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SHORT COMMUNICATION

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X-ray diffraction, FTIR and ^1H MAS NMR investigations during fast dynamic exchange between Na^+OH^- ion pairs and H_2O molecules in sodalites

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Keywords: hydro sodalite, ion exchange, IR spectroscopy, NMR spectroscopy, X-ray diffraction

We report sodalite phases formed at the intermediate stages during the fast dynamic exchange between Na^+OH^- ion pairs and H_2O molecules while transforming a series of hydro-hydroxy sodalites into hydro sodalites. The applicability of an ion-exchange technique has been addressed, which is much faster than the previously employed exchange methods. The results of X-ray diffraction, FTIR and ^1H MAS NMR spectroscopy are complimentary showing the successive steps of the exchanges. The X-ray data Rietveld refinements demonstrate that the framework composition did not change at the intermediate stages of the $\text{Na}^+\text{OH}^-/\text{H}_2\text{O}$ exchange, thus distinguished the ion-exchange from re-crystallization.

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Introduction

Hydro sodalites $\text{Na}_6[\text{T}^1\text{T}^2\text{O}_4]_6(\text{H}_2\text{O})_8$ ($\text{T}^1 = \text{Al}, \text{Ga}; \text{T}^2 = \text{Si}, \text{Ge}$) [1–7] are synthetic analogues to the mineral sodalite [8–10] offer typical zeolitic ion-exchange in aqueous solution. They are unique mainly from two standpoints: (I) they do not enclathrate anionic guest species such as Cl^- , OH^- , NO_2^- but neutral H_2O molecules and, (II) reversible dehydration/hydration phenomena and the consequent anomalous effect on framework geometry are only known from hydro sodalites [1–3]. Synthesis of pure hydro sodalite from binary oxide sources using alkaline media is somewhat difficult compared to its other synthetic analogues (e.g. halide sodalites [11]), in particular, when gallosilicate [6] or alumogallosilicate [7] frameworks are concerned. Therefore, it has been a common practice producing hydro sodalites from their hydro-hydroxy $\text{Na}_{6+x}[\text{T}^1\text{T}^2\text{O}_4]_6(\text{OH})_x(\text{H}_2\text{O})_{8-4x}$ phases ($0 < x < 2$) either by ion-exchange in Teflon-coated steel autoclaves [1–3] or by Soxhlet extraction [4,5] at mild conditions. However, due to lack of information of the intermediate phases formed during the exchanges sometimes it may be misleading considering re-crystallization as ion-exchange or leaching processes. For instance, it takes as long as 24 hours for the transformation of $\text{Na}_8[\text{GaSiO}_4]_6\text{I}_2$ into $\text{Na}_6[\text{GaSiO}_4]_6(\text{H}_2\text{O})_8$ sodalite using the autoclave procedure at 473 K and autogeneous pressure [7], however, such transformation should not be considered as ion-

exchange. Instead, it has been demonstrated as a re-crystallization process [7] since the large iodide anion (206 pm [12]) could not leach through the effective six-ring windows (~190 pm) without destroying the β -cages (also known as ‘toc’ or ‘sod’ as modern designation [13]).

Herein, we investigate the intermediate phases formed during the fast dynamic exchanges between Na^+OH^- ion pairs and H_2O for the transformation of hydro-hydroxy sodalites into hydro sodalites.

Experimental Section

A series of $\text{Na}_6[\text{Al}_{1-y}\text{Ga}_y\text{SiO}_4]_6(\text{H}_2\text{O})_8$ sodalites were produced from the corresponding $\text{Na}_{6+x}[\text{Al}_{1-y}\text{Ga}_y\text{SiO}_4]_6(\text{OH})_x(\text{H}_2\text{O})_{8-4x}$ sodalites ($y = 0 - 1$ in both cases) by an ion-exchange method carried out in an open 100 ml beaker containing an acidic solution (pH ~6.5) at room conditions [7]. The $\text{Na}^+\text{OH}^-/\text{H}_2\text{O}$ exchange took place between the solution and the β -cages of the sodalites through the bottleneck of the six-ring apertures. The pH of the solution instantly increased due to gradual depletion of Na^+OH^- ion pairs from the hydro-hydroxy sodalite cages to maintain $[\text{Na}_3\text{O}(\text{H}_2\text{O})_4]^{3+}$ non-framework configuration per hydro sodalite cage. The exchange accelerated upon external acid (1 M CH_3COOH) addition within a controlled pH between 5.5 and 6.5. The target hydro sodalites were obtained within 1 – 2 hours.

The X-ray powder diffraction data were collected on a STOE STADI P diffractometer using a transmission geometry in Debye-Scherrer mode, a focusing Ge(111) monochromator and $\text{CuK}\alpha_1$ radiation. 4000 data points were collected with a step width of 0.02° in the 2θ range from 10° to 90° . During Rietveld refinements using RIETAN-97 [14], cell parameter, atomic positional coordinates (xyz), displacement parameters, zero point of the counter, scale

factor, maximum twelve background parameters and six profile parameters (U, V, W, X, Y, asymmetry) were optimized. Fourier transform infrared (FTIR) spectra were obtained on a Bruker IFS 66v/S spectrometer using the KBr method. Magic angle spinning nuclear magnetic resonance for ^1H isotope (^1H MAS NMR) spectra were recorded on a Bruker Avance ASX 400 spectrometer using standard 4 mm MAS probes, 2 μs pulse, 5 s recycle delay and a spinning rate more than 5 kHz. TMS was used as an external standard.

Results and Discussion

Prior to $\text{Na}^+\text{OH}^-/\text{H}_2\text{O}$ exchanges, the starting hydroxy sodalites were prepared from binary oxide sources (Al_2O_3 , Ga_2O_3 , Na_2SiO_3) at 473 K and autogeneous pressure in the Teflon-coated steel autoclaves [15]. There were small amounts of CO_3^{2-} directed cancrinite impurities along with the starting hydroxy sodalites, which were produced from the aerial carbonation of NaOH and removed by the exchange method carried out in acidic media. The weight fractions of the constituent crystalline phases were obtained from the powder X-ray data Rietveld refinements (Table 1). The framework composition did not change at the intermediate stages during the $\text{Na}^+\text{OH}^-/\text{H}_2\text{O}$ exchanges, thus distinguished the exchange from re-crystallization (i.e. the initial composition differs from the resulting exchanged one [7]). Two distinct lattice parameters clearly show that the intermediate phases comprise of both the starting hydroxy and the transformed hydro sodalites (Fig. 1). Complimentary results can also be seen both in the FTIR and ^1H MAS NMR spectra (Fig. 2). A sharp absorption band at 3636 cm^{-1} showing OH^- imbibed inside the hydroxy sodalites. With increasing ion-exchange time, the intensity of the OH^- stretching mode gradually decreases to disappearance, and the H_2O deformation mode ($\sim 1650\text{ cm}^{-1}$) increases for the transformation of hydro sodalites. Concomitantly, the intensity of broad CO_3^{2-} bands ($\sim 1400 - 1500\text{ cm}^{-1}$) of small amounts of cancrinite impurities, and/or surface carbonates of the sodalites decrease to decay, ensuring pure hydro sodalites. In the ^1H MAS NMR spectra, chemical shifts at 4.2 ppm and -1.0 ppm have been respectively assigned to H_2O and OH^- enclathrated in the β -cages [7,16], where the OH^- signal completely disappeared for hydro sodalite with increasing exchange time.

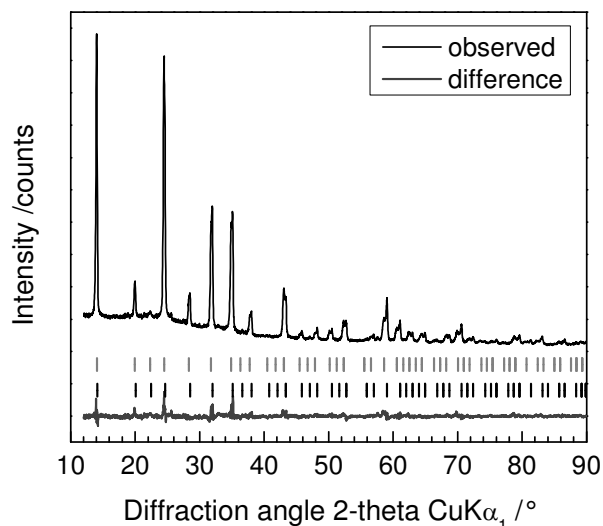


Figure 1. Rietveld plots of a hydro-hydroxy alumogallosilicate sodalite while transforming into its hydro containing phase (Table 1) at an intermediate stage during the $\text{Na}^+\text{OH}^-/\text{H}_2\text{O}$ exchange. The vertical solid lines depict the symmetry ($P43n$) allowed positions of Bragg reflections.

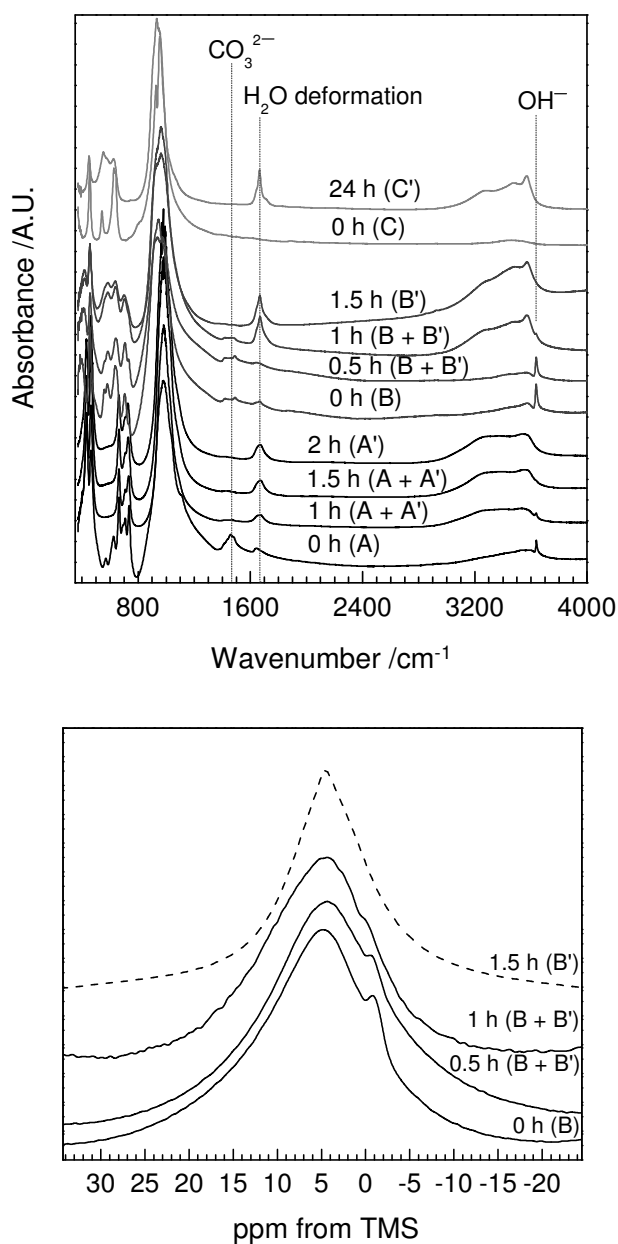


Figure 2. FTIR (top) and ^1H MAS NMR (down; the dashed spectrum was measured at different spinning rate than the other three spectra) of some sodalites during the $\text{Na}^+\text{OH}^-/\text{H}_2\text{O}$ exchange. A, B and C are $\text{Na}_{6.7(1)}[\text{AlSiO}_4]_6(\text{OH})_{0.7(1)}(\text{H}_2\text{O})_{5.1(1)}$, $\text{Na}_{7.1(1)}[\text{Al}_{0.44(1)}\text{Ga}_{0.56(1)}\text{SiO}_4]_6(\text{OH})_{1.1(1)}(\text{H}_2\text{O})_{3.6(1)}$ and $\text{Na}_8[\text{GaSiO}_4]_6\text{L}_2$ starting sodalites, respectively; A', B' and C' refer to their transformed hydro sodalite phases of $\text{Na}_6[\text{AlSiO}_4]_6(\text{H}_2\text{O})_8$, $\text{Na}_6[\text{Al}_{0.43(1)}\text{Ga}_{0.57(1)}\text{SiO}_4]_6(\text{H}_2\text{O})_8$ and $\text{Na}_6[\text{GaSiO}_4]_6(\text{H}_2\text{O})_8$, respectively.

In comparison with the previously described ion exchange/leaching processes using sodalite matrices where amorphization and/or dramatic reduction of average crystal size were common phenomena [2,3], we applied an open beaker method and checked some intermediate phases formed during the $\text{Na}^+\text{OH}^-/\text{H}_2\text{O}$ exchanges, which is ~ 12

times faster than autoclave exchange method [1–3], and ~60 times faster than Soxhlet extraction [4,5]. Moreover, it is simple, non-destructive, and seems to be cheaper.

Table 1. Results of the powder X-ray data Rietveld refinements of the starting hydro-hydroxy sodalite, sodalite phases at an intermediate stage, and the transformed hydro sodalite during the Na⁺OH⁻/H₂O exchange.

Atom	Site	Occupancy	x	y	z	B[pm ² 10 ⁴]
Starting phase: R _{wp} = 0.051						
Na _{7.0(2)} [Al _{0.76(1)} Ga _{0.24(1)} SiO ₄] ₆ (OH) _{1.0(2)} (H ₂ O) _{4.0(2)} ; a = 889.78(2) pm;						
Na	8e	0.88(2) ^a	0.1758(3)	0.1758	0.1758	1.0(1)
Al/Ga	6c	0.76/0.24(1)	¼	½	0	1.14(8) ^b
Si	6d	1	¼	0	½	1.14(8) ^b
O1	24i	1	0.1515(4)	0.1419(4)	0.4339(3)	0.9(1) ^c
O2	24i	0.21(2) ^a	0.0504(19)	0.1105(49)	0.8975(39)	0.9(1) ^c

Intermediate phases: R _{wp} = 0.056						
Phase I: Na _{7.0(1)} [Al _{0.75(1)} Ga _{0.25(1)} SiO ₄] ₆ (OH) _{1.0(1)} (H ₂ O) _{4.0(1)} ; a = 890.29(4) pm						
Na1	8e	0.88(1) ^a	0.1770(5)	0.1770	0.1770	4.0(2)
Al/Ga	6c	0.75/0.25(1)	¼	½	0	1.17(2) ^b
Si1	6d	1	¼	0	½	1.17(2) ^b
O1	24i	1	0.1515(6)	0.1419(5)	0.4360(6)	1.74(8) ^c
O2	24i	0.21(1) ^a	0.0992(39)	0.0598(36)	0.8384(28)	1.74(8) ^c
Phase II: Na ₆ [Al _{0.76(2)} Ga _{0.24(2)} SiO ₄] ₆ (H ₂ O) ₈ ; a = 884.14(3) pm						
Na	8e	0.75	0.1513(6)	0.1513	0.1513	4.1(2)
Al/Ga	6c	0.75/0.25(2)	¼	½	0	1.17(2) ^b
Si	6d	1	¼	0	½	1.17(2) ^b
O1	24i	1	0.1501(3)	0.1401(4)	0.4301(5)	1.74(8) ^c
O2	8e	1	0.3849(5)	0.3849	0.3849	4.2(4)

Final phase: R _{wp} = 0.035						
Na ₆ [Al _{0.75(1)} Ga _{0.25(1)} SiO ₄] ₆ (H ₂ O) ₈ ; a = 884.03(3)						
Na	8e	0.75	0.1602(6)	0.1602	0.1602	4.6(2)
Al/Ga	6c	0.74/0.24(1)	¼	½	0	1.8(2)
Si	6d	1	¼	0	½	2.0(2)
O1	24i	1	0.1501(4)	0.1403(4)	0.4311(4)	2.3(2)
O2	8e	1	0.3819(4)	0.3819	0.3819	2.9(4)

^{a,b,c}linear constraints were used during the Rietveld refinements in the space group P43n

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