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# Hydrothermal synthesis and characterization of a new aluminium–boron oxyfluoride

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Under hydrothermal conditions a new crystalline aluminium–boron oxyfluoride has been synthesized in whose structure there are strong Lewis sites.

Crystalline microporous oxides find much use in catalysis, adsorption and ionic exchange.[1] Studies exist[2,3] that give information about the production of new microporous aluminium–boron oxychlorides with anion-exchange properties and good catalytic activities in the selective synthesis of but-2-ene from ethanol. The present paper reports on the synthesis and characterization of a new aluminium–boron oxyfluoride (referred to subsequently as AlBF).

The hydrothermal synthesis of the substance was carried out using a reaction mixture with a molar ratio of $3B_2O_3 : 1Al_2O_3 : 3NH_3 : 24HF : 270H_2O$ in an autoclave under autogenous pressure at 160 °C for 3 days. The pH value of the solution was maintained within the limits 3.0–3.5. The product was isolated by centrifugation, washed up to the absence of fluorine ions and dried at a temperature of 100 °C. The product samples were identified by X-ray powder diffraction (Cu K , DRON-2M), IR spectroscopy (Perkin-Elmer 325), $^{27}$Al, $^{11}$B MAS NMR spectroscopy (Bruker CXP-200), mass spectrometry, thermal analysis and adsorption techniques. Chemical shifts in the $^{27}$Al, $^{11}$B MAS NMR spectra were measured with reference to $Al(H_2O)_6^{3+}$ and $B(OCH_3)_3$, respectively. The surface acidity was studied by temperature-programmed desorption (TPD) of ammonia, temperature-programmed reaction (TPR) of dehydration of isopropyl alcohol and IR spectroscopy of adsorbed $CD_3CN$.

On the basis of our chemical analysis data the composition of the product is represented by the formula $Al_2BO_2F_5$–HF–$H_2O$. Figure 1 displays an X-ray pattern of the synthesized aluminium–boron oxyfluoride. Comparison of the pattern with the familiar patterns of aluminates, borates and aluminoborates indicates that AlBF has a novel structure. In conformity with the interpretation of the AlBF powder diffraction patterns all the spectral lines are sufficiently and correctly identified as possessing tetragonal *syngony* with unit cell parameters $a = 6.3653$ and $b = 10.8502$ Å.

In the $^{27}$Al MAS NMR spectrum of AlBF there is a signal at –38 ppm that is assigned to octahedrally coordinated aluminium. The broadening of the signal and its shift towards stronger field with respect to the $Al(H_2O)_6^{3+}$ signal (0 ppm) is related to the substitution of fluorine atoms for part of the oxygen atoms in the aluminium coordination sphere. Note that in the $^{27}$Al MAS NMR spectrum of crystalline $AlF_3$ the octahedral aluminium signal is detected at –12 ppm (with $\nu_{1/2} = 7.5$ kHz). The infrared absorption spectrum of AlBF (Figure 2) displays bands due to the stretching vibrations of Al–F ($\nu_{as} = 601$ cm$^{-1}$ and $\nu_s = 355$ cm$^{-1}$) and of Al–O ($\nu_{as} = 715$ cm$^{-1}$ and $\nu_s = 654$ cm$^{-1}$) which are characteristic of aluminium in an octahedral environment.[4]

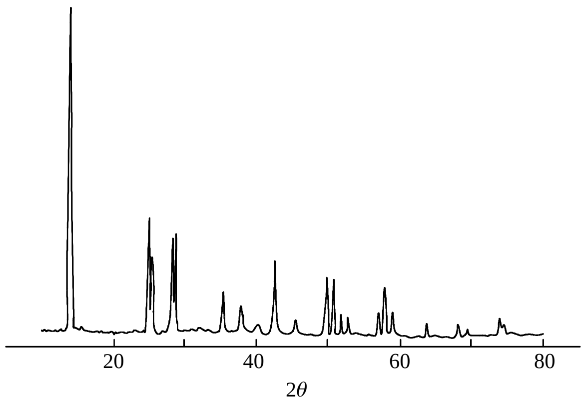

**Figure 1** X-ray powder diffraction pattern of AlBF.

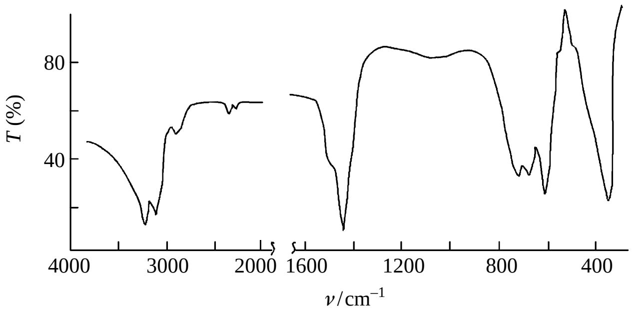

**Figure 2** Transmission infrared spectrum of AlBF in the region from 4000 to 300 cm$^{-1}$.

The strong band at 1490–1432 cm$^{-1}$ and the very weak band at 1120–1080 cm$^{-1}$ for the B–O stretching vibrations (Figure 2) are characteristic of trigonal and tetrahedral boron, respectively.[4] In the $^{11}$B MAS NMR spectrum there is also a narrow signal at –19 ppm for tetrahedral boron and a broad signal with side bands for trigonal boron. It is known that structures with trigonal boron are characterized by high values of their quadrupole coupling constants, *e.g.* for $BO_3$ this value is equal to 2.8 MHz.[5] An increase in the symmetry order of the electron surrounding the boron nuclei leads to a shift of the signal towards the strong field, to a substantial decrease of the quadrupole coupling constants (for $BO_4$ down to 0.1–0.5 MHz) and to a considerable narrowing of the spectral lines.[5,6] The appearance of the intense line at –19 ppm may be attributed to an increase of the symmetry order of the electron surrounding boron as a result of coordination of HF molecules with trigonal boron atoms that act as Lewis acids. The presence of HF molecules in the AlBF structure is corroborated by the absorption bands at 3241–3125 cm$^{-1}$ in its IR spectrum (Figure 2).[4]

The isotherm for $H_2O$ adsorption on AlBF obtained belongs to the Langmuir-type and is similar to the isotherms in the case of zeolites. Adsorption of hexane is not observed which allows us to admit a microporous structure of the sample with a pore diameter < 4.3 Å.

Up to *ca.* 300 °C the crystalline structure of the oxyfluoride is stable. At temperatures above 300 °C the AlBF crystal structure changes substantially. Mass spectrometric analysis of the gas phase over the sample indicates that release of $H_2O$, HF and $BF_3$ takes place (in the IR spectrum of AlBF calcined at 450 °C vibrations of boron ions are absent). The high content of fluorine in AlBF and formation of $BF_3$ during calcination gives grounds for assuming the presence of B–F bonds in the oxyfluoride structure. Complete failure of the oxyfluoride crystal structure occurs above 750 °C.

The TPD spectrum of AlBF is characterized by a peak of ammonia release at 320 °C; the peak of $NH_3$ molecules hydrogen-bonded with structural hydroxyl groups of oxides which is usually observed in the interval of 80–120 °C is absent from this spectrum. These observations are indicative of the hydrophobic character of the oxyfluoride surface. The presence of acid sites in AlBF is confirmed by a test reaction of isopropyl alcohol dehydration. According to the TPR spectrum the formation of propylene occurs at temperatures in the interval of 120–170 °C with a peak at 155 °C.

After adsorption of deuterioacetonitrile the IR spectrum of oxyfluoride vacuum-treated preliminarily at 200 °C has three bands at 2270, 2315 and 2360 $cm^{-1}$. The band at 2270 $cm^{-1}$ disappears after vacuum treatment of the sample at room temperature and is assigned to physically sorbed acetonitrile. The bands at 2315 and 2360 $cm^{-1}$ are assigned to $CD_3CN$ molecules coordinatively bonded at Lewis sites of two types. The highly shifted band at 2360 $cm^{-1}$ can be related to Lewis sites that are formed by ions of trigonal boron bonded with one or two atoms of fluorine.

To summarize: a novel crystalline aluminium–boron oxyfluoride having the composition $Al_2BO_2F_5$–HF–$H_2O$ (AlBF) has been hydrothermally synthesized. In the structure of AlBF there are strong Lewis sites and coordinatively bonded molecules of hydrogen fluoride.

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