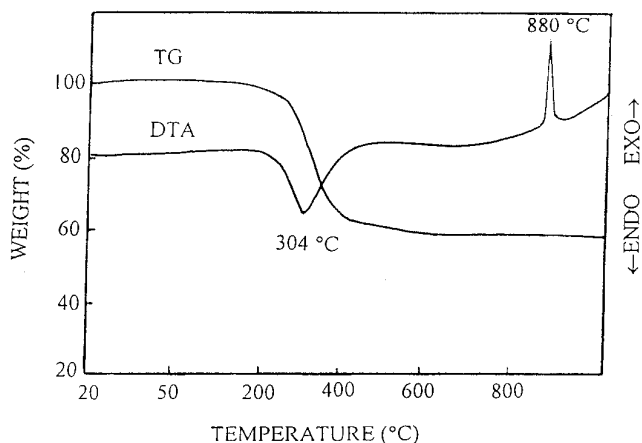


FIG. 8. DTA-TG curves of BAC(3).

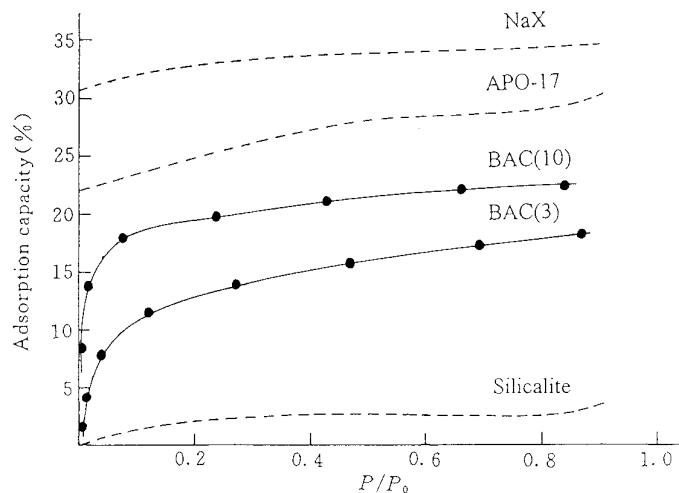


FIG. 9. H₂O adsorption isotherm for BAC(3).

in terms of XRD and IR analyses may be attributed to the evolution of HCl and H₂O. The exothermic effect near 880°C can be considered as a phase-transition effect of the solid since no corresponding weight loss appears on the TG curve. This result is in agreement with the XRD and IR analyses that at 800°C BAC(3) is converted via amorphous phase to crystalline $\text{Al}_{18}\text{B}_4\text{O}_{33}$.

The H₂O adsorption isotherm for the boron-aluminum oxochloride BAC(3) is shown in Fig. 9. For comparison, NaX, Silicalite, and APO-17, as well as BAC(10), are included. The hydration-dehydration of the highly crystalline BAC(3) is reversible and its adsorption isotherm shape as well as BAC(10), like that of NaX, Silicalite, and APO-17, is type I, typical of micropore-filling (17, 18). However, the H₂O adsorption capacity for BAC(3) is lower than that for BAC(10). Some molecules of known kinetic diameter

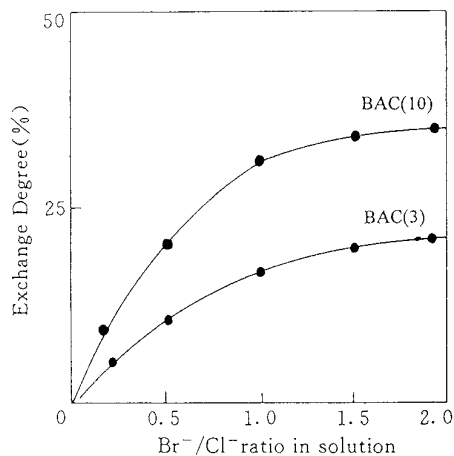


FIG. 10. Ion-exchange isotherm for BAC(3).

such as *n*-hexane and cyclohexane were used as probe molecules to determine the micropore size, but the results show that BAC(3) hardly adsorbs these molecules, suggesting that the pore size of BAC(3) is much smaller than that of zeolite NaX or APO-17.

Chemical analysis reveals that the existence of a certain amount of Cl⁻ anions but no Na⁺ or Ca²⁺ in the as-synthesized microporous BAC(3). Furthermore, ion-exchange studies indicate that about 20% Cl⁻ anions in BAC(3) could be exchanged by Br⁻ anions, and the exchange isotherm shape is similar to that for most zeolites (19) (Fig. 10). For comparison, Fig. 10 also gives the isotherm for microporous BAC(10). Both microporous boron-aluminum oxochlorides have anion exchange properties, implying that they possess positively charged frameworks, unlike other microporous crystals, almost all with negatively charged or neutral frameworks, such as aluminosilicates and aluminophosphates.

CONCLUSION

A novel microporous boron-aluminum oxochloride named BAC(3) has been synthesized hydrothermally from the system B₂O₃-Al₂O₃-Na₂O/CaO-H₂O, and some crystallization conditions are discussed. The main role of Na₂O or CaO, like that of NH₃·H₂O, is to adjust the pH value of the reaction mixture. Anions Cl⁻ are essential for the formation of microporous BAC(3), which cannot be replaced by NO₃⁻, SO₄²⁻, or PO₄³⁻. The microporous boron-aluminum oxochloride BAC(3) has a molar composition of 0.2B₂O₃·1.0Al₂O₃·0.6HCl·5.7H₂O, and its framework is built up from triangular BO₃ and tetrahedral BO₄ with B₃/B₄ of 2.6, as well as octahedral AlO₆. This framework structure is unstable above 300°C, with the decomposition of HCl and H₂O from the solid. Boron-aluminum oxochloride BAC(3) has a characteristic micropore structure, and the Cl⁻ anions can be exchanged by Br⁻ anions. Thus, boron-aluminum oxochloride BAC(3) is a novel microporous crystal with a cationic framework.

ACKNOWLEDGMENTS

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REFERENCES

1. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannan, and E. M. Flanigen, *J. Am. Chem. Soc.* **104**, 1146 (1982).
2. S. T. Wilson, B. M. Lok, C. A. Messina, T. R. Cannon, and E. M. Flanigen, *ACS Symp. Ser.* **218**, 799 (1983).
3. R. Xu, J. Chen, and F. Shou, "Chemistry of Microporous Crystals" (T. Inui, Ed.), p. 63. Kodansha, Tokyo 1991.
4. J. Chen and R. Xu, *J. Solid State Chem.* **80**, 149 (1989).
5. G. Yang, L. Li, J. Chen, and R. Xu, *J. Chem. Soc. Chem. Commun.*, 810 (1989).
6. J. Chen, L. Li, G. Yang, and R. Xu, *J. Chem. Soc. Chem. Commun.*, 1217 (1989).
7. R. H. Jones, J. Chen, J. M. Thomas, A. George, M. B. Hursthouse, R. Xu, S. Li, Y. Lu, and G. Yang, *Chem. Mater.* **4**, 808 (1992).
8. R. L. Bedard, S. T. Wilson, L. D. Vail, J. M. Bennett, and E. M. Flanigen, "Zeolites: Facts, Figures, Future" (P. A. Jacobs and R. A. van Santen, Eds.), p. 375. Elsevier, Amsterdam, 1989.
9. E. M. Flanigen, B. M. Lok, T. R. Patton, and S. T. Wilson, "Proceedings of the 7th International Zeolite Conference" (Y. Murakami, A. Lijima, and J. W. Ward, Eds.), p. 103. Kodansha/Elsevier, Tokyo/Amsterdam, 1986.
10. J. Yu, R. Xu, Q. Kan, Y. Xu, and B. Xu, *J. Mater. Chem.* **3**, 77 (1993).
11. J. Yu, K. Tu, and R. Xu, "Proceedings of the 10th International Zeolite Conference" (J. Weitkamp, H. G. Karge, H. Pfeifer, and W. Holderich, Eds.), Part A, p. 315. Elsevier, Amsterdam, 1994.
12. P. E. Werner, L. Eriksson, and M. Westdahl, *J. Appl. Crystallogr.* **18**, 367 (1985).
13. C. A. Fyfe, L. Berni, H. G. Clark, J. A. Davies, G. C. Gobbi, J. S. Hartman, P. J. Hayes, and R. E. Waislyshen, *Adv. Chem. Ser.* **211**, 405 (1983).
14. J. Yu, R. Xu, J. Chen, and Y. Yue, *J. Mater. Chem.*, **6**, 1996, in press.
15. C. A. Fyfe, G. C. Gobbi, J. Klinawski, J. M. Thomas, and S. Ramdas, *Nature* **96**, 530 (1982).
16. N. V. Kochetkova, V. A. Anoknin, V. A. Pergudor, G. V. Cherepkov, *Zh. Prikl. Khim.* **54**, 140416 (1981).
17. S. Brunauer, L. S. Deming, W. S. Deming, and K. Teller, *J. Am. Chem. Soc.* **62**, 1723 (1940).
18. S. Brunauer, P. H. Emmett, and K. Teller, *J. Am. Chem. Soc.* **60**, 309 (1939).
19. D. W. Breck, in "Zeolite Molecular Sieves," p. 529. Wiley, New York, 1974.