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Synthesis and Characterization of a Novel Microporous Alumino-borate

Wang Jianhua, Feng Shouhua, and Xu Ruren*

Department of Chemistry, Jilin University, Changchun, P.R. China

A novel microporous alumino-borate, named B–C7, has been synthesized from $CaO–Al_2O_3–B_2O_3–(TEA)_2O–H_2O$ systems (TEA = tetraethylammonium), and characterized by means of *X*-ray powder diffraction, infrared, composition, thermal analyses, and gas adsorption.

Microporous crystalline inorganic solids are known to be very useful materials for catalysis, adsorption, and ion-exchange. Both traditional aluminosilicate zeolites[1] and recently discovered aluminophosphate molecular sieves,[2] contain Si, Al, and P as their framework atoms, although they can be partially substituted by B or by metals. It has been found that a mineral borate, hilgardite, consists of a three-dimensional borate framework which has channels parallel to the *c*-axis with a diameter of 5.2 Å.[3] Another borate-based zeolite, borate–sodalite, was synthesized from a high temperature reaction.[4] So far, there have been no reports on the hydrothermal synthesis of microporous alumino-borates. We report here the synthesis and characterization of a novel microporous alumino-borate, which we named B–C7.

Hydrothermal crystallization of a reaction mixture with molar composition $0.6CaO·1.0Al_2O_3·6.0B_2O_3·0.5TEAOH·150H_2O$ (TEAOH = tetraethylammonium hydroxide) was carried out in a stainless steel autoclave under autogenous pressure at 200 °C for 6 days. The crystalline product was filtered, washed with distilled water, and dried at ambient temperature. The product was identified by means of *X*-ray powder diffraction, i.r., composition, and thermal analyses. The adsorption properties were determined on a CAHN 2000 Vacuum Electrobalance, and the micropore distribution was calculated with a micropore adsorption program based on the N_2 adsorption isotherm at −196°C.

The *X*-ray powder diffraction pattern of B–C7 is shown in Figure 1. By comparison with the characteristic *X*-ray powder diffraction patterns of the borates and alumino-borates known so far, it was found that the alumino-borate has a unique, novel structure. The bulk composition of B–C7, in oxide molar ratio obtained from chemical analysis, is $1.0CaO$, $1.0Al_2O_3$, $9.6B_2O_3$, $4.3H_2O$. Surface composition analysis for the sample by ESCA (electron spectroscopy for chemical analysis) gave a B/Al molar ratio of 9.8, which coincided well with the B/Al molar ratio (9.6) of its bulk composition. The

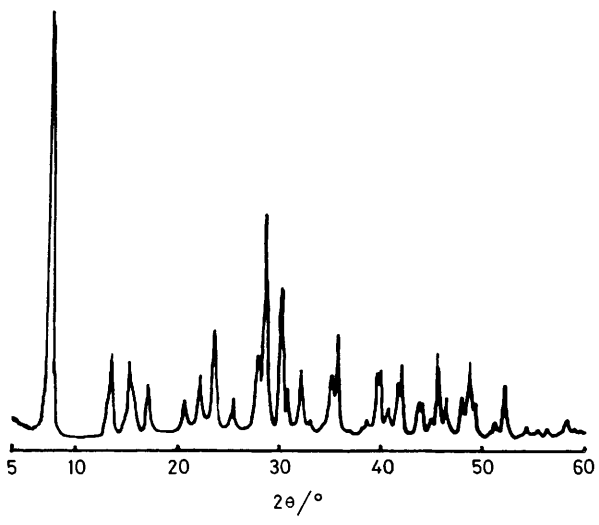

Figure 1. *X*-ray powder diffraction pattern of B–C7

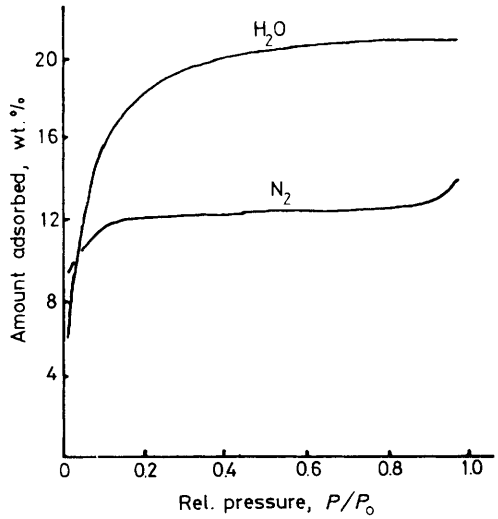

Figure 2. H_2O and N_2 adsorption isotherms for B–C7 (H_2O at 20 °C and N_2 at −196 °C)

alumino-borate can be thought of as consisting of certain building units having the same B_2O_3–Al_2O_3 composition. The characteristic i.r. absorptions of the alumino-borate at 1298—1384 cm^{-1} and 1071—1101 cm^{-1} are assigned to the vibration band of triangular BO_3 and tetrahedral BO_4, respectively; this indicates that the basic building units of B–C7 are BO_3 and BO_4. The detailed crystal structure of B–C7 still remains to be solved.

The synthesis of B–C7 was associated with a certain quaternary ammonium alkali, TEAOH, but the elemental analysis of the crystalline product showed there are no TEA^+ cations or TEAOH molecules in the structure. DTA–TG (differential thermal analysis–thermogravimetric) analysis showed that the synthetic alumino-borate lost a large amount of zeolitic water at about 400 °C and structurally collapsed at 733 °C.

The determination of H_2O and N_2 adsorption isotherms of B–C7 (Figure 2) showed that it possesses characteristic micropore adosorption properties. The Langmuir type adsorption isotherms are similar to those of zeolite molecular sieves. The result of micropore distribution calculations based on the N_2 adsorption isotherm indicated that the micropore size of B–C7 lies between 5—6 Å and the specific area is 340 $m^2 g^{-1}$.

In summary, a novel microporous crystalline alumino–borate, named B–C7, has been hydrothermally synthesized from CaO–Al_2O_3–B_2O_3–$(TEA)_2O$–H_2O systems. The structure consists of BO_3 and BO_4 as basic building units and has regular intercrystalline pore size from 5 to 6 Å.

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