

Basic Nitrite Sodalite— $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)_x$ —A Suitable Material for the Uptake of Carbon Dioxide

JOSEF-CHRISTIAN BUHL

*Institut für Mineralogie, Universität Münster, Corrensstr.24,
D-4400 Münster, Germany*

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The solid solution series basic sodalite–nitrite sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})_{2-x}(\text{NO}_2)_x$ has been synthesized under hydrothermal conditions at 470 K (autogeneous pressure). The observed composition range $0 \leq x \leq 2$ could be varied by using different amounts of sodium nitrite in the starting reaction mixture. Besides the crystal data and the thermoanalytical properties of this new material its sorption capacity for carbon dioxide has been investigated. At elevated temperatures (970 K) an intracage reaction of the enclathrated sodium hydroxide with carbon dioxide could be estimated, yielding to an uptake of 25 mg CO_2 per gram sodalite, whereas no CO_2 absorption could be estimated at room temperature. The reaction mechanism involves the partial destruction of the $\text{NaOH} \cdot \text{H}_2\text{O}$ complex followed by the formation of Na_2CO_3 within the sodalite cages, as demonstrated by X-ray powder diffraction, IR spectroscopy, and thermoanalytical results. © 1991 Academic Press, Inc.

Introduction

The chemical behavior of a given sodalite species is determined by the properties of the guest molecules within the aluminosilicate framework. Studies of the salt enclathration and the resulting effects on chemical and thermal properties became of interest recently for the development of new ion exchangers, adsorbents, or materials with special physical properties like photochromism (1–6). Because of the structural similarities of sodalites and zeolites A, X, and Y, studies on sodalites are also important for a better understanding of zeolite sorbents.

Although various articles are available on the synthesis of salt-filled sodalites and their thermoanalysis, only a few deal with sorption properties of sodalites (7, 8). Because of the scarcity of experimental data this paper reports on the synthesis of basic nitrite soda-

lite solid solutions and its intracage reactions with carbon dioxide at elevated temperatures, indicating this new material as a suitable sorbent for CO_2 . These properties are a result of a special combination of two types of guest molecules ($\text{NaOH} \cdot \text{H}_2\text{O}$ and NaNO_2), a “reactive” one and an “inert” one which stabilizes the sodalite host structure. As suitable guest species hydrated sodium hydroxide (“reactive component”) and sodium nitrite (“stabilizing component”) were selected, because the thermal properties of pure basic sodalite as well as the pure nitrite sodalite are already known (3, 4).

Experimental

The hydrothermal transformation of kaolinite (FLUKA 60609) in an 8 M solution of sodium hydroxide (Merck 6495) was used

for synthesis. Different amounts of sodium nitrite (Riedel-deHaen 31443) up to 3.45 g were added to form the solid solution series of compositions $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})_{2-x}(\text{NO}_2)_x$; $0 \leq x \leq 2$. Teflon-coated steel autoclaves (50-ml vol) filled with 1 g of kaolinite (degree of filling with NaOH solution: 100%) were used. After a reaction period of 24 h at a temperature of 473 K the products were washed and dried at 350 K to remove weakly absorbed surface water. The polycrystalline samples were prepared for subsequent X-ray powder diffraction, using the Guinier technique ($\text{CuK}\alpha_1$ radiation, internal Si standard, LSQS refinement of the unit cell parameter and determination of the relative intensities by densitometry). The chemical composition of the aluminosilicate framework of the samples was detected by ED analysis (Camscan SEM, equipped with a KEVEX ED analysis; 10 kV and 0.4 nA, 300 cps at 200-s scan time), whereas the concentrations of the guest molecules were analyzed by thermogravimetry in combination with stepwise IR spectroscopy to distinguish between OH^- , H_2O , NO_2^- , and CO_3^{2-} . All products were analyzed by X-ray powder diffraction, IR spectroscopy, and thermogravimetry in an inert atmosphere (Ar) as well as in carbon dioxide.

The uptake of carbon dioxide has been described for the sample of the composition $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$. Therefore this species was heated on a Mettler thermoanalyzer TA 146 up to 970 K in a CO_2 stream of 10 liters/hr for up to 1 hr. Additional ^{29}Si MAS NMR spectra of the initial sample and the resulting carbonate containing product were measured on a Bruker CXP-300 spectrometer to detect structural deviations developed during heating. The spectra were recorded with a multinuclear double bearing probehead. Chemical shifts were referenced to $\text{TMS} = 0$ ppm with Q_8M_8 (trimethyl-silyl ester of double four-ring silicate) as an intermediate reference.

Results

Synthesis and Characterization of Basic Nitrite Sodalite Solid Solutions

The experimental parameters and results of the hydrothermal syntheses are summarized in Table I for five selected compositions. Sodalites have been obtained exclusively in every run. The lattice constants calculated from X-ray powder diffraction are also added in this table. A complete solid solution series between common basic sodalite ($a_0 = 8.890(1)$ Å (9)) and nitrite sodalite ($a_0 = 8.931(2)$ Å (4)) could be observed as a function of the initial concentration of sodium nitrite. The X-ray powder data of basic nitrite sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ (sample 3, table I) are summarized in Table II.

Due to the mild reaction conditions the products were always obtained as white polycrystalline powders, since single crystals can only be observed at stronger conditions, i.e., pure nitrite sodalite at 570 K and 0.1 GPa pressure (4). The grain size of the polycrystallites is in the range of 1.0 μm . ED analysis of Na_2O , SiO_2 , and Al_2O_3 gave the typical values of $\text{Si} = 6.02$, $\text{Al} = 5.98$, and $\text{Na} = 7.90$ for the cell content, based on $\text{Si} + \text{Al} = 12$, indicating an Si/Al ratio of 1.0 (analysis of sample No. 3, Table I). The concentrations of the guest species calculated from thermogravimetry are in good agreement with the compositions estimated from the unit cell parameter calculations (see Table I). The IR spectroscopic characterization of the products indicates their different imbibed guest molecules, as shown in Fig. 1a for product 3 (Table I) (absorption band at 3640 cm^{-1} , OH^- ; 3600 cm^{-1} - 3000 cm^{-1} as well as 1650 cm^{-1} , H_2O ; and 1270 cm^{-1} , NO_2^- (4)). The vibrations of the aluminosilicate framework are typical for sodalite, as described by Henderson and Taylor (1978) (10).

In addition to the structural information from IR spectroscopic data the ^{29}Si MAS

TABLE I

THE PRODUCTS OF THE HYDROTHERMAL SYNTHESSES AT 473 K FOR 24 HR IN 8 M NaOH, AUTOGENEOUS PRESSURE

No.	Initial NaNO ₂ (g)	Composition of the products	Cell parameter (Å)
1	0.0	Na ₈ [AlSiO ₄] ₆ (OH · H ₂ O) ₂	8.890(1)
2	0.345	Na ₈ [AlSiO ₄] ₆ (OH · H ₂ O) _{1.8} (NO ₂) _{0.2}	8.893(1)
3	0.690	Na ₈ [AlSiO ₄] ₆ (OH · H ₂ O)(NO ₂)	8.913(1)
4	1.0	Na ₈ [AlSiO ₄] ₆ (NO ₂) ₂	8.931(1)
5	3.45	Na ₈ [AlSiO ₄] ₆ (NO ₂) ₂	8.931(1)

NMR spectrum of basic nitrite sodalite is shown in Fig. 2a. The single peak with a chemical shift of $\delta = -85.4$ ppm indicates the alternating ordering of the Si and Al atoms in the TO₄ framework, i.e., Si(4Al) units (11). The chemical shift also correlates well with the Si–O–Al bond angle and the unit cell parameter (11).

Thermoanalysis of Basic Nitrite Sodalite in an Inert Atmosphere

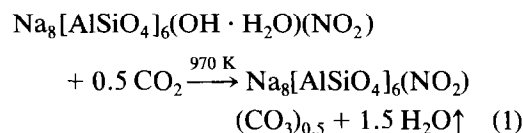
The results of the simultaneous thermoanalysis in an Ar atmosphere are given in Fig. 3. As can be seen from this figure, during heating a two-step decomposition reaction occurs in the 790 K–1150 K interval with DTA maxima at 850 and 1020 K. The total loss in weight according to both steps is 6.6 wt% (thermogravimetry). Stepwise IR spectra, taken from this material after the first and second decomposition step, clearly indicates the decomposition of the (NaOH · H₂O) guest molecules during the first step and the total destruction of the sodalite framework according to the decomposition of the nitrite at elevated temperatures in the second step.

Some deviations in the water content from batch to batch up to 0.5 H₂O should be taken into account. This is a result of physically adsorbed surface water (see also the bending mode near 1650 cm⁻¹ in Fig.

1a), of water from small admixtures of amorphous material as well as water from "defects" in the occupancy of the sodalite cages during crystallization. Under the mild conditions used here some sodalite cages can accommodate 4H₂O instead of one NaNO₂ or NaOH · H₂O. The thermal decomposition behavior also has been studied by high temperature X-ray powder diffraction on a Guinier–Simon film, where the totally new pattern of a stuffed carnegieite phase (Na₂O)_{1/6}NaAlSiO₄ (12) could be revealed at elevated temperatures (1020 K), followed by the reflections of a nepheline like phase.

Thermal Analysis in Carbon Dioxide; the Imbibition of CO₂

The thermochemical results in a CO₂ atmosphere are shown in Fig. 4. In contrast to the measurements in an inert atmosphere a weight uptake of 2.3 wt% can be stated here, according to the imbibition of carbon dioxide during isothermal heating at 970 K in a CO₂ stream of 10 liters/hr according to Reaction (1)



within the sodalite cages. The X-ray powder data of this new carbonate-intercalated

TABLE II
 X-RAY POWDER DATA OF $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ AND
 $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_2)(\text{CO}_3)_{0.5}$

$\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ cubic, $a_0 = 8.913(1) \text{ \AA}$				$\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_2)(\text{CO}_3)_{0.5}$ cubic, $a_0 = 9.000(1) \text{ \AA}$			
$h k l$	$2\theta_{\text{obs}}$	d_{obs}	I/I_0	$h k l$	$2\theta_{\text{obs}}$	d_{obs}	I/I_0
1 1 0	14.040	6.302	75	1 1 0	13.909	6.362	87
2 0 0	19.906	4.457	14	2 0 0	19.711	4.500	11
2 1 0	22.285	3.986	5	2 1 0	22.057	4.027	6
2 1 1	24.443	3.639	100	2 1 1	24.209	3.674	100
2 2 0	28.297	3.152	3	2 2 0			
3 1 0	31.720	2.819	47	3 1 0	31.390	2.848	42
2 2 2	34.840	2.573	69	2 2 2	34.475	2.599	68
3 2 1	37.733	2.382	29	3 2 1	37.340	2.406	19
4 0 0	40.448	2.228	2	4 0 0	40.022	2.251	13
3 3 0	43.019	2.101	63	3 3 0	42.570	2.122	48
4 1 1				4 1 1			
4 2 0	45.473	1.993	4				
3 3 2	47.827	1.900	3				
4 2 2	50.096	1.819	16	4 2 2	49.578	1.837	6
4 3 1	52.293	1.748	27	4 3 1	51.744	1.765	31
5 1 0				5 1 0			
5 2 1	56.504	1.627	3				
4 4 0	58.534	1.576	25	4 4 0	57.915	1.591	22
4 3 3	60.520	1.529	26	4 3 3	59.882	1.543	19
5 3 0				5 3 0			
4 4 2	62.468	1.486	20	4 4 2	61.798	1.500	14
6 0 0				6 0 0			
5 3 2	64.382	1.446	19	5 3 2	63.664	1.461	18
6 1 1				6 1 1			
6 2 0	66.266	1.409	4	6 2 0	65.519	1.424	3
5 4 1	68.123	1.375	12	5 4 1	67.684	1.383	2
5 3 3	69.042	1.359	5				
6 2 2	69.956	1.344	16				
6 3 1	71.768	1.314	9	6 3 1	70.933	1.328	8
4 4 4	73.561	1.287	9	4 4 4	72.683	1.299	10
5 4 3	75.338	1.261	4	5 4 3	74.456	1.273	7
5 5 0				5 5 0			
7 1 0	76.221	1.248	9	7 1 0			
7 1 1							
5 5 2	78.850	1.213	19	5 5 2	78.389	1.219	3
6 3 3				6 3 3			
7 2 1	80.590	1.191	6	7 2 1	79.641	1.203	4
6 4 2				6 4 2			
7 3 0	82.321	1.170	7	7 3 0	81.275	1.183	4

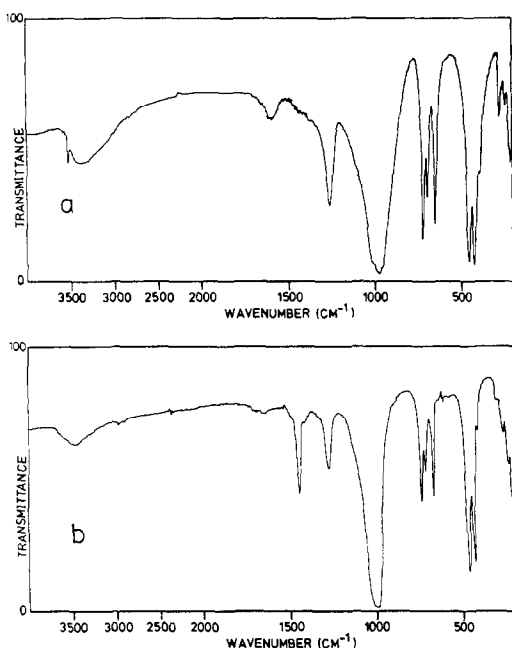
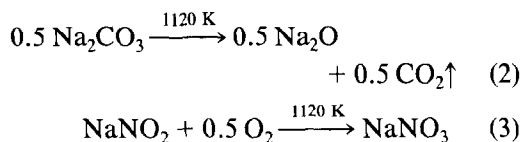


FIG. 1. IR spectroscopic characterization of basic nitrite sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ (a) and carbonate-imbibed sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_2)(\text{CO}_3)_{0.5}$ (b).

sodalite are given in Table II. The IR spectrum as well as the ^{29}Si MAS NMR spectrum are shown in Figs. 1b and 2b. Besides the NO_2^- absorption, one can see the evaluation of the CO_3^{2-} band at 1450 cm^{-1} and the disappearance of the OH^- and H_2O vibrations, compared with Fig. 1a. The single peak at $\delta = -87.7\text{ ppm}$ in the ^{29}Si MAS NMR spectrum (Fig. 2b) gives evidence for the unchanged sodalite framework with $\text{Si}/\text{Al} = 1.0$ after the heating procedure.

Additional thermoanalytical studies in air indicate the possibility of a "regeneration" of the carbonate-filled nitrite sodalite by a heating process at 1120 K . Two reactions can be observed under these conditions: The decomposition of sodium carbonate (2) and the oxidation of the nitrite guest anions to nitrate (3),



The high temperature oxidation of the nitrite to nitrate inside a sodalite matrix is already known for pure nitrite sodalites (13). The sodalite framework remains unchanged during heating. The composition of the sodalite solid solution at 1120 K in air can be written as $\text{Na}_8[\text{AlSiO}_4]_6(\text{O})(\text{NO}_3)$. This material now can react again with carbon dioxide by

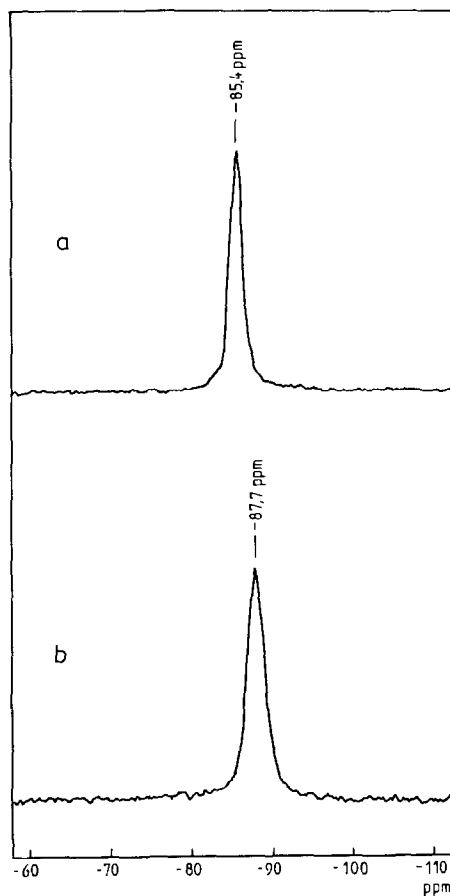


FIG. 2. ^{29}Si MAS NMR spectra of basic nitrite sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ (a) and carbonate-imbibed sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_2)(\text{CO}_3)_{0.5}$ (b).

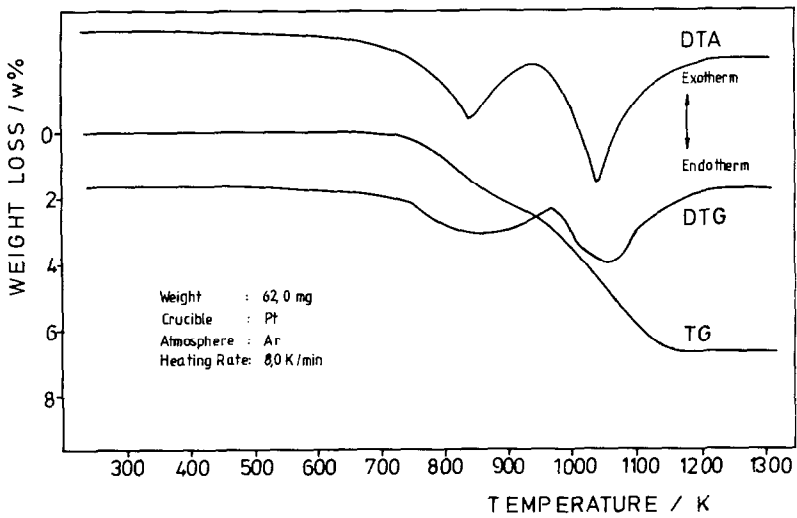


FIG. 3. Simultaneous thermal analysis of basic nitrite sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ in an argon atmosphere.

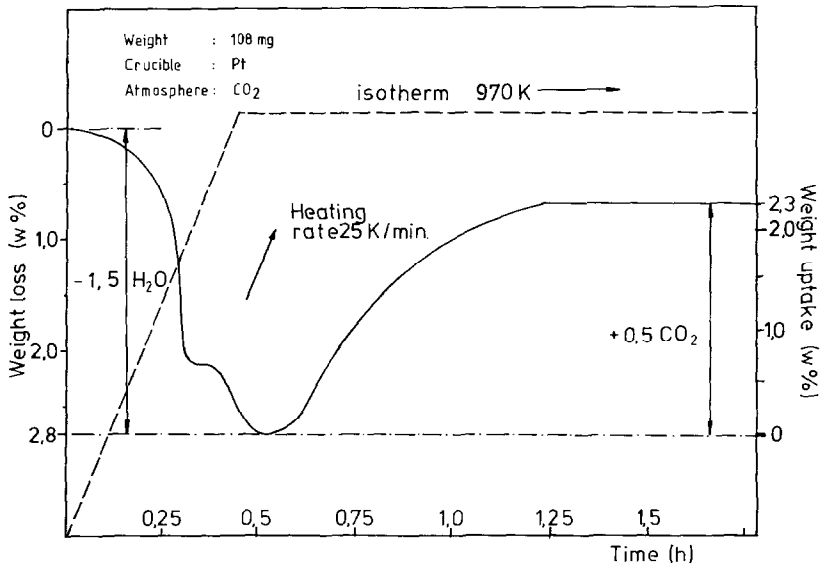


FIG. 4. Simultaneous thermal analysis of basic nitrite sodalite $\text{Na}_8[\text{AlSiO}_4]_6(\text{OH} \cdot \text{H}_2\text{O})(\text{NO}_2)$ in carbon dioxide.

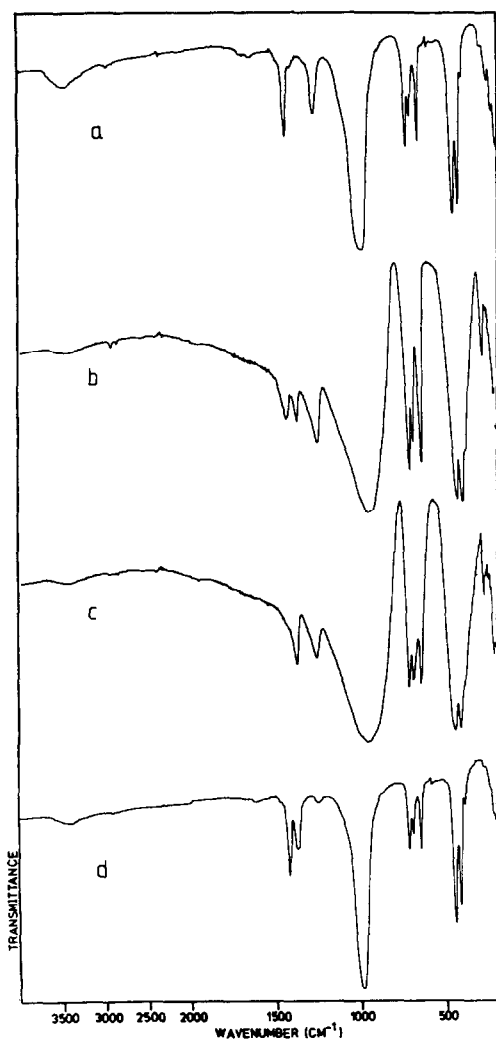
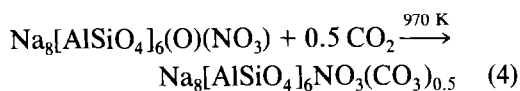


FIG. 5. IR spectroscopic investigation of the "regeneration" and "modification" process of $\text{Na}_8[\text{AlSiO}_4]_6(\text{NO}_2)(\text{CO}_3)_{0.5}$ during heating in air at 1120 K: (a) initial substance; (b) sample (a), heated up at 1120 K; (c) sample (b), after tempering for 30 min; (d) sample (c) after heating in CO_2 at 970 K.

cooling it down to 970 K in the presence of CO_2 according to



The series of IR spectra in Figs. 5a–5d illus-

trate this modification and regeneration process.

The calculation of the amount of carbon dioxide, which can be incorporated by the high temperature reaction within the sodalite cages gives about 25 mg CO_2 per gram of sodalite. Some facts should be mentioned in this connection: The carbon dioxide is bonded here in the form of stable carbonate molecules and not only adsorbed on a surface of a channel system as in the case of the zeolite sorbents. At high temperatures the sorption capacity of zeolites is decreasing drastically (14). Thus the intracage reactions of sodalite, presented in this paper, can be regarded as an interesting model system for the modification of zeolites to improve their capacity for reducing the carbon dioxide content of waste gases. Experiments to introduce the corresponding guest anions into the sodalite cages of zeolites A and X are in progress now.

Acknowledgments

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