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The properties of salt-filled sodalites. Part 4. Synthesis and heterogeneous reactions of iodate-enclathrated sodalite $Na_8[AlSiO_4]_6(IO_3)_{2-x}(OH \cdot H_2O)_x$; $0.7 < x < 1.3$

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Abstract

Sodalite solid solutions $Na_8[AlSiO_4]_6(IO_3)_{2-x}(OH \cdot H_2O)_x$; $(0.7 < x < 1.3)$ have been obtained in the system Na_2O–$2SiO_2$–Al_2O_3–$NaIO_3$–H_2O under hydrothermal conditions and characterized by X-ray powder diffraction, IR and MAS-NMR spectroscopy, as well as by simultaneous thermoanalysis in different gas atmospheres. Syntheses have been performed by the alkaline transformation of kaolinite at a temperature of 473 K in the presence of different amounts of sodium iodate salt. The composition range could only be varied down to $x = 0.7$, even with high amounts of sodium iodate in the initial mixtures. For the synthesis of a solid solution with a low content of iodate, a certain high concentration of the template salt has been found to be essential for the formation of a homogeneous sodalite solid solution.

As well as its synthesis, the thermal properties of basic iodate sodalite have been investigated. A discontinuity of the thermal expansion could be detected as a result of temperature-induced host–guest interactions. Whereas at room temperature and during the initial heating process the aluminosilicate framework of sodalite is partially collapsed, at elevated temperatures ($T = 773$ K) an onset of a maximal expansion of the unit cell volume was apparent from the high-temperature X-ray powder diffraction results.

Further investigations of the thermal behaviour of basic iodate sodalite ($Na_8[AlSiO_4]_6(IO_3)_{2-x}(OH \cdot H_2O)_x$; $x = 1$) in different gas atmospheres gave evidence for intra-cage heterogeneous reactions, resulting in the formation of carbonate, nitrate or sulphite anions inside those sodalite cages, formerly filled with the "hydrated-hydroxide". During this high temperature process, the decomposition of the iodate to iodide could be observed inside the sodalite cavities, causing high thermal stability in the resulting carbonate/iodide–, nitrate/iodide– or sulphite/iodide–sodalite solid solution.

Keywords: Hydrothermal synthesis; Intra-cage reactions; Intercalation reactions; Sodalites; Thermal decomposition; Thermal expansion

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1. Introduction

Sodalites are microporous solids with certain guest molecules in their cage-like voids. In addition to the immense number of studies published on the theoretical and experimental principles of host–guest interactions in zeolite chemistry in recent years, current research is aimed at practical applications of sodalites in industrial processes. Extensive research in the field of pigments, and the synthesis of nanocomposites and special host matrices for quantum dot materials can be mentioned here [1–5].

The application of sodalites as reservoir materials according to their large variety of chemical compositions has recently become another interesting focus of research [6–9]. The present contribution reports on the synthesis and thermal properties of iodate-enclathtrated basic sodalite solid solution. The thermal behaviour of this interesting compound suggests the encapsulation of CO_2, NO, and also SO_2 into the sodalite cavities via high-temperature intra-cage reactions. As the result of these heterogeneous reactions, waste gases could be entrained in the sodalite matrix in the form of carbonate, nitrate and sulphite. On this basis, the new sodalite can be regarded as a model system for waste gas immobilization at elevated temperatures.

2. Experimental

The system Na_2O–$2SiO_2$–Al_2O_3–$NaIO_3$–H_2O has been investigated under hydrothermal conditions at a temperature of 473 K and an autogeneous pressure of up to 10 Mpa in teflon-coated steel autoclaves of 50 ml interior volume. The alkaline transformation of kaolinite was used to obtain polycrystalline sodalite powder. The addition of different amounts of sodium iodate was performed to influence the degree of cage-filling of the products according to the enclathration of the iodate during the crystallization process. Despite the presence of iodate anions, the highly alkaline solution inserted for sodalite synthesis contains hydrated-hydroxide $(OH{\cdot}H_2O)^-$ anions as another suitable template for intercalation into the sodalite cages [10, 11]. The autoclaves were filled with 1.0 g of kaolinite (Fluka 60609) and up to 8.0 g of sodium iodate (Merck 6525); 45 ml of an 8 M solution of sodium hydroxide (Merck 6495) were added before the autoclaves were heated for a reaction period of 24 h. The reaction products were then washed with distilled water and dried at 353 K. This washing process has to be executed carefully by filtering, without stirring or centifuging, to prevent an OH/H_2O exchange in the products, as known from the basic hydrosodalites [11]. The various parameters of the syntheses are summarized in Table 1.

The products were characterized by X-ray powder diffraction, using a Guinier–Jagodzinski camera (Cu $K\alpha_1$ radiation, internal Si standard). The lattice constants were calculated by least-squares refinement.

MAS-NMR of the ^{29}Si nucleus was performed on the basic iodate sodalite sample to be used for further thermoanalytical studies, in order to check additional structural data of the sodalite solid solution, in particular the quantitative ratio of Si/Al. The NMR experiment was carried out on a Bruker CXP-300 FT NMR spectrometer at 59.5

Table 1
The products of the hydrothermal syntheses

No.	Initial $NaIO_3$ (g)	Composition of the product	Cell parameter/Å
1	0.5	$Na_8[AlSiO_4]_6(IO_3)_{0.7}(OH\cdot H_2O)_{1.3}$ $Na_8[AlSiO_4]_6(OH\cdot H_2O)_2$	8.954(1) 8.889(2)
2	1.0	$Na_8[AlSiO_4]_6(IO_3)_{0.8}(OH\cdot H_2O)_{1.2}$	8.967(1)
3	2.0	$Na_8[AlSiO_4]_6(IO_3)(OH\cdot H_2O)$	8.984(1)
4	4.0	$Na_8[AlSiO_4]_6(IO_3)_{1.3}(OH\cdot H_2O)_{0.7}$	9.013(2)
5	8.0	$Na_8[AlSiO_4]_6(IO_3)_{1.3}(OH\cdot H_2O)_{0.7}$	9.013(2)

MHz using a single-pulse sequence with 2–3 μs pulse duration and 3–7 s pulse delay. The spinning rate of the MAS probe head was 3.5 kHz and the chemical shift was related to the tetramethylsilane standard.

The cage-filling species, iodate and hydroxide, were analysed qualitatively by IR spectroscopy on a Perkin-Elmer Spectrometer 683 using KBr pellets; the quantitative analysis was performed by thermogravimetry, using a Mettler Thermoanalyzer TA 146. The latter equipment was also employed to investigate the thermal properties of basic iodate sodalite in an inert atmosphere (Ar) as well as in carbon dioxide (gas flow rates always 5 l h^{-1} with 100 mg sodalite). A first sample was heated up to 1273 K in Ar at a heating rate of 8 K min^{-1} to study the total thermal stability of basic iodate sodalite. The thermal intra-cage reactions of sodalite in different waste gases were performed at lower temperatures in the 823–973 K interval, to prevent decomposition of the sodalite structure. The sample was therefore rapidly heated up at a heating rate of 25 K min^{-1} to the reaction temperature and held at this constant value for times of up to one hour.

In contrast to these experiments in a flowing gas atmosphere of the non-toxic gases argon or carbon dioxide, sealed tube experiments were applied to test the thermal reaction behaviour of basic iodate sodalite in the toxic and corrosive gases nitrogen oxide and sulphur dioxide. Quartz-glass tubes of 8 cm^3 interior volume were filled with 100 mg of the sodalite powder and with a molar gas mixture of $NO + O_2$ or pure sulphur dioxide at normal pressure before being placed in a furnace for heating in the 823–953 K interval for times of up to one hour. An additional high-temperature X-ray powder diffraction experiment was performed up to a temperature of 1223 K (heating rate 16 K h^{-1}) on an Enraf– Nonius Guiner–Simon camera to measure the cell volume of basic iodate sodalite during heating.

3. Results and discussion

3.1. Synthesis and characterization

Polycrystalline powders of sodalite were exclusively observed as the products of the reactions in every case. The chemical composition of the sodalites and the initial amount of sodium iodate salt are summarized in Table 1. The cell parameters according to X-ray powder diffraction are included in this table.

It was surprising to find that the composition range of sodalite could only be varied in the interval $0.7 < x < 1.3$, even at very high amounts of iodate in the starting materials. Thus a complete solid solution series between basic sodalite (ideal composition $Na_8[AlSiO_4]_6(OH \cdot H_2O)_2$) and iodate sodalite (ideal composition $Na_8[AlSiO_4]_6(IO_3)_2$) could not be synthesized under the conditions described above. This behaviour is in contrast to the enclathration of guest anions during the crystallization of other salt-enclathrated sodalites: as a typical case, the chlorate–sodalite system should be mentioned here, where a molar ratio of 1.0 for the kaolinite/sodium chlorate amounts yielded pure chlorate sodalite [12]. In contrast, the remarkable excess of 8 g of sodium iodate per g of kaolinite in the starting reaction mixture here did not result in a higher degree of filling of the sodalite cavities with this template, when compared with the synthesis with only 4 g of the iodate (see Table 1). A limited mobility of the heavy iodate anions because of low thermal convection in the autoclaves during the crystallization process seems to be responsible for this behaviour. Kinetic studies of the hydrothermal phase formation of sodium iodate are in progress to clarify this unusual situation.

Ensuring formation of a homogeneous sodalite solid solution in the direction of low initial salt concentrations, the necessity of a certain minimum of the template salt can be inferred from the results of experiment No. 1, Table 1. Here a limited iodate concentration yielded a two-phase heterogeneous product of pure basic sodalite together with basic iodate sodalite.

The powder diffraction data of a basic iodate sodalite of composition $Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O)$ are summarized in Table 2. This sample was used for all the thermoanalytical studies, described below. The data in Table 2 were taken from a Guinier film, using an internal Si standard for data evaluation and LSQS-refinement of the unit-cell parameter. From another X-ray diffraction photograph, taken without an internal standard, one can clearly see two further reflections 220 and 332, overlapping with the pattern of the Si standard on the first film. All the observed reflections are consistent with space group $P\bar{4}3n$. For a further structural characterization of iodate inside the sodalite cages, a high degree of positional disorder can be expected for the enclathrated non-cubic iodate (C_{3v} symmetry [13]) in order to fulfil the cubic symmetry 23 at the centre of each sodalite cage on average.

The IR spectrum of basic iodate sodalite is given in Fig. 1a. Besides the typical vibrations of the sodalite framework [14], the enclathrated guests can be clearly distinguished on the basis of their characteristic absorption bands. A band in the $775\,cm^{-1}$ region results from the vibrations of the iodate anions [13]. Hydroxyl groups, water molecules and carbonate impurities from the NaOH solution can also be analysed qualitatively due to their well-known absorption bands (OH^-, $3640\,cm^{-1}$; H_2O, 3000, -3600 and $1650\,cm^{-1}$; CO_3^{2-}, $1450\,cm^{-1}$).

Fig. 2 shows the ^{29}Si MAS NMR spectrum of basic iodate sodalite (sample No. 3, Table 1). A narrow single resonance signal with a highly symmetrical line shape at a chemical shift of $\delta_{iso} = -86.5$ ppm for Si(4Al) building units confirms the strictly alternating ordering of the tetrahedral Si and Al atoms of the sodalite framework according to an Si/Al ratio of 1.0. This is consistent with Loewenstein's aluminium

Table 2
X-ray powder data of basic iodate sodalite at 298 K: $Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O)$, cubic, $a_0 = 8.984(1)$ Å; data obtained from a Guinier film, internal Si standard

hkl	$2\Theta_{obs}$	d_{obs}/Å	d_{calc}/Å	I/I_0
110	13.980	6.33	6.32	24
200	19.760	4.489	4.492	15
211	24.247	3.6678	3.6677	67
310	31.470	2.8404	2.8410	29
222	34.560	2.5932	2.5934	47
321	37.436	2.4001	2.4010	13
330/411	42.661	2.1177	2.1175	30
422	49.671	1.8340	1.8338	5
431/510	51.859	1.7616	1.7619	21
440	58.041	1.5879	1.5881	16
433/530	59.982	1.5410	1.5407	9
442/600	61.913	1.4975	1.4973	8
532/611	63.819	1.4573	1.4574	9
541	67.511	1.3863	1.3862	6
622	69.321	1.3545	1.3544	13
444	72.889	1.2967	1.2967	5
543/550/710	74.631	1.2707	1.2705	7
552/633/721	78.115	1.2225	1.2226	7
651/732	84.940	1.1408	1.4110	2

avoidance rule [15]. From this highly symmetrical resonance signal, it can be deduced that domains of pure basic sodalite and pure iodate sodalite do not exist in the structure. Thus this sample exhibits the character of a regular solid solution, despite the two different types of cage-filling anions. This is an important result for the interpretation of the high-temperature reaction behaviour of this sodalite phase, as described below.

3.2. Thermal properties of basic iodate sodalite in an inert atmosphere

The results of simultaneous thermal analysis of basic iodate sodalite (90 mg of sample No. 3, Table 1) are given in the thermogram of Fig. 3. The measurements were taken at a heating rate of 8 K min^{-1} in an inert atmosphere (Ar) and include thermogravimetry (TG), differential thermogravimetry (DTG; range, 5 mg min^{-1}) and differential thermoanalysis (DTA; range, 50 μV). A complex overlapping process of thermal decomposition reactions can be observed during heating. In the temperature region 723–1103 K, the dehydration and dehydroxylation of the $(OH \cdot H_2O)^-$ anions occur together with the loss of oxygen of the enclathrated iodate. From the DTA characteristics, an exothermic/endothermic crossover can be estimated for these reactions. They can be distinguished by the following equations for the decomposition

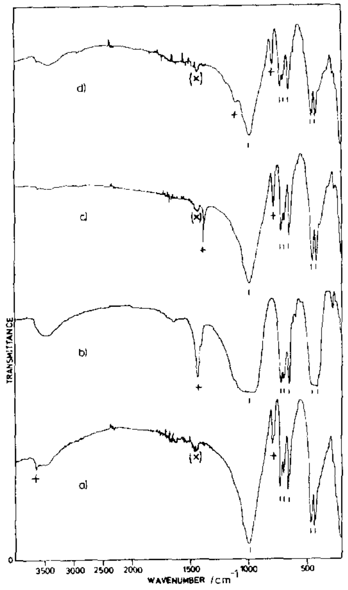

Fig. 1. The IR spectra of the sodalites: I, vibrations of the framework; +, absorption bands of the enclathrated guests; x, carbonate impurities, enclathrated during synthesis under open conditions. (a) Basic iodate sodalite $[Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O)$, as synthesized (No. 3, Table 1). (b) Carbonate/iodide sodalite, obtained after heating basic iodate sodalite at 973 K in a flowing atmosphere of CO_2 (gas flow rate: 5 l h^{-1}). (c) Nitrate/iodate sodalite, obtained after heating basic iodate sodalite at 823 K in an NO/O_2 atmosphere (sealed tube experiment, normal pressure at room temperature). (d) Sulphite/iodate sodalite, obtained after heating basic iodate sodalite at 873 K in an SO_2 atmosphere (sealed tube experiment, normal pressure at room temperature).

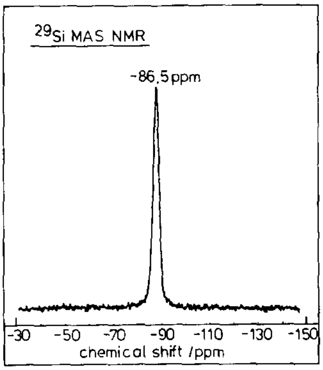

Fig. 2. ^{29}Si MAS-NMR spectrum of basic iodate sodalite $Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O)$ (No. 3, Table 1).

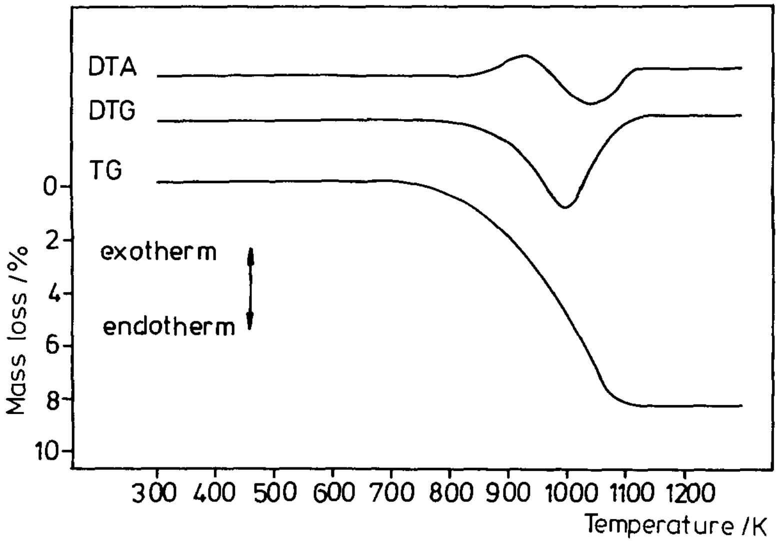

Fig. 3. Simultaneous thermal analysis of basic iodate sodalite $Na_8[AlSiO_4]_6(I_3)(OH\cdot H_2O)$ in an argon atmosphere.

of the, "hydrated hydroxide", together with the release of oxygen from the iodate

$$Na_8[AlSiO_4]_6(IO_3)(OH\cdot H_2O) \rightarrow Na_8[AlSiO_4]_6(IO_3)(O)_{0.5} + 1.5\,H_2O\uparrow$$

$$Na_8[AlSiO_4]_6(IO_3)(O)_{0.5} \rightarrow Na_8[AlSiO_4]_6(I)(O)_{0.5} + 1.5O_2\uparrow$$

The iodate decomposition is characterized by a resulting formation of iodide inside these sodalite cages. Due to the matrix effect of the sodalite framework, the iodate decomposition proceeds at a somewhat higher temperature as compared with the solid sodium iodate salt [16, 17].

The theoretical weight loss (6.8% for both combined reactions) is only in poor agreement with the practical results of Fig. 3, which indicates a total mass loss of 8%. This phenomenon is already known for basic sodalite, grown under open conditions in a highly alkaline NaOH solution [11]. The incorporation of carbonate impurities in a few of the sodalite cages, as well as the exchange of some of the enclathrated sodium hydroxide by water molecules ($NaOH\cdot H_2O \rightarrow 4H_2O + Na^+$-vacancy, as observed for hydrosodalite [11]), are responsible for the observed deviation in mass loss. Whereas the extent of the latter effect is a result of the washing procedure of the sample after synthesis, the incorporation of carbonate impurities depends on the reaction temperature. Under the experimental conditions used here, up to 10% of the sodalite cages can be affected by these unavoidable results of preparing the samples under open conditions. Both "impurities" of basic iodate sodalite can be detected qualitatively in the IR spectrum of Fig. 1a, as already mentioned above (absorption of the carbonate at 1450 cm^{-1}; absorption bands of regular water molecules are at 1650 cm^{-1} as well as 3000–3600 cm^{-1}).

Additional powder diffraction data, obtained from a heating experiment on a Guinier–Simon camera indicate the thermal stability of $Na_8[AlSiO_4]_6(I)(O)_{0.5}$ up to a temperature of 1130 K at a very low heating rate of 16 K h^{-1} (0.27 K min^{-1}) during this experiment. Thus the thermal destruction of the sodalite solid solution $Na_8[AlSiO_4]_6(I)(O)_{0.5}$ and the resulting formation of a nepheline-like phase can be observed at a lower temperature as compared with pure iodide sodalite, which has been proved to be stable up to temperatures higher than 1223 K [18].

Besides the total collapse of the sodalite framework at elevated temperatures, a remarkable thermal expansion of the cell volume has been revealed from the X-ray heating powder diffraction experiment. The plot of the course of the unit cell volume, calculated from the Guinier–Simon photograph, is shown in Fig. 4. A discontinuity can be observed at a temperature of 773 K, where the maximum of thermal expansion is obtained. In the following temperature interval up to the thermal destruction of the sodalite framework, the increase in the cell volume is drastically diminished, a behaviour already known for pure iodide sodalite [19]. If the sodalite framework remains in its partially collapsed state at lower temperatures, a high degree of thermal expansion results from the tetrahedra "tilt" during heating, caused by the big cage anions forcing the cations in the direction of the six-membered rings of the sodalite cages. If the cations reach the position of these rings in the plane of the framework oxygens at a temperature of 773 K, a maximal tilt-angle is reached and a further expansion on the basis of tetrahedral tilt is impossible. The observed discontinuity in thermal expansion results from the onset of a much lower expansion rate during further heating (see Fig. 4). It is remarkable that even in a sodalite solid solution, containing only 50% cage fillings with big anions, i.e. the iodate or the resulting iodide, this discontinuous thermal characteristic proceeds in the same manner as for sodalites filled to a degree of 100% with big anions [18].

From the results of the X-ray powder diffraction heating experiment, another important fact should be mentioned. Formation of iodide via the thermal decomposi-

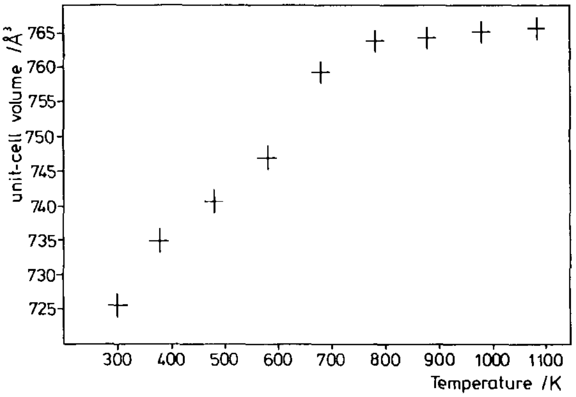

Fig. 4. The evaluation of the unit-cell volume of basic iodate sodalite $Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O)$ during heating as observed from high-temperature X-ray powder diffraction results.

tion of iodate is not notable at the onset of the discontinuity of the unit-cell volume at 773 K, but can first be observed during further heating at 873 K, indicated by a change in the intensities of some reflections on the high-temperature X-ray powder diffraction photograph. In particular, the diminishing of the intensities of the reflections 310, 222 and 530 at elevated temperatures should be mentioned here. The resulting powder pattern of $Na_8[AlSiO_4]_6(I)(O)_{0.5}$ shows close similarities with the well-known pattern of pure iodide sodalite [19].

3.3. Thermal properties of basic iodate sodalite in waste gas atmospheres of carbon dioxide, nitrogen oxide or sulphur dioxide

The basic iodate sodalite of composition $Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O)$ is expected to be a suitable material for intra-cage anion exchange reactions during heating in gas atmospheres, as already found for the CO_2 uptake of other basic sodalite solid solutions [9, 20]. The basis for a high-temperature reactivity is the enclathration of the two types of cage-filling anions, the hydrated hydroxyl groups on the one hand and the iodate anions on the other. Whereas the latter stabilize the sodalite host framework on the basis of the formation of thermal stable iodide anions according to the intracage reaction: $NaIO_3 \rightarrow NaI + 1.5O_2\uparrow$, the "hydrated hydroxyl groups" in the remaining 50% of the sodalite cavities undergo thermal destruction, followed by reaction with the gas molecules from the atmosphere. In the case of carbon dioxide, this intra-cage event can be described in form of the reaction: $2Na(OH \cdot H_2O) + CO_2 \rightarrow Na_2CO_3 + 3H_2O$ at elevated temperatures, i.e. the formation of carbonate in 25% of the sodalite cavities occurs. As a result of charge balance, 25% of the adjacent cages remain empty. They can be filled with water, absorbed from the atmosphere, as is well-known in noselites. In order to summarize this thermal behaviour, one can regard the iodate/iodide as a framework-stabilizing template and the "hydrated hydroxide" as the reactive template inside the sodalite cages.

The heterogeneous intra-cage reactions of basic iodate sodalite in the different gas atmospheres were performed at a temperature lower than 1130 K to prevent the thermal destruction of the sodalite structure. The samples were therefore rapidly heated (heating rate 25 K min^{-1}) up to the reaction temperatures between 823 and 973 K, and held for one hour in the different waste gas atmospheres. The heating procedure has been optimized for the individual reactions to observe a maximal conversion of the gas inside the sodalite cavities at the lowest temperature. The conditions and results of the heterogeneous reactions of basic iodate sodalite in the different gas atmospheres are summarized in Table 3. In the case of the carbon dioxide atmosphere, the optimal carbonate formation conditions could be observed according to the total reaction

$$Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O) + 0.5CO_2 \xrightarrow{973\,K} Na_8[AlSiO_4]_6(I)(CO_3)_{0.5} + 1.5H_2O\uparrow + 1.5O_2\uparrow$$

This intra-cage reaction scheme is illustrated in Fig. 5. The favoured reaction temperature is 973 K. At low temperatures ($T < 773$ K), the reaction rate is limited in every case

Table 3
The conditions and resulting sodalites of the heterogeneous reaction of basic iodate sodalite in different waste gases. Educt: basic iodate sodalite $Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O)$, $a_0 = 8.984(1)$/Å

Atmosphere	Temperature/K	Duration/h	Composition	Unit-cell parameter/Å
Ar	973	1.0	$Na_8[AlSiO_4]_6(I)(O)_{0.5}$	9.050(1)
CO_2	973	1.0	$Na_8[AlSiO_4]_6(I)(CO_3)_{0.5}$	8.995(2)
$NO+O_2$	823	0.5	$Na_8[AlSiO_4]_6(IO_3)(NO_3)$	8.955(2)
$NO+O_2$	953	1.0	$Na_8[AlSiO_4]_6(I)(NO_3)$	9.035(1)
SO_2	873	0.5	$Na_8[AlSiO_4]_6(IO_3)(SO_3)_{0.5}$	9.023(3)

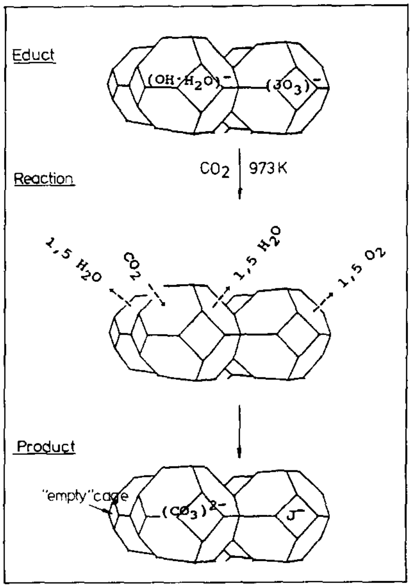

Fig. 5. Schematic view of the intra-cage reactions of basic iodate sodalite in CO_2 at a temperature of 973 K (the cations are omitted for clarity). Carbonate formation results after the thermal destruction of the $(OH \cdot H_2O)^-$ anions and the entrance of CO_2 into these cages. Every second cavity, formerly filled with $(OH \cdot H_2O)^-$ remains empty for charge balance. At the same time, the iodate inside the other cages decomposes to the framework-stabilizing iodide anions.

because of the stability of the hydroxide in the sodalite solid solution under these conditions.

The same reaction behaviour can be obtained in a nitrogen oxide/oxygen gas mixture as well as in sulphur dioxide. The reactions could already be observed at 823 K (in nitrogen oxide) or 873 K (sulphur dioxide) after a short reaction time of 30 min. Under these conditions, the decomposition of the iodate to iodide did not take place on a large scale, as can be checked qualitatively from the results of IR spectroscopy of the reaction products, discussed below, and the conversion is not yet fully quantitative. The principal reactions investigated in the nitrogen oxide–oxygen mixture can be described according to the following scheme

$$Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O) + NO + O_2 \xrightarrow{823\,K} Na_8[AlSiO_4]_6(IO_3)(NO_3) + 1.5H_2O\uparrow$$

whereas the reaction of basic iodate sodalite in sulphur dioxide can be summarized as follows

$$Na_8[AlSiO_4]_6(IO_3)(OH \cdot H_2O) + SO_2 \xrightarrow{873\,K} Na_8[AlSiO_4]_6(IO_3)(SO_3)_{0.5} + 1.5H_2O\uparrow$$

The IR spectra of the reaction products, i.e. the resulting carbonate-iodide sodalite, the nitrate-iodate sodalite and the sulphite-iodate sodalite, are summarized in Fig. 1b–d. In the spectra of Fig. 1b one can clearly see the asymmetric streching mode of the trigonal planar carbonate group ($1450\,cm^{-1}$). The absorption band due to the enclathrated nitrate at $1380\,cm^{-1}$ can be detected in the spectra of nitrate iodate sodalite (Fig. 1c) and the absorption of the SO_3^{2-} anions is at $1100\,cm^{-1}$ in Fig. 1d. In every case, one can also describe the extent of the reaction from the change of the unit-cell parameter of the products, as compared with the starting basic iodate sodalite. The change of the cubic lattice parameter results from an adjustment of the sodalite framework to the different size and geometry of the newly formed guest anions inside the sodalite cages. The "flexibility" of the sodalite framework is described in the literature on the basis of "tetrahedra tilt" [21,22]. The unit-cell parameters of the high-temperature reaction products are given in Table 3. The amounts of waste gas which can be incorporated per gram of the initial basic iodate sodalite are 19.9 mg of carbon dioxide or 27.1 mg of nitrogen oxide NO (56.0 mg of NO + O_2), as well as 29.0 mg of SO_2 respectively.

The observed reaction behaviour of the basic iodate sodalite in waste gases can be regarded as a model system for the application of sodalites as "special reservoir materials". The results, presented here in this case study of basic iodate sodalite, are even of interest for future modifications of zeolites A or X/Y via the incorporation of both guest anions in the zeolite β-cages to improve their reactive properties for waste gas uptake at elevated temperatures or several other applications.

References

[1] F. Hund, Z. Anorg. Allg. Chem., 509 (1984) 225.
[2] G. Geismar and J. Westphal, Chem. Zeit., 111 (1987) 277.
[3] M.T. Weller, G. Wong, C.L. Adamson, S.M. Donald and J. J. B. Roe, J. Chem. Soc. Dalton Trans., (1990) 593.
[4] A. Stein, G.A. Ozin and G.D. Stucky, J. Am. Chem. Soc., 114 (1992) 8119.

[5] G. van de Goor, P. Behrens and J. Felsche, Microporous Mater., 2 (1994) 493.
[6] H. Pöllmann, Ber. Dtsch. Miner. Ges., Beih. z. Eur. J. Mineral., 3 (1991) 213.
[7] J. Neubauer and H. Pöllmann, Ber. Dtsch. Miner. Ges., Beih. z. Eur. J. Mineral., 4 (1992) 206.
[8] J.-Ch. Buhl, Thermochim. Acta, 189 (1991) 75.
[9] J.-Ch. Buhl, J. Solid State Chem., 94 (1991) 19.
[10] I. Hassan and H.D. Grundy, Acta Crystallogr. Sect. C, 39, (1983) 3.
[11] G. Engelhardt, J. Felsche and P. Sieger, J. Am. Chem. Soc., 114 (1992) 1173.
[12] T. Veit, J.-Ch. Buhl and W. Hoffmann, Catal. Today, 8 (1991) 405.
[13] W.E. Dasent and T.C. Waddington, J. Chem. Soc., (1960) 2429.
[14] C.M.B. Henderson and D. Taylor, Spectrochim. Acta A, 33 (1973) 283.
[15] W. Loewenstein, Am. Miner., 39 (1954) 92.
[16] R. Näsänen, A. Uggla and A. Salo, Suomen Kemistilethi, B31 (1958) 176.
[17] K. Watanabe and S. Shimizu, Denki Kagaku (Japan), 33 (1965) 292.
[18] C.M.B. Henderson and D. Taylor, Phys. Chem. Miner., 2 (1978) 337.
[19] E.R. Vance, D.K. Agrawal and J.G. Pepin, Phys. Status Solidi, 63 (1981) K189.
[20] J.-Ch. Buhl, Mater. Res. Bull., 28 (1993) 1319.
[21] D. Taylor, Mineral. Mag., 38 (1972) 593.
[22] D. Taylor, C.M.B. Henderson, Phys. Chem. Miner., 2 (1978) 325.