The first synthetic microporous yttrium silicate containing framework sodium ions

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The synthesis and structural characterization of AV-1, the first synthetic microporous yttrium silicate containing stoichiometric amounts of framework sodium cations, are reported.

Recently, much research has been carried out aimed at preparing inorganic microporous framework solids containing metal atoms in different coordination geometries. Two such families of materials are of considerable interest, microporous titanosilicates (known at ETS materials) and derivatives contain Ti^{4+} usually in octahedral coordination,[1,2] while porous molybdophosphates display an amazing variety of crystal structures.[3] We have been interested in the synthesis of microporous framework silicates of several elements of the Periodic Table.[4,5] When attempting to prepare yttrium silicates we have obtained a synthetic analogue (named AV-1, Aveiro microporous solid no. 1) of the rare mineral montregianite (Mont St-Hilaire, Québec, Canada), $Na_4K_2Y_2Si_{16}O_{38}\cdot10H_2O$, which possesses a most unusual structure.[6,7] In montregianite the sodium (and yttrium) cations are an integral part of the framework. In sharp contrast, in zeolites and zeolite-type materials the charge-balancing sodium cations usually reside within the channels and, thus, are not part of the framework.

AV-1 of composition (determined by bulk chemical analysis and TG) $Na_2KYSi_8O_{19}\cdot5H_2O$, was prepared in Teflon-lined autoclaves under hydrothermal conditions. An alkaline solution was prepared by mixing 5.07 g sodium silicate solution (27% m/m SiO_2, 8% m/m Na_2O, Merck), 18.26 g H_2O, 0.20 g KOH (Carlo Erba), 0.29 g NaOH (Merck) and 0.22 g NaCl (Aldrich). $Y_2(SO_4)_3\cdot8H_2O$ (Aldrich) (1.73 g) was added to this solution and stirred thoroughly. The gel with composition 0.53 $Na_2O : 0.078\ K_2O : 1.0\ SiO_2 : 0.12\ Y_2O_3 : 44\ H_2O$ was autoclaved for 6 d at 230 °C. The crystalline product was filtered, washed with distilled water and dried at ambient temperature, the final product being an off-white microcrystalline powder.

The crystal structure of montregianite consists of two different types of layers alternating along the [010] direction (Fig. 1): (*a*) a double silicate sheet, where the single silicate sheet is of the apophyllite type with four- and eight-membered rings, and (*b*) an open octahedral sheet composed of $[YO_6]$ and three distinct $[NaO_4(H_2O)_2]$ octahedra. The layers are parallel to the (010) plane. The K atoms are ten-coordinate and the six water molecules (not shown) are located within large channels formed by the planar eight-membered silicate rings.

The powder X-ray diffraction patterns of AV-1 and montregianite[6] (Fig. 2) are similar. The small differences observed are mainly due to the fact that extensive framework substitution of Y and Si by Ca, Mg, Ba and Al, respectively, occurs in the mineral.[6] The unit-cell parameters of AV-1 have been calculated assuming a monoclinic unit cell ($P2_1/n$, $Z = 2$)[7] and cell dimensions $a = 9.595$, $b = 23.956$, $c = 9.583$ Å, $\beta = 93.850°$.

The AV-1 ^{29}Si solid-state MAS NMR spectrum (Fig. 3) displays two groups of resonances in the ranges δ −96 to −102 and −105 to −108. The spectrum can be deconvoluted into eight peaks with equal intensities, revealing the presence in AV-1 of eight non-equivalent Si sites. In accord with this observation, the crystal structure of montregianite calls for the presence of eight unique Si sites with equal populations.[7] Two silicate tetrahedra [Si(1) and Si(4)], one each within the four-membered rings belonging to a single sheet, have upward-pointing apices [O(1)] which are shared with the apices of the two downward-pointing corresponding tetrahedra [Si(4) and Si(1), respectively] in the second silicate sheet.[7] Clearly, Si(1) and Si(4) are Si(4Si) environments (Si linked to four other Si *via* oxygen bridges) and the ^{29}Si MAS NMR resonances at δ −105.5 and −106.9 are attributed to them. The assignment of the peaks at high frequency is more difficult. Si(6) is of the type Si(3Si, 1Y). Si(6)–O(12) is the shortest non-bridging bond length (1.562 Å) involving the most charge-deficient oxygen which is bonded to a Y atom.[7] Considering the well known correlation between the ^{29}Si chemical shifts and the SiO bond lengths in silicates,[8] we tentatively assign the peak at δ −100.8

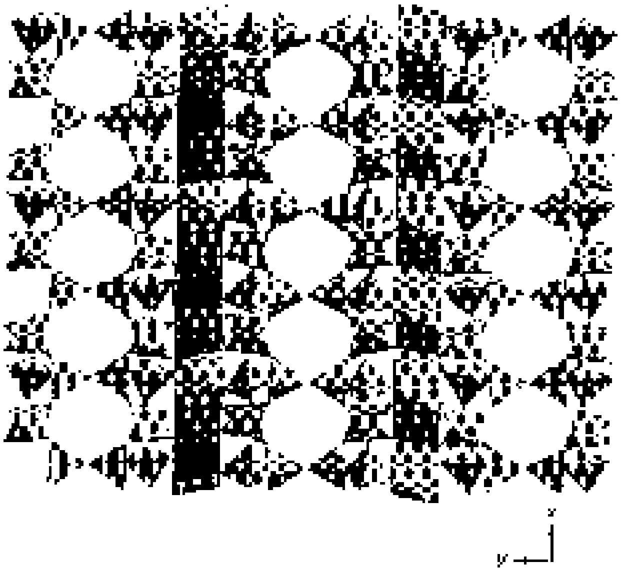

Fig. 1 Polyhedral representation of the montregianite (and AV-1) structure viewed along [001] showing the alternating octahedral sheet and double silicate sheet along [010]

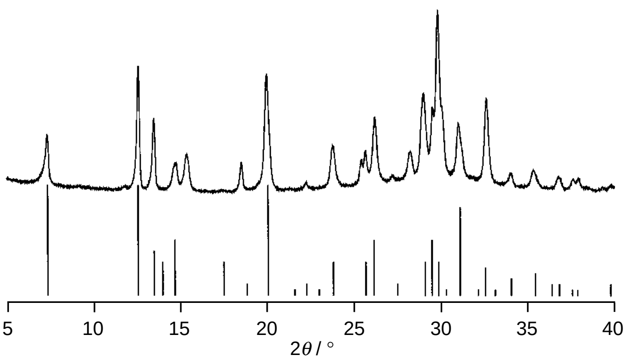

Fig. 2 Powder XRD pattern of AV-1. For comparison, the solid lines depict the montregianite reflections.[6]

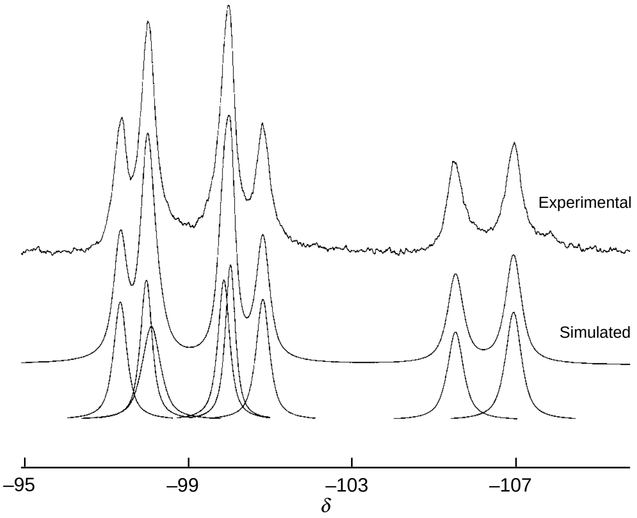

Fig. 3 Experimental and simulated ^{29}Si MAS NMR spectrum of AV-1 recorded at 79.5 MHz on a Bruker MSL 400P. Chemical shifts are quoted in ppm from SiMe$_4$.

to Si(6). The other five unique Si atoms are connected to three other silicons *via* bridging oxygens.[7] However, the fourth oxygen atom is non-bridging and is bonded to one Y and two Na atoms. [Si(2a) and Si(2b)] and [Si(5a) and Si(5b)] have very similar local environments and thus the resonances overlapping at δ *ca.* −98 and *ca.* −100 are probably associated with these sites. The resonance at δ −97.3 is assigned to the remaining Si(3) site.

The ^{23}Na triple-quantum (3Q) MAS NMR spectrum[9] of AV-1 (not shown) displays two resonances with intensities close to 1 : 1. Although montregianite contains three non-equivalent Na sites the [Na(2A)O$_4$(H$_2$O)$_2$] and [Na(2B)O$_4$(H$_2$O)$_2$] octahedra (populations 0.47 and 0.45, respectively) are very similar in configuration and it is unlikely that they can be distinguished by solid-state ^{23}Na NMR.[7] The [Na(1)O$_4$(H$_2$O)$_2$] site (population 0.95) forms a weak seventh bond with O(5B) and is, thus, distorted. The 3Q peak S1 displays a relatively broad powder pattern and, hence, is ascribed to the distorted Na(1) site. S2 is assigned to sites Na(2A) and Na(2B). The single-quantum ('normal') spectrum (not shown) can be simulated assuming the presence of two resonances, ascribed to sites Na(1) and [Na(2A) and Na(2B)], with intensities of *ca.* 1 : 0.9 and the following parameters: isotropic chemical shifts: δ 1.8 and 9.0 (from 1 M aqueous NaCl); quadrupole coupling constants 1.92 and 1.24 MHz; asymmetry parameters 0.50 and 1.0, respectively.

The Raman spectrum of AV-1 (not shown) displays a main, strong and sharp, peak at 607 cm^{-1} which we assign to relatively undistorted [YO$_6$] octahedra. Indeed, in montregianite the [YO$_6$] octahedron is fairly regular.[7]

The Fourier transform infrared spectra of AV-1 (not shown) and montregianite[6] are very similar. In particular, the medium intensity band at 1630 cm^{-1}, due to the H–O–H bending, confirms that water is present in the structure. Three O–H stretching bands are observed at 3610, 3510 and 3460 cm^{-1}.

Thermogravimetry (TG) and differential scanning calorimetry (DSC) data (not shown) provide further evidence that the structures of AV-1 and montregianite[6] are very similar. The dehydration of AV-1 is essentially complete at *ca.* 450–500 °C and the total mass loss is 11.4%. AV-1 materials calcined at 650 °C and rehydrated overnight at room temperature display TG and DSC curves similar to the parent solid. Three stages of dehydration occur, at *ca.* 20–80 °C (loss of disordered zeolitic water molecules adsorbed within the channels), 80–200 °C and 200–450 °C.

In conclusion, the novel synthetic microporous yttrium-silicate AV-1 and the rare mineral montregianite possess the same structure. These materials contain stoichiometric amounts of sodium cations which are an integral part of the framework and, thus, are fundamentally different from zeolites and other zeolite-type solids.

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Footnote and References

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