



A mild conditions synthesis route to produce hydrosodalite from kaolinite, compatible with extrusion processing

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ABSTRACT

Hydrosodalites are a family of zeolitic materials which have a diverse range of possible applications such as water desalination. Typical synthesis methods are relatively complex, using hydrothermal production and pre-processing and it is desirable to use lower energy and more cost-effective processing routes. For the first time, a low temperature, non-hydrothermal synthesis procedure for hydrosodalites, compatible with extrusion processing, is demonstrated. Kaolinite precursor, without calcination, was activated with a sodium hydroxide solution and formed at a workability consistent with extrusion. The cured samples were characterised using a range of advanced analytical techniques including PXRD, SEM, TGA, 27Al and 29Si-MAS-NMR, and FTIR to confirm and quantify conversion of the precursor to product phases. The synthesis consistently formed a 8:2:2 basic hydroxysodalite phase and the reaction was shown to follow a largely linear relationship with Na:Al until full conversion to the hydrosodalite phase was approached. The hydrosodalite became more ordered for Na:Al \geq 1. There is good agreement between quantitative measurements made using PXRD, TGA and 29Si-MAS-NMR methods, providing confidence in the results. It has been shown that it is possible to synthesise hydrosodalite materials in a consistent and predictable manner, using non-hydrothermal methods, at the viscosity used for extrusion processing. This novel processing route could reduce production costs, production impacts and open up new applications for this important family of materials.

1. Introduction

Hydrosodalites are a member of the zeolite family. Their defining features are their aluminosilicate framework of cubic symmetry (S.G. *P*-43n) [1], formed by alternating SiO₄ and AlO₄ tetrahedras shown in Fig. 1 [2]. These sodalite cages (β -cages) can contain a wide range of guest species [3,4]. The sub-family of hydrosodalites itself contains two separate groups within the general chemical formula $Na_{6+x}(Al_6Si_6O_{24})(OH)_x \cdot nH_2O$. These are: basic hydrosodalite (or hydroxysodalite hydrate) for $x = 2$, $n = 8$, with a chemical formula of $Na_8(Al_6Si_6O_{24})(OH)_2 \cdot 2H_2O$ (abbreviated as 8:2:2), and non-basic hydrosodalite for $x = 0$, $n = 2$, with a chemical formula $Na_6(Al_6Si_6O_{24}) \cdot 8H_2O$ (abbreviated as 6:0:8) [1,5]. The cage structure of sodalites gives them desirable properties including selective adsorption [3], fluorescence [6] and thermal stability. Previous research has considered applications as diverse as wastewater treatment [7], water desalination [8,9], admixtures in cement mortars [10], and use in optics and computation [11].

It is well established that kaolinite can be reacted with sodium

hydroxide solutions to form hydrosodalite under hydrothermal conditions [12]. Kaolinite is a phyllosilicate mineral, with an ideal chemical formula $Al_2(Si_2O_5)(OH)_4$. Each layer is formed of a gibbsite and silica sheet, with the unit cell having the *C*1 space group [13], as shown in Fig. 1. Hydrogen bonding between layers forms large stacks, giving little opportunity for interlayer cation adsorption [14]. Kaolinite is a common clay mineral found in soils and deposits, and is an inexpensive feedstock if not highly purified. Purified kaolinite is readily available and is used in ceramics, paper production, medicines and numerous other applications.

The synthesis of zeolitic products is generally by alkali activation of an aluminosilicate and the product phase is strongly determined by the processing conditions used. Hydrosodalite has been shown to be favoured over formation of other zeolitic phases by the following processing conditions: synthesis time between 24 and 72 h [15]; solid:liquid ratios of > 5 [16]; NaOH solution concentrations of > 3 M, and synthesis temperatures of 150–200 °C [17]. Hydrothermal synthesis is by far the most commonly used method [17], whilst more complex two-step synthesis methods have also been used involving alkali pre-fusion

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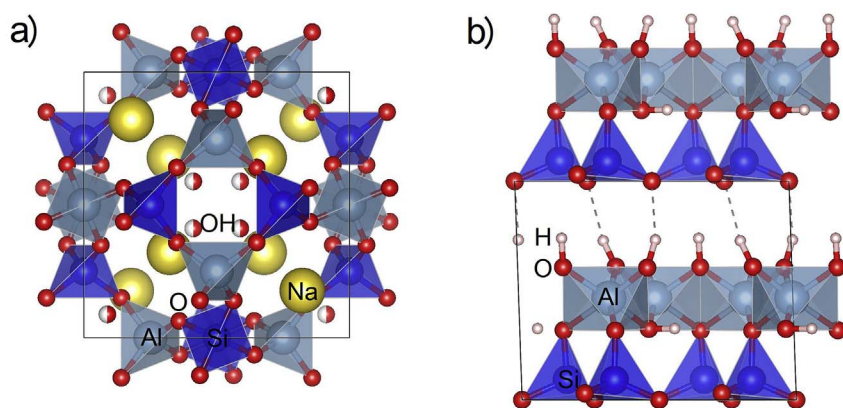


Fig. 1. The structures of a) sodalite (8:2:2 hydroxysodalite), using structural parameters by Kendrick and Dann [35], and b) kaolinite, using structural parameters by Bish [13]. Both structures are viewed along the a axis with coordination polyhedra shown for Al and Si. Images were generated in VESTA.

at elevated temperatures [18]. It is also common to calcine kaolinite by heating above 700 °C to form metakaolin, in order to increase reactivity before synthesis [19].

Even for hydrosodalite which prefers low solid:liquid ratios [16], synthesis routes typically use an excess quantity of NaOH solution, which makes them incompatible for processing involving extrusion, a technique which is frequently used for production of ceramics. Extrusion is an adaptable, continuous processing technique, which requires that a clay-based feedstock is a wetted mixture in its plastic state [20]. In the plastic state, a clay-based material is able to be moulded without cracking and has the ability to hold its new shape without support [21]. This is typically done at a moisture content between the plastic limit and liquid limit [22], which is the moisture content range over which the clay can be moulded but will not flow as a liquid. Extrusion processing could increase the types of products and applications where hydrosodalites could be used.

Given that calcination and mid-temperature synthesis both involve an additional heating step, a synthesis route at low temperature involving no thermal pre-treatment could be desirable for reducing energy and for practicality. The proportions of phases formed by the reaction of kaolinite with sodium hydroxide have previously been investigated in relation to the nature of kaolinite used [23], or addition of different volumes of an activating solution at given pH [24], rather than the Na:Al molar ratio for a mixture of constant workability. Whilst Heller-Kallai and Lapidés demonstrated proof of concept for non-hydrothermal synthesis [23], a systematic understanding of the reaction for these conditions has not previously been developed. A synthesis route using lower temperature and atmospheric conditions would make production cheaper and less energy-intensive.

In this study, hydrosodalite-kaolinite samples were made with a range of Na:Al ratios from 0.25 to 1.5. They were characterised to determine the amounts of hydrosodalite formed and unreacted kaolinite for each Na:Al ratio, comparing measurements made using PXRD, 29Si MAS-NMR and TGA.

2. Experimental

2.1. Materials

Imerys Speswhite (mined from Cornwall, U.K.) kaolinite was used as the aluminosilicate precursor. The chemical composition was determined by energy dispersive X-rays (JEOL SEM6480LV with Oxford INCA X-Act SDD X-ray detector). It showed minor amounts of iron, potassium and magnesium present (Table 1) believed to be unreactive in the present conditions. Specific surface area was 11.9 m²g⁻¹, measured using the BET method [32]. It was activated using sodium hydroxide pellets of > 98% purity (Sigma-Aldrich, product no. 06203).

Table 1

Chemical composition of kaolinite precursor in oxide wt%.

Oxide	Al ₂ O ₃	Fe ₂ O ₃	K ₂ O	MgO	SiO ₂	Total
wt % (std error)	40.11 (0.15)	0.95 (0.06)	2.06 (0.09)	0.04 (0.04)	56.83 (0.15)	100

Table 2

Composition of hydrosodalite samples for chemical characterisation.

Name	0.25-Na:Al	0.5-Na:Al	0.75-Na:Al	1-Na:Al	1.25-Na:Al	1.5-Na:Al
Na:Al molar ratio	0.25	0.5	0.75	1	1.25	1.5
Concentration of activating solution (molarity)	5.2	9.5	13.2	16.2	18.3	19.7

2.2. Synthesis procedure

The compositions in Table 2 were determined to provide samples of pre-determined Na:Al ratio, whilst maintaining the wet mix workability at the plastic limit. This was done by initially undertaking Atterberg plastic limit measurements [22] for kaolinite over a range of sodium hydroxide solution concentrations [25]. From these data a best fit line was plotted to extrapolate the volume of solution required to reach plastic limit consistency for a given concentration (Fig. 2). A correction was made to exclude the mass of the sodium hydroxide from the solids mass in the plastic limit calculations [26]. Only small changes in plastic limit were observed, as expected due to kaolinite's low cation exchange capacity [14].

The kaolinite was activated by adding a sodium hydroxide solution. Solutions of different concentrations were prepared by adding sodium

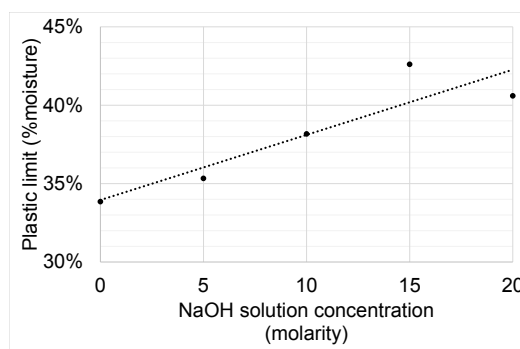


Fig. 2. The change in kaolinite's plastic limit with sodium hydroxide solution concentration.

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