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Synthesis of Basic Cancrinite in a Butanediol−Water System

Michael Fechtelkord,* Britta Posnatzki, and Josef-Christian Buhl

Institut für Mineralogie, Universität Hannover, Welfengarten 1, 30167 Hannover, Germany

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Cancrinite has been synthesized in a 1,3- or 1,4-butanediol/water mixture at temperatures of 353−493 K and reaction times of 24−168 h. Two main series have been performed. In the first series the silica sources (tetraethoxysilane, Aerosil, and precipitated silica) were combined directly with the alumina sources (aluminum *sec*-butoxide and aluminum isopropoxide) in the synthesis. In the second series "organic" gels formed from tetraethoxysilane and aluminum *sec*-butoxide/aluminum isopropoxide as well as "inorganic" gels formed from hydrolyzation of tetraethoxysilane with aqueous sodium and aluminum nitrate solution or from combination of sodium metasilicate with sodium aluminate were dried and used for synthesis. The products were characterized by X-ray powder diffraction as well as ^{29}Si and ^{27}Al MAS NMR spectroscopy. The results show that the sensitivity to the synthesis temperature, duration, and alkalinity depends mainly on the reactivity potential and solubility of the silica/alumina source used in the synthesis. While the directly applied reactants show the highest sensitivity to synthesis temperature and so forth, the gels show even the best synthesis results and cancrinite is formed in a wide range of synthesis parameters (temperature, duration, and sodium hydroxide concentration). A strong relationship between seeding kinetics, crystallization kinetics, and thermodynamic properties of cancrinite seems to be responsible for that behavior under the mild reaction conditions used here. Cancrinite formation as a kinetically controlled process is preferred if both the alumina and silica source dissolve slowly and steadily in the same proportions.

Introduction

Cancrinite is found in nature with the ideal chemical composition $Na_6Ca(AlSiO_4)_6CO_3{\cdot}2H_2O$ and belongs to the group of feldspathoid minerals.[1] Its crystal structure has similarities to those of the zeolites, where sodium and calcium cations, carbonate anions, and water molecules can be regarded as the guest components in a three-dimensional aluminosilicate host framework. The cancrinite structure is formed by layers of 6-membered rings called the secondary building units SBU-6 in the zeolite nomenclature.[2] The edges of the 6-membered rings of these two-dimensional layers are occupied by corner-sharing aluminum and silicon tetrahedra in an alternating manner connected by oxygen atoms. Stacking of these layers in an ABA′B′ sequence leads to the hexagonal cancrinite framework with its two main structural features: the ϵ-cages and the large 12-membered ring channel along the crystallographic *c*-axis. On the other hand, stacking these layers in an ABCA′B′C′ sequence leads to the cubic sodalite framework with its characteristic β-cage. The structural relation between both structure types often results in a cocrystallization of sodalite and cancrinite in the synthesis. Sodalite is the thermodynamically more stable phase. It is difficult to synthesize a cancrinite without a template because the one-dimensional channel needs a "backbone" for stabilization.

Synthetic cancrinite is usually prepared under hydrothermal conditions in the laboratory by imitating the geochemical formation process in nature. Conventional syntheses in aqueous solvents are characteristically carried out in a wide temperature range of 363−770 K under autogenous pressure.[3,4] Typically, amorphous silicon dioxide is used as the reactant since it displays a reactive partner because of its large surface area. Alumina sources are often hydrated aluminum oxides. Besides the nature of the reaction partners, the alkalinity of the mixture influences the product formation specifically. Both, pH value and solubility of reactants is determined mainly by the presence of mineralizing agents such as OH^-.[5,6]

Water is the "classic solvent" for zeolite syntheses, but recent studies have increasingly focused on the use of nonaqueous solvents in zeolite syntheses.[7−10] In some

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* To whom correspondence should be addressed. E-mail: M.Fechtelkord@mineralogie.uni-hannover.de. Present address: Department of Chemistry, UBC, 2036 Main Mall, Vancouver, British Columbia V6T 1Z1, Canada.

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cases, the organic solvent can influence the phase formation according to a structure-directing role in addition to its solvating role.[7] The addition of organic solvents in the hydrothermal synthesis changes the viscosity and polarity of the medium, which can affect the crystallization process. The higher viscosity and lower polarity of many nonaqueous solvents can reduce convection currents, decrease solubility of the reactants, and influence diffusion rates, all giving rise to a slower mass transfer.

The use of 1,3- and 1,4-butanediol for the synthesis of cancrinite in nonaqueous media was carried out first by Liu et al.[8] and Milestone et al.[9] and recently by Burton et al.[10] They noticed that the formation of cancrinite is preferred if molecules of a certain size are present in the nonaqueous solvent. 1,3-Butanediols and 1,4-butanediols are very suitable here because they contain more than three carbon atoms. Furthermore, they applied reactive silica and alumina sources. Fumed silica for example is a highly voluminous and porous material with a large specific surface of 100−400 m^2/g. Aluminum isopropoxide is known as a reactive alumina source in the synthesis of micro- and mesoporous alumophosphates.[11,12]

Another approach of controlling the reaction pathway is the introduction of sol−gels into the synthesis. They display a preliminary well-connected network, which dissolves very slowly during synthesis, a property that favors kinetically controlled reactions rather than thermodynamically controlled ones. The addition of certain amounts of water plays another important role because it influences the polarity and viscosity of the solvent as well as the mobility of the mineralizer OH^-. Organic bases often fail as mineralizers due to their own reactivity in the solvent during synthesis and due to their low basicity. As an example sodium methylate is oxidized to formate under typical hydrothermal temperature and pressure conditions,[13] which favors the formation of sodalite.[14]

The aim of our work is to show a new way of cancrinite synthesis under application of organic solvents (in this case: a 1,3- or 1,4-butanediol/water mixture), which provides a template-free channel system after calcination. Our studies followed two different approaches: First, the silica and alumina sources are introduced directly into the synthesis by adding them simultaneously. Second, sol−gels were formed first and then introduced into the reaction mixture. Besides fumed silica and aluminum isopropoxide as used in the literature,[8−10] we applied a large variety of reactants such as tetraethoxysilane, precipitated silica, and aluminum *sec*-butoxide. Moreover, four different sol−gels were introduced into the cancrinite synthesis for the first time. These gels present both sodium-containing gels formed from pure inorganic reactants and sodium-free gels formed from organic aluminum and silicon containing reactants. The gels were characterized in detail by ^{27}Al, ^{29}Si MAS, and {^{1}H} ^{29}Si CPMAS NMR spectroscopy. In addition, we studied the effect of a variety of different parameters such as water influence, synthesis temperature and duration, and alkalinity of the reaction mixture on the product formation, which was characterized by X-ray powder diffraction.

Table 1. Silica and Alumina Sources for the Direct Synthesis, Base Concentrations, Synthesis Temperature, Duration, and Products Formed in a 1,3- or 1,4-Butanediol/Water Mixture (1:1)

silica source	alumina source	NaOH (mol/L)	synthesis temp (K)	synthesis time (h)	product[a]
A1 TEOS	Al *sec*-butoxide	5	393	48	INT + SOD
		2.5	393	60	a + INT
		5			INT + CAN
		7.5			CAN + SOD
		10			SOD
		5	423	48	CAN + SOD
		5	453	168	SOD (+ CAN)
A2 TEOS	Al isopropoxide	5	393	24	INT
		5	393	48	CAN
		2.5	393	60	INT + CAN
		5			CAN
		7.5			CAN + SOD
		10			SOD
		5	453	168	SOD (+ CAN)
B1 Aerosil	Al *sec*-butoxide	5	393	60	GIS (+ CAN)
		7.5			CAN
		10			CAN
		12.5			CAN (+ SOD)
		15			SOD + CAN
		5	453	168	ANA
		10			CAN
B2 Aerosil	Al isopropoxide	5	393	60	GIS + CAN
		7.5			CAN
		10			CAN
		12.5			CAN
		15			CAN (+ SOD)
		5	453	168	ANA
		10			CAN
C1 precipitated silica	Al *sec*-butoxide	5	393	60	GIS + CAN
		7.5			CAN
		10			CAN
		12.5			CAN
		15			CAN
		10	453	168	CAN
C2 precipitated silica	Al isopropoxide	5	393	60	GIS + CAN
		7.5			CAN
		10			CAN
		12.5			CAN
		15			CAN + SOD
		10	453	168	CAN

[a] a, amorphous phase; ANA, analcime; CAN, cancrinite; GIS, gismondine-type phase; INT, intermediate phase; SOD, sodalite; ( ), only under application of 1,3-butanediol.

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Table 2. Sol−Gel Compositions, Base Concentrations, Synthesis Temperature, Duration, and Products Formed in a 1,3- or 1,4-Butanediol/Water Mixture (1:1)

series	precursor−gel composition	NaOH (mol/L)	synthesis temp (K)	synthesis time (h)	product[a]
O1	TEOS	5	393	48	CAN
	Al *sec*-butoxide	10			CAN
		15			CAN
		5	393	60	CAN
		7.5			CAN
		10			CAN
		5	453	168	CAN
O2	TEOS	2.5	493	24	CAN
	Al isopropoxide	5			CAN + SOD
		10			SOD
		2.5	393	60	CAN
		5			CAN
		7.5			CAN + SOD
		10			SOD
		5	453	168	CAN
S1	TEOS	2.5	393	60	GIS
	1 M $NaNO_3$ (aq)	5			CAN
	1 M $Al(NO_3)_3$ (aq)	7.5			CAN + SOD
		5	453	168	CAN
S2	Na_2SiO_3	2.5	393	60	INT
	$NaAlO_2$	5			CAN + SOD
		7.5			CAN (+ SOD)
		2.5	393	80	INT
		5			CAN
		5	453	168	CAN

[a] CAN, cancrinite; GIS, gismondine-type phase; INT, intermediate phase; SOD, sodalite; ( ), only under application of 1,3-butanediol.

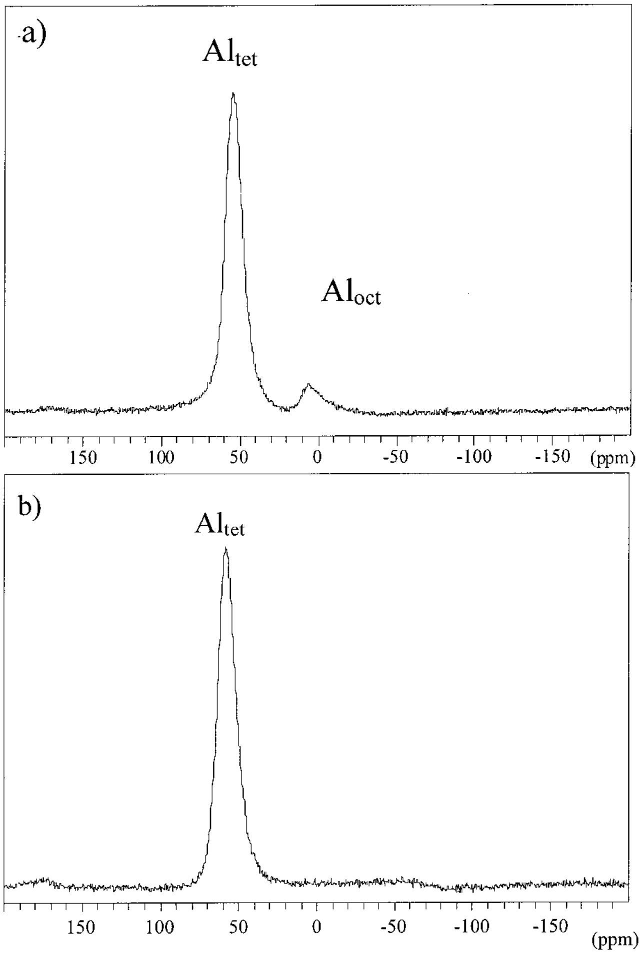

Figure 1. ^{27}Al MAS NMR spectra of O2 gel (a) and of S2 gel (b). Resonances of tetrahedral and octrahedral aluminum are labeled with Al_{tet} and Al_{oct}.

Experimental Section

Synthesis. In the syntheses with directly applied reactants, three series were carried out and analyzed. In series A, tetraethoxysilane ($C_8H_{20}O_4Si$, TEOS; Fluka 86578) was used together with aluminum isopropoxide ($C_9H_{21}O_3Al$, Fluka 06251) or aluminum *sec*-butoxide ($C_{12}H_{27}O_3Al$, Fluka 06190). In series B, fumed silica (SiO_2, Aerosil R812; Degussa) was selected as silica source and in series C precipitated silica (SiO_2, Fluka 833340). All three silica sources were applied together with the same two alumina sources at a ratio of Si/Al = 5 to obtain an increased Si/Al ratio in the cancrinite product. Sodium hydroxide (NaOH, Fluka 71691) was introduced as a mineralizing agent. The two different alumina sources were chosen to compare between the solubility of the solid isopropoxide and dispersion of the liquid *sec*-butoxide in the reaction as well as their reactivity and the influence of the remaining organic residues on the cancrinite formation. The synthesis series numbers, the applied reactants, the sodium hydroxide concentration, the synthesis temperature, duration, and the products formed are summarized in Table 1.

A second approach focused on the application of sol−gels. Two different series were investigated. For the gels of series "O" molar amounts of TEOS and aluminum *sec*-butoxide (O1) or aluminum isopropoxide (O2) were dissolved in an ethanol/water mixture (volume ratio 1:2) at a Si/Al ratio of 5. After that a basic hydrolysis was initiated by the addition of a saturated aqueous ammonium hydroxide solution (NH_3(aq), Merck 105426). The solution was stirred for 15 min and left without stirring for another 24 h. The resulting gel was dried first at 313 K, then at 353 K for 24 h, and finally at 393 K for 48 h. The dried gel was ground in a mortar before introduction into the main synthesis. For the preparation of gel series "S1" 1 M aluminum nitrate ($Al(NO_3)$, Merck 101063) and sodium nitrate ($NaNO_3$, Merck 106537) aqueous solutions were mixed together with TEOS in a molar ratio of 1:1:5 in an ethanol/water mixture (volume ratio 1:2).[15] After addition of basic ammonium hydroxide solution, the reaction mixture was treated in the same way as the O1 and O2 series. In addition, the nitrate and the residual organic compounds were removed by combustion in a platinum crucible over a Bunsen burner at ≈1073 K. A fine-grained oxide powder results from this procedure. For the S2 series amounts of sodium metasilicate (Na_2SiO_3, Fluka 71744) and sodium aluminate ($NaAlO_2$, Riedel de Haen 13404) were dissolved separately in a molar ratio of 5:1 in water and mixed together very slowly. After 15 min of stirring, the gel was stored without stirring for 24 h and dried in the same way as the O1 and O2 gels. The gel compositions of the synthesis series, series numbers, the sodium hydroxide concentration, the synthesis temperature, duration, and the formed products are listed in Table 2. In the synthesis the dried gels were mixed together with 1,4-butanediol ($C_4H_8(OH)_2$, Fluka 18960) and 1,3-butanediol (Fluka, 18940) and a certain amount of sodium hydroxide and water.

The organothermal synthesis was carried out at the described temperatures and autogenous pressure in 50 mL of Teflon-coated steel autoclaves under static conditions. The products were washed with acetone to remove organic residues and 500 mL of deionized water and dried overnight at 353 K.

Characterization. The products were analyzed by X-ray powder diffraction using a Philips PW 1800 diffractometer (Cu $K\alpha_1/\alpha_2$, 40 kV, 40 mA).

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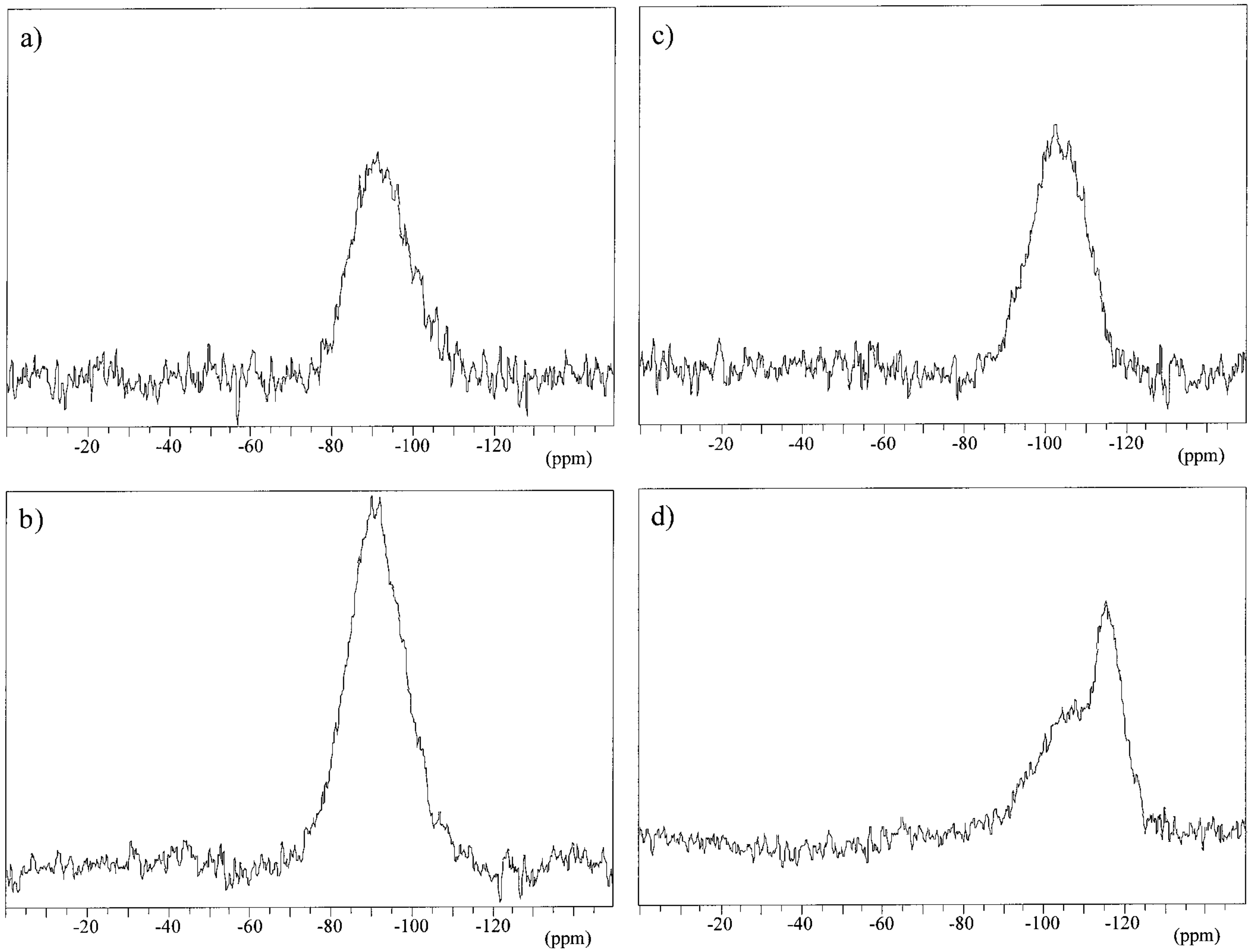

Figure 2. ^{29}Si MAS NMR spectra of S1 gel (a), S2 gel (b), O1 gel (c), and O2 gel (d).

The NMR spectra were recorded on a Bruker ASX 400 NMR spectrometer. ^{29}Si MAS NMR measurements were performed using a Bruker 7-mm standard MAS probe at 79.49 MHz with a single-pulse duration of 2 μs (28° tip angle, $\pi/2$ pulse length: 6.8 μs) and a 10-s recycle delay. To ensure that the 10-s delay is sufficient with regard to the spin−lattice relaxation time (T_1) of the sol−gels, the experiments were repeated with a delay of 120 s; 800 scans were accumulated at a spinning frequency of 3.5 kHz in both cases. In the case of the longer delays no significant lineshape changes were observable. Tetramethylsilane was used as an external standard. {^{1}H} ^{29}Si CPMAS NMR experiments were carried out with a ^{1}H 90° pulse length of 6.5 μs and contact times of 1.0 and 2.5 ms. The ^{27}Al MAS NMR spectra were obtained at a transmitter frequency of 104.26 MHz in a 4-mm standard MAS probe. Typical conditions were pulse lengths of 0.6 μs and recycle delays of 100 ms. A total of 10 000 scans were accumulated at a MAS rotation frequency of 12 kHz.

Results and Discussion

Physical and Chemical Properties of the Gels. All gels are completely amorphous as determined by X-ray powder diffraction. Solid-state NMR spectroscopy is an appropriate tool to obtain structural information from amorphous samples. The ^{27}Al and ^{29}Si MAS NMR spectra give direct information about the local structural environments of these nuclei.

Differences between sodium-free gels and gels with sodium cations can be clearly observed in the ^{27}Al MAS NMR spectra of the gel O2 and S2 (Figure 1). The ^{27}Al MAS NMR spectra of the gels O1 and S1 show similar signal behavior. All the spectra show aluminum in a tetrahedral coordination (58.5 ppm),[16] but in addition the spectrum of the O1 and O2 gel show some octahedrally coordinated aluminum (6.5 ppm).[17] The signal at 58.5 ppm can be attributed to Al(OSi)$_4$ units. The large line broadening ($\Delta\nu_{1/2}$ = 1400 Hz) shows the amorphous character of the sample (bond distance and angle variations) in comparison to the crystalline product ($\Delta\nu_{1/2}$ = 700 Hz). The existence of AlO$_4^-$ units from unreacted or hydrolyzed Al source can be excluded because they would give rise to a signal around 75 ppm.[17] The octahedral signal could be caused by Al^{3+} cations, which must exist to balance the negative charge of the amorphous aluminosilicate framework. In the S2 gel composition sodium cations serve as charge balance for the negative network charge. If sodium cations are not present, aluminum serves as a cation and network builder on either side like in the O1 and O2 gel composition. However, the ^{27}Al MAS NMR shift may also be attributed to the presence of hydrolyzed and unreacted Al source (probably Al(OH)$_3$).

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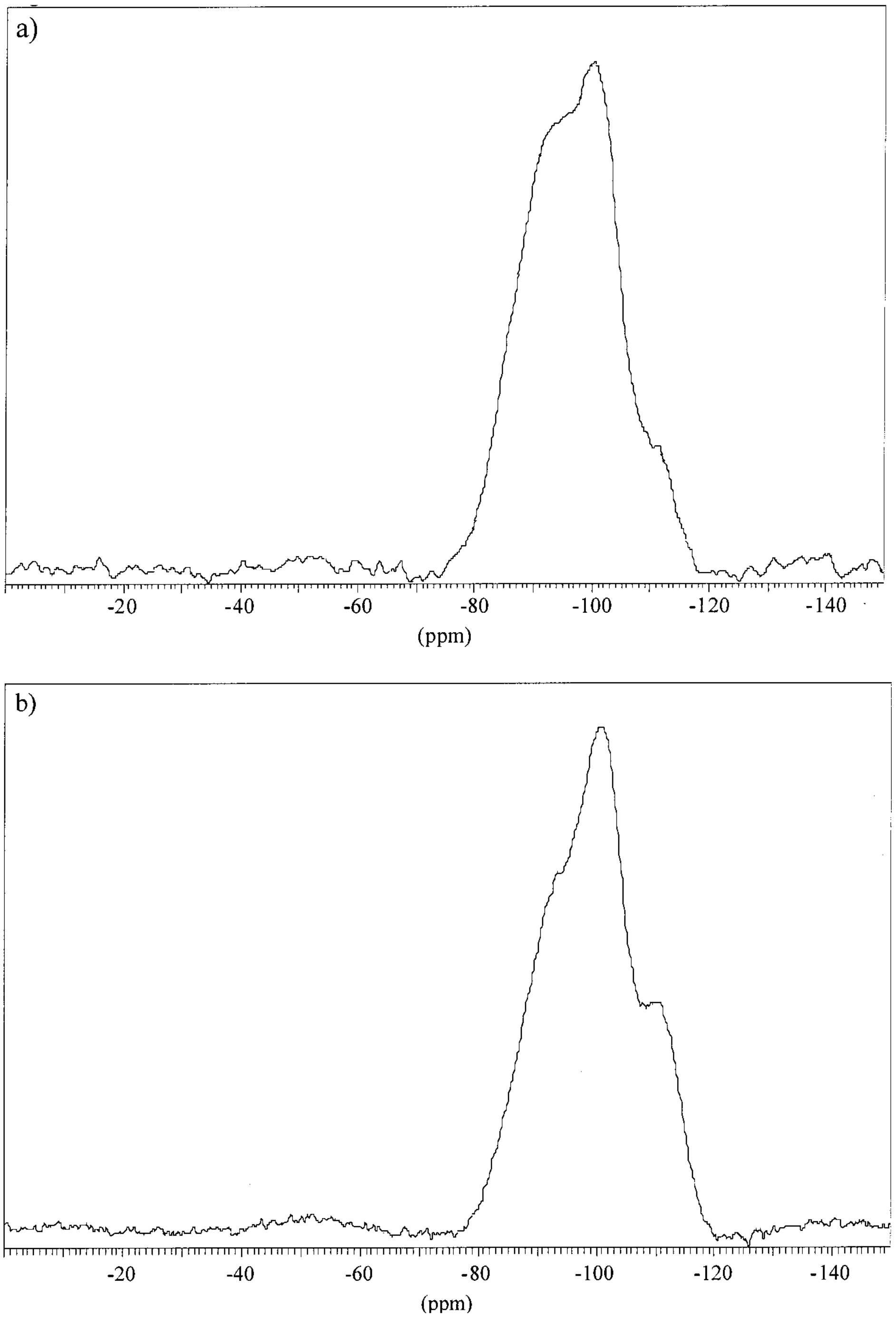

Figure 3. $\{^1H\}^{29}Si$ MAS NMR spectra of O2 gel with contact times of 1.0 (a) and 2.5 ms (b).

The ^{29}Si MAS NMR spectra (Figure 2) for both S gel compositions show a broad signal with a center of gravity at −91 ppm ($\Delta\nu_{1/2} = 1400$ Hz), displaying the distribution of bond distances and angles as well as different $Si\{(OAl)_x(OSi)_{4-x}\}_{4-y}(OH)_y$ units ($1 \leq x \leq 4$, $1 \leq y \leq 4$). The signal width of the crystalline product for comparison is $\Delta\nu_{1/2} = 160$ Hz. The center of gravity of the ^{29}Si MAS signal of the O gels is shifted to a higher field (−102 ppm, $\Delta\nu_{1/2} = 1400$ Hz), suggesting a more silicon-rich amorphous network.[18] This is not quite surprising because parts of the aluminum must balance the negative network charge (as concluded from ^{27}Al MAS NMR spectra) and therefore is not fully bonded in the framework. Another interesting aspect is the difference shown in the spectra between gels O1 and O2. The ^{29}Si MAS NMR signal of the O1 gel composition shows a Gaussian lineshape whereas the O2 resonance shows a major signal at −112 ppm with a shoulder at −105 ppm. This implies an inhomogeneous nonstatistical Si distribution in the gel framework, which is possibly due to a reduced solubility of the solid aluminum isopropoxide in the hydrolyzing mixture, which leads to a faster condensation of silicon building units and thus to either silicon-rich or aluminum-rich areas.

Both gel types (O and S) consist of SiO_4 tetrahedra with varying bond angles and distances. The oxygen

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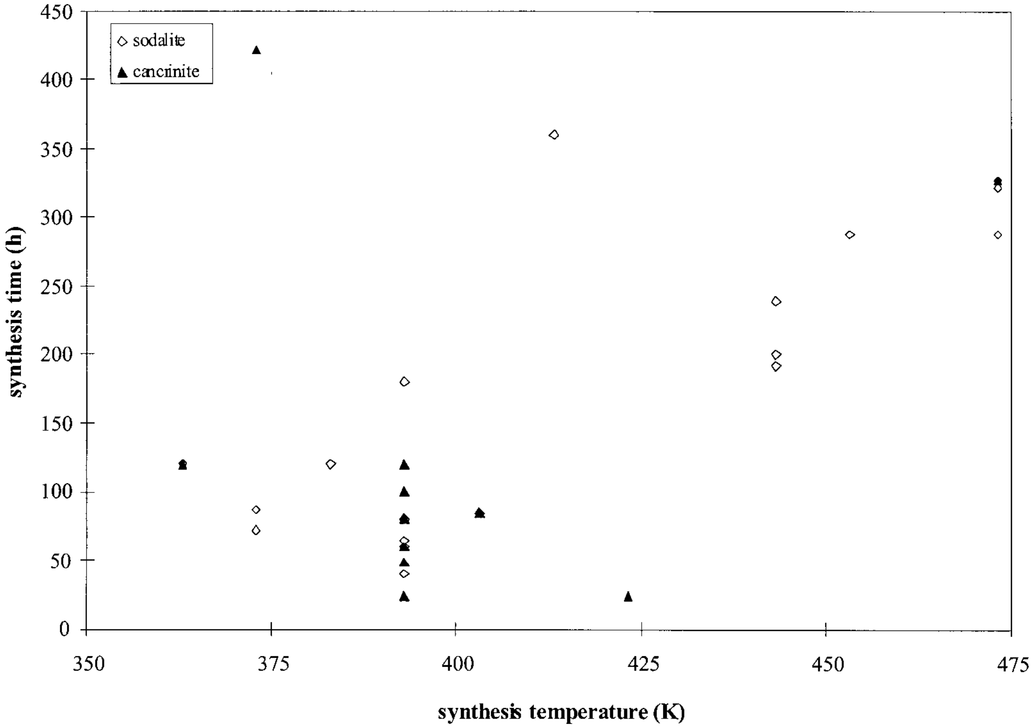

Figure 4. Plot of synthesis duration against synthesis temperature containing the different products (sodalite and cancrinite) of several synthesis experiments.

bonds to the next nearest neighbor may also be substituted by nonbridging oxygens in the form of hydroxyl groups. The second coordination site could be occupied by aluminum or silicon and a statistical or nonstatistical distribution, respectively, are expected in the case of homogeneous materials (O1, S1, and S2) or inhomogeneous materials (O2). Therefore, a definite assignment of the signals to $Q^n(m\mathrm{Al})$ units is not possible. In the case of the investigated gels all the above-mentioned parameters influence the chemical shift. A clear relationship between the second coordination sphere and the position of the peak maximum cannot be established and only limited information can be drawn from the mostly featureless and broad resonance line. An estimation of the Si/Al ratio from the ^{29}Si MAS NMR spectra is impossible. We checked the Si/Al ratio by microprobe analysis, which showed ratios of 2.5 for the S gels and 1.6 and 5.4 for the O1 and O2 gel. However, the result is not very reliable due to the high porosity of the gels.

To obtain more information about the existence of silanol groups, we investigated the four gels additionally by $\{^1\mathrm{H}\}$ ^{29}Si CPMAS NMR spectroscopy. The existence of silanol groups can be clearly deduced from the spectra of the O1 and O2 gel. Figure 3 shows the spectrum of the O2 gel with contact times of 1.0 and 2.5 ms. The resonance is structured into three different Gaussian lines at −93, −102, and −112 ppm, which can be attributed to Q^2, Q^3, and Q^4 units with two nonbridging silanol groups, one nonbridging silanol group and fully linked silicon tetrahedra. The dependence of signal intensity on the contact time supports the assignment. The local site (Q^2) with the most protons in the next nearest neighborhood experiences the fastest polarization transfer and hence shows stronger relative intensity contribution at the contact time of 1.0 ms, compared to the experiment carried out with the longer contact time of 2.5 ms. In contrast, the spectra of the S1 and S2 gel (not shown) show similar lineshapes as in the normal single-pulse experiment, which excludes the existence of silanol groups. The existence and nonexistence of silanol groups is mainly dependent on the different condensation processes and on the treatment of the gels. Whereas the organic gels hydrolyze and condense slowly and were dried only at mild temperatures (393 K), the S1 gel was burnt out at nearly 1073 K (evaporation of water and full condensation) and the S2 gel was precipitated from the inorganic salts (fast condensation), which excludes nearly the existence of silanol groups.

Influence of Synthesis Parameters (Duration, Temperature, and Water Content). The temperature and duration of the crystallization period plays an important role in the formation field of cancrinite and sodalite. Figure 4 shows the products formed in a plot of duration against temperature in several synthesis experiments without added salt. Cancrinite is preferably formed at temperatures below 423 K and at a duration of 150 h. This agrees with results in the classic hydrothermal synthesis of salt-containing cancrinites, which were synthesized at temperatures below 373 K and in 24−48 h.[19] However, in the studies of Liu et al.,[8] Milestone et al.,[9] and Burton et al.[10] cancrinite was formed at temperatures of 443−453 K. Through variation of temperature and duration it seems possible to guide the synthesis, to improve the formation of the desired cancrinite product, and to suppress the cocrystallization of sodalite. The kinetically stabilized cancrinite phase is slowly substituted by the thermodynamically more stable sodalite at higher temperatures and longer synthesis duration (Ostwald rule). Moreover, at higher temperatures more dense structures are formed due to the decreasing stabilizing water

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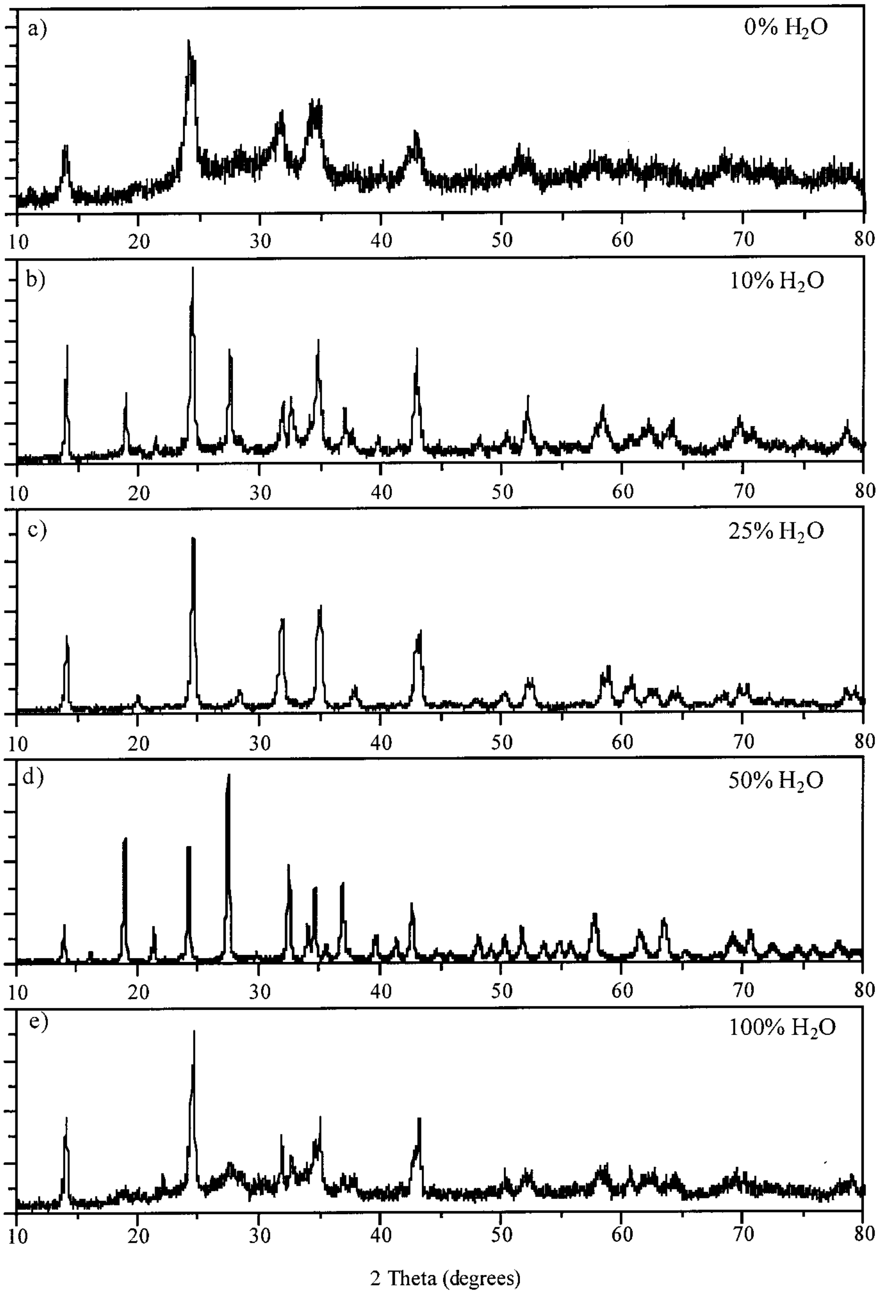

Figure 5. X-ray diffraction powder patterns of synthesis products from O1 gels in 1,3-butanediol with different amounts of water: 0 (a), 10 (b), 25 (c), 50 (d), and 100 vol % (e) with respect to the 1,3-butanediol/water volume.

amount in the solvent phase.[20] Some data points in Figure 4 that do not fulfill these conditions show that this conclusion is not valid in general because the choice of reactants, solvents, and the amount of mineralizing agent are other important influencing parameters.

The application of a pure organic solvent leads to solubility problems of the mineralizing agent or the precursor. In this case, the introduction of small amounts of water can accelerate the crystallization process, whereas the nature of the product formed is independent of the water content in the solvent. Several zeolite compounds are known which can be successfully synthesized in an organic solvent/water mixture.[21−34] Figure 5 illustrates the influence of the water content in a synthesis of a O1 gel in 1,3-butanediol. The X-ray

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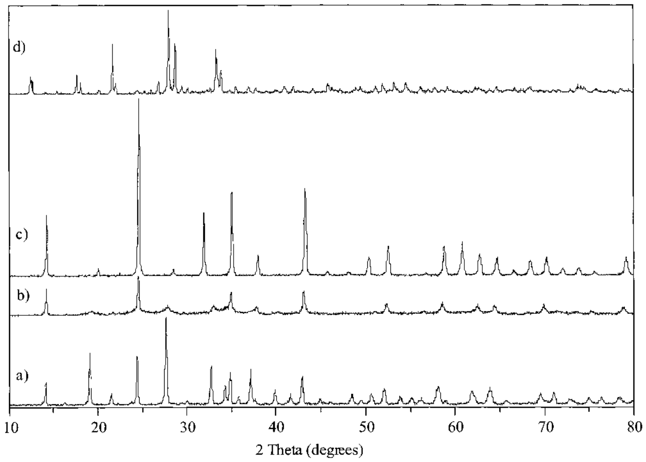

Figure 6. X-ray diffraction powder patterns of cancrinite CAN (a), intermediate phase INT (b), sodalite SOD (c), and gismondine-type mineral GIS (d).

powder pattern shows broad reflections of a nearly amorphous compound if water is totally absent in the solvent. Upon increasing water content, the diffraction pattern indicates the increasing crystallinity of the compound. On the other hand, water contents higher than 50% have a destabilizing effect. The highly amorphous nature of the sample implies the solution was too basic and that solvation of sodium cation and hydroxyl anion is not sufficiently enough. High water contents counteract the stabilizing impact of the 1,3-butanediol solvent.

Products Synthesized with Directly Applied Reactants (Series A, B, and C). Syntheses series A using TEOS as silica source shows a strong influence of duration and base concentration. Besides cancrinite and amorphous compounds, sodalite and an intermediate phase are formed[35,36] (Table 1). Figure 6 shows some typical X-ray diffraction pattern. Characteristic reflections for sodalite (Figure 6c) and cancrinite (Figure 6a) are in the 2θ range of 58°−65°. Sodalite shows four reflections in this region. Cancrinite can be easily distinguished from sodalite because the second reflection at $2\theta = 60°$ is missing. A characteristic of the intermediate phase is that its powder pattern shows only those reflections which are common in the diffraction pattern of sodalite and cancrinite (Figure 6b).[36] One obvious point that can be concluded easily is that a sodium hydroxide concentration of above 5 mol/L favors the formation of sodalite. Co-crystallization of sodalite and cancrinite takes place. Very high base concentrations above 7.5 mol/L result in a pure sodalite formation. The reason for that tendency can be attributed to the structure-directing role of the hydroxyl anion, which leads to the formation of basic hydro-sodalite, if it is present in high concentration. A second point that is obvious is the dependence of product formation on the synthesis duration. Short durations of 24 h lead to the intermediate phase. Different phase compositions are present after 48 h, depending on the base concentration and temperature. Longer synthesis times change the phase compositions again. In summary, it may be stated that the series A with TEOS is extremely sensitive to other parameters. In addition, series A1 using aluminum *sec*-butoxide as alumina source never yields a pure cancrinite phase.

The direct syntheses series B and C (Table 1) where solid silica sources Aerosil and precipitated silica were used do not show such extreme sensitivity to temperature, duration, and base concentration as seen for series A (Table 1). However, another phase appears in the syntheses if the base concentration is below or equal to 5 mol/L. The phase has been identified as gismondine-type zeolite.[37,38] The characteristic X-ray powder pattern is shown in Figure 6d. In a range of 7.5−12.5 mol/L in sodium hydroxide concentration cancrinite is formed almost exclusively. Higher base concentrations lead to additional crystallization of sodalite for reasons already described above. In both series the base concentration only plays a structure-directing role. ^{29}Si MAS NMR experiments show only a single resonance for all products, indicating a completely ordered alumosilicate framework with a Si/Al ratio of 1.

Results of Products Obtained from Syntheses with Gels (Series O and S). In the cancrinite synthesis starting from gels it turns out that there seems to be less dependence on synthesis temperature and time than in the direct reactant series (Table 2). One general observation from the X-ray powder diffracton patterns is that the same alkalinity dependence appears as found in the direct reactant series A, B, and C. At a NaOH concentration higher than 5 mol/L sodalite cocrystallizes partially. Gismondine and the intermediate phase are formed only in the case of the S-gel series, which contains already sodium cations. The crystallization is favored at low base concentrations (≤2.5 mol/L). The formation of either gismondine or intermediate phases depends on temperature, duration, and gel composition. In the case of the O1 gels (aluminum *sec*-butoxide and TEOS), which are very homogeneous, cancrinite formation occurs exclusively, whereas in the case of the more inhomogeneous O2 gel (aluminum isopropoxide) sodalite precipitates at higher sodium hydroxide concentrations. All cancrinites synthesized from gels show a fully ordered framework and a Si/Al ratio of 1 as detected by ^{29}Si MAS NMR.

Conclusions

The synthesis results show that the sensitivity of parameters such as temperature, duration, and base concentration depends mainly on the reactivity potential and solubility of the applied silica/alumina source. The direct reactant series shows here the highest sensitivity. Tetraethoxysilane is highly reactive and in combination with aluminum *sec*-butoxide, which dissolves very fast

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as well, no pure cancrinite can be derived from the synthesis no matter what other parameters were varied. Introducing the solid aluminum isopropoxide (which dissolves more slowly) allows pure cancrinite to be obtained in some syntheses. The same tendency emerges if the silica source is solid as in the case of series B and C. The likelihood of pure cancrinite formation increases as a function of decreasing solubility of the reactants, with gels giving the best results. They dissolve slowest and the framework building molecular units in the solvent are present in a restricted amount. The difference between both types of gels indicates that the sodium-containing gels are even more sensitive to the temperature, duration, and pH value of the solution.

A strong influence of the kind of solvent chosen (1,3- or 1,4-butanediol) on the product distribution was not observed. In some cases under application of 1,3-butanediol cocrystallization of sodalite takes place. The Si/Al ratio of all cancrinite products is 1, independent of all other applied parameters. This in contrast to the studies of Liu et al.[8] and Milestone et al.[9]

The presented data show the interesting relations between kinetically controlled metastable phase formation under mild conditions (low temperature) on one hand and crystallization of the thermodynamically stable equilibrium phases on the other hand. Cancrinite formation is preferred if both alumina and silica sources dissolve slowly and steadily and at comparable rates. A preformed amorphous alumosilicate network such as that present in the O1 and O2 gels seems to be tailor-made for this demand. Sodium-free pure aluminosilicate gels yield the best results.

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