Synthesis and Thermal Decomposition of Sodalites $Na_8[SiAlO_4]_6{\cdot}(XO_4)_2$, X = Cl, Mn

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Sodalites containing the ions MnO_4^- and ClO_4^- have been synthesised and characterised by powder X-ray diffraction, IR, UV and solid state NMR spectroscopy; both materials may be heated to 500 °C before undergoing intracage decomposition to manganate and chloride ion containing sodalites, respectively.

Aluminosilicate sodalites are of the general formula $[M]_n^{8+}[SiAlO_4]_6{\cdot}X_m^{2-}$ where M represents mono or divalent cations of overall charge 8+ and X represents anionic species of overall charge 2−. These aluminosilicates are unusual in that both cations and anions are contained within the zeolitic framework; X is most commonly a halide but sodalites containing SCN, NO_2, OH and other small inorganic/organic ions are known.[1] Recent interest has centred on the hydroxide containing sodalites $Na_8[SiAlO_4]_6{\cdot}(OH)_2{\cdot}nH_2O$,[2,3] sodium cluster formation in sodalites[4,5] and nitrite/nitrate sodalites.[6,7]

The noselite subgroup of general formula $[M^{2+}]_4[SiAlO_4]_6{\cdot}(MO_4^{2-})$ contain divalent tetrahedral species such as chromate and sulphate in alternate sodalite cages. Barrer and Cole[1] have synthesised from kaolinite a perchlorate sodalite $Na_8[SiAlO_4]_6{\cdot}(ClO_4)_2$ and partially characterised its thermal properties showing slightly increased stability of the perchlorate ion in the sodalite cage. A similar reaction with sodium permanganate produced a cancrinite structure rather than a sodalite unit cell. In this communication we report the direct synthesis of sodalites containing the permanganate and perchlorate ions and show that isolation of the permanganate ion in an aluminosilicate framework permits the stabilisation of this highly oxidising ion to much higher temperatures.

The materials were synthesised following the method described by Hund;[8] a concentrated solution of either sodium permanganate or sodium perchlorate and sodium silicate was added to a freshly prepared sodium aluminate solution. The reaction mixture was refluxed for 24 hours and the solid product filtered and washed thoroughly.

Powder X-ray diffraction patterns were collected using a Siemens D5000 powder diffractometer fitted with a primary monochromator and using Cu-Kα_1 radiation. In each case a simple cubic pattern was obtained which could be indexed on unit cells of dimensions 9.101(1) $\{Na_8[SiAlO_4]_6(ClO_4)_2\}$ and 9.111(1) Å $\{Na_8[SiAlO_4]_6(MnO_4)_2\}$; observed and calculated d spacings are given in Table 1. In common with other sodalites reflections with $h + k + l = 2n + 1$ are not observed in the powder X-ray pattern as they are very weak (at best $I(h + k + l = 2n + 1)/I_0 = 1\%$) and arise solely from the Si–Al ordering. The observed value from sodium perchlorate sodalite is somewhat larger than that reported of 9.02 Å.[1]

The cell parameter in the sodalite structure reflects the dimensions of the cage species through control of the Si–O–Al bond angle[9] and this bond angle may be estimated from the ^{29}Si resonance frequency in the MAS NMR spectrum. Such data were collected from each of the new sodalite materials and a single frequency was found in each compound; −90.03 $\{Na_8[SiAlO_4]_6(ClO_4)_2\}$ and −90.61 ppm $\{Na_8[SiAlO_4]_6(MnO_4)_2\}$. These values are in line with the determined lattice constant[9] and the thermochemical radii of the permanganate and perchlorate ions ClO_4^-, 2.36 and MnO_4^-, 2.40 Å. A Si–O–Al bond angle close to 148° is indicated in both cases.

Infrared spectra of the sodalites showed the expected composite of the sodalite lattice and cage anion. In addition to the typical sodalite frequencies in the 500–1500 cm^{-1} range the perchlorate sodalite had discernible absorptions at 1116 and 631 cm^{-1} (assigned to the IR active tetrahedral ClO_4 ν_3 and ν_4 modes) whilst the permanganate derivative had an additional absorption at 911 cm^{-1} (ν_3). The anion frequencies are close to those observed for these species in other inorganic compounds and indicate little interaction with the lattice. The UV spectrum of the permanganate sodalite showed strong absorptions at 225 and 320 nm typical of the permanganate ion; both features demonstrated well resolved vibrational structure.

The thermal behaviour of both new sodalites was characterised up to 700 °C by heating samples and observing the effects on the X-ray, IR and UV spectra. Little change was observed by these techniques in samples heated to 500 °C and maintained at that temperature for 24 hours. For the perchlorate sodalite above this temperature a rapid decrease in cell parameter to 8.91(1) Å was observed accompanied with

Table 1 Observed and calculated d spacings for $Na_8[SiAlO_4]_6(ClO_4)_2$ and $Na_8[SiAlO_4]_6(MnO_4)_2$

			$Na_8[SiAlO_4]_6{\cdot}(ClO_4)_2$			$Na_8[SiAlO_4]_6{\cdot}(MnO_4)_2$		
h	k	l	d_{calc}	d_{obs}	I/I_0	d_{calc}	d_{obs}	I/I_0
1	1	0	6.435	6.446	5	6.442	6.444	6
2	0	0	4.550	4.555	6	4.555	4.562	7
2	1	1	3.715	3.718	100	3.719	3.720	100
2	2	0	3.217	3.221	2	—	—	—
3	1	0	2.878	2.878	5	2.881	2.889	6
2	2	2	2.627	2.628	20	2.630	2.630	17
3	2	1	2.432	2.432	4	2.435	2.435	7
4	0	0	2.275	2.276	5	2.278	2.278	10
3	3	0	2.1449	2.1448	14	2.147	2.147	14
3	3	2	1.9402	1.9411	3	1.942	1.942	6
4	2	2	1.8576	1.8573	1	1.859	1.858	5
4	3	1	1.7847	1.7839	5	1.787	1.785	7
5	2	1	1.6615	1.6609	4	1.663	1.663	7
4	4	0	1.6087	1.6087	6	1.610	1.610	7
4	3	3	1.5607	1.5607	2	—	—	—
4	4	2	1.5167	1.5163	3	—	—	—
5	3	2	1.4763	1.4765	5	1.4779	1.4778	6
6	2	2	1.3719	1.3714	3	1.3734	1.3737	6

loss of the characteristic perchlorate vibrations from the IR patterns. The final lattice parameter is similar to that observed for the parent sodalite $Na_8[SiAlO_4]_6{\cdot}Cl_2$ (8.88 Å) and analysis of the thermolysis product indicated the presence of Cl^- on dissolution in dilute acid. Differential thermal analysis measurements using a Stanton Redcroft DTA 673 confirm an onset for decomposition of 620 °C.

The purple permaganate sodalite again showed little change after extensive periods at temperatures up to 500 °C. Above this temperature, however, the 911 cm^{-1} band in the IR spectrum is replaced by an absorption at 841 cm^{-1} and new absorptions appear in the UV spectrum at 260 and 350 nm as the sample becomes dark green. The lattice parameter of this dark green sample was slightly contracted from that of the permanganate starting material at 9.104(3) Å. These results strongly imply the formation of manganate from permanganate at at around 600 °C and at higher temperatures further decomposition to MnO_2 is likely.

In both these new sodalites, containing highly oxidising anions, decomposition and reduction only occurs above 600 °C; at this temperature both oxygen and cations can diffuse rapidly through the sodalite lattice as seen in nitrite sodalite.[6,7] These decomposition temperatures are higher, particularly for permanganate (alkali metal permanganates typically decompose between 200 and 250 °C), than those observed for these species in simple inorganic salts showing the stabilisation offered by isolation in the sodalite cavity.

Both permanganate and perchlorate sodalites undergo facile ion exchange with lithium from aqueous solutions with a marked decrease in the unit cell parameter.

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