

Stability of Layered Sodium Disilicate during Hydration Process As Studied by Multinuclear Solid State NMR Spectroscopy

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Solid-state ^1H , ^{23}Na , and ^{29}Si NMR spectroscopies, combined with X-ray powder diffraction (XRD) technique, were used to study the hydration process of a layered sodium disilicate SKS-5 (having a crystal structure of $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$). NMR and XRD experiments suggest that SKS-5 is very sensitive to absorbed water molecules and the crystal structure of SKS-5 converts gradually from $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ to a new phase during the hydration process. Although the new phase contains about 9% $\text{Na}_2\text{Si}_4\text{O}_9$, its crystal structure is still unclear. The hydration of SKS-5 begins with the formation of hydrogen-bonded water (with the silicate framework), accompanied by a partial hydrolysis of the Si–O–Si linkages in the framework that generates isolated and hydrogen-bonded silanols (with proton bonded to oxygen atom in the adjacent layer). With an increase of the hydration degree, the above process proceeds and the concentrations of hydrogen-bonded water and hydrogen-bonded silanol increase significantly. When the hydration time is extended to 6 months, the conversion from SKS-5 to the new phase is accomplished and a new kind of hydrogen-bonded silanols (with the proton bonded to nonbridging oxygen at the same silicon atom) appears. The hydrogen-bonding network formed during the hydration process may probably strengthen the stability of the new phase. The silicon sites in the new phase are confirmed to be mainly Q^2 [$(\text{SiO})_2\text{Si}(\text{OH})\text{O}^-\text{Na}^+$] and Q^3 [$(\text{SiO})_3\text{SiO}^-\text{Na}^+$] groups. The coordination of sodium ions is also significantly altered after the hydration. The results of ^{23}Na NMR experiments agree well with the data from ^1H and ^{29}Si NMR experiments, and five sodium sites with different local environments can be resolved by the ^{23}Na MAS and two-dimensional ^{23}Na multiple quantum MAS spectra in different hydration periods. Probably, the hydrolysis of the SKS-5 framework and the variation of the sodium coordination lead to the structural conversion during the hydration process.

1. Introduction

Sodium disilicates are a group of materials with complex polymorphism, at least eight different modifications have been reported as a function of temperature, pressure, and synthesis conditions.¹ In these modifications, the well-known layered sodium disilicates are SKS-5 ($\alpha\text{-Na}_2\text{Si}_2\text{O}_5$), SKS-6 ($\delta\text{-Na}_2\text{Si}_2\text{O}_5$), and SKS-7 ($\beta\text{-Na}_2\text{Si}_2\text{O}_5$), which were first synthesized by Hoechst Corporation in 1986.^{2,3} Because these layered disilicates combine high performance per unit weight and high degree of multifunctionality, they were verified to be excellent detergent builders and used to replace sodium triphosphate (STP) for the reason of environmental compatibility in the past few years.^{2–4} The superior properties of these materials, such as water-softening effect, buffer effect, dispersing-ability, and prevention of soil re-deposition, can all be attributed to their special crystal structures and high content of sodium ions. Therefore, the stability of these layered disilicates should be receiving much attention since their utilities as detergent builders can be deeply influenced by structural change or collapse. In the factors that can influence the stability of these materials, water should be a crucial element because all the layered silicates (including the

layered disilicates) can absorb water easily in the atmosphere due to their special layer structures. In fact, absorbed water can not only alter the coordination of cations in layered silicates,⁵ but, more seriously, may also lead to hydrolysis of the silicate framework as those happened in silicate glasses.^{6,7} Although absorbed water should play an important role in influencing the stability of layered silicates, to the best of our knowledge, there are few studies of interaction between absorbed water and layered silicates published until now.

SKS-5 is an anhydrous layered sodium disilicate and its chemical formula is $\text{Na}_2\text{Si}_2\text{O}_5$. The crystal structure of this layered disilicate is the same as $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$,^{2,3} which consists of a distorted trigonal bipyramidal pentahedral sodium sheet layered between two tetrahedral silicate sheets. Figure 1 shows one silicate sheet of $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ that was suggested by Pant and co-workers on the basis of the X-ray diffraction data.⁸ In the silicate layer, each tetrahedral silicon atom is bonded to other three tetrahedral silicon atoms via bridging oxygen atoms, leaving one coordination oxygen atom in a nonbridging form (having a negative charge on the oxygen atom). The 5-coordinated sodium ions reside between the silicate layers for charge compensation. In the crystal structure of SKS-5, there is only one equivalent site for both silicon atoms and sodium ions. Since the crystal structure of SKS-5 is relatively simple, it is very suitable for this material to be used as a model substance to study the effect of absorbed water on the stability of layered silicates.

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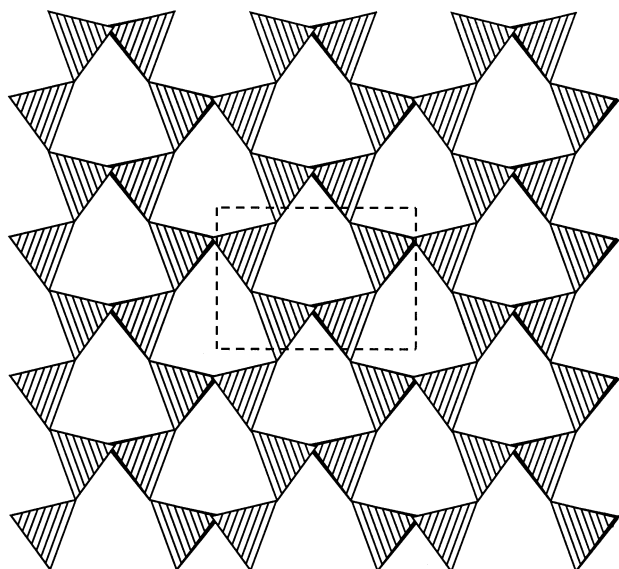


Figure 1. Single tetrahedral layer of the SiO_4 tetrahedra in the layered sodium disilicate SKS-5. The dashed line denotes a unit cell that is displayed in a crystallographic c - a plane. Oxygen atoms are located in the corners of tetrahedra and silicon atoms are located in the center of tetrahedra (sodium ions are not shown).

In the present study, ^1H MAS, ^{29}Si MAS, $^1\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS, ^{23}Na MAS, and ^{23}Na multiple-quantum MAS (MQMAS) NMR spectroscopies,^{9,10} combined with X-ray diffraction (XRD) technique, were applied to study the interaction between absorbed water and SKS-5 by exposing the as-received sample to the atmosphere for various periods. The purpose of using the weak hydration condition is to highlight the slight structural change during the hydration process. The results of the NMR and XRD experiments show that SKS-5 is very sensitive to absorbed water, and the crystal structure of this layered disilicate converts gradually from α - $\text{Na}_2\text{Si}_2\text{O}_5$ to a new phase. In addition, the coordination of sodium ions that are of central interest for ion exchange is also significantly changed during the hydration process.

2. Experimental Section

2.1. Sample Preparation. The as-received SKS-5 (in an anhydrous form and with a molar ratio of $1\text{Na}_2\text{O}:2\text{SiO}_2$) was synthesized according to the methods described in the literature.^{2,3} The crystal size of the sample is about 3–5 μm in diameter as revealed by transmission electron microscopy (TEM). By exposing the as-received sample at room temperature (20 ± 3 $^\circ\text{C}$) to the atmosphere (with a relative humidity between 35 and 50%) for different periods, a series of samples with hydration time ranging from 10 days to 6 months were prepared. The amounts of water up-take in the different hydrated samples were measured by thermogravimetry with temperatures ranging from 30 to 1300 $^\circ\text{C}$, and the corresponding data were listed in Table 1. Some dehydrated samples were obtained by dehydrating the corresponding hydrated samples at room temperature and at a pressure below 10^{-3} Pa for 8 h. Rehydration treatment was carried out by keeping the dehydrated sample in a desiccator filled with aqueous NH_4NO_3 solution for 4 h before NMR experiment.

2.2. X-ray Diffraction. The X-ray powder diffraction (XRD) patterns were acquired with a Rigaku D/max-IIIc diffractometer using a $\text{Cu K}\alpha$ radiation operating with 32.5 kV. The scanning rate was $2^\circ/\text{min}$ for $5^\circ < 2\theta < 50^\circ$ with a resolution of 0.02° .

2.3. NMR Spectroscopy. All solid-state NMR experiments were carried out using a Varian Infinity-plus 400 spectrometer operating at a magnetic field strength of 9.4 T. For ^1H and ^{23}Na NMR experiments, a Chemagnetics 4 mm double-resonance probe was used. ^{29}Si NMR experiments were performed utilizing a Chemagnetics 7.5 mm triple-resonance probe. The resonance frequencies for ^1H , ^{23}Na , and ^{29}Si were 400.12, 105.84, and 79.48 MHz, respectively. Magic angle spinning (MAS) rates were 14 kHz for ^1H NMR, 10 kHz for ^{23}Na NMR, 6 kHz for ^{29}Si MAS NMR, and 5 kHz for $^1\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS NMR experiments. The ^1H and ^{29}Si chemical shifts were referenced to tetramethylsilane (TMS) and the ^{23}Na chemical shifts to a dilute aqueous NaCl solution (1 M).

^1H MAS spectra were recorded with a Hahn echo pulse sequence ($\pi/2$ - τ - π - τ -acquire), where τ equals one rotor period (rotor synchronized). The $\pi/2$ pulse width was 2 μs , and 5–60 s recycle delays were used for signal accumulation, depending on the T_1 relaxation time of the ^1H signals in the samples. ^{23}Na MAS spectra were acquired with a short $\pi/12$ radio frequency pulse (0.3 μs), and 400 scans were accumulated with a 10 s recycle delay. ^{29}Si single pulse experiments were performed with a 4.5 μs pulse width ($\pi/2$) and a 600 s recycle delay, and ^1H decoupling with field strength of 39 kHz was applied during the acquisition period. The Hartmann–Hahn condition in the $^1\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS NMR experiments was optimized with kaolinite using a contact time of 1 ms and a 5 s recycle delay. Deconvolution of the ^1H MAS and ^{29}Si MAS spectra were performed by using the built-in software in Spinsight.

Two three-pulse sequences with and without ^1H decoupling (shown in Figure 2) were used for ^{23}Na multiple-quantum MAS (MQMAS) experiments.⁵ The radio frequency (rf) pulses used to excite the three-quantum coherences ($\pm 3Q$) and to transfer them back to zero quantum had a field strength of 147 kHz. A selective $\pi/2$ pulse with a 10 kHz field strength was applied after the z-filter period (200 μs).¹¹ For high power ^1H decoupling, a rf field strength of 64 kHz was used. To produce pure absorption-mode line-shapes in the two-dimensional spectra, the hypercomplex method was applied for data collection,¹² and all two-dimensional data were processed with a shearing transformation prior to the complex Fourier transformation.¹³ Typically 96 scans were acquired for each t_1 increment and two-dimensional data sets consisted of $128 t_1 \times 1024 t_2$. Simulation of the second-order quadrupolar patterns in F_2 projections of two-dimensional MQMAS spectra was performed using the Varian software STARS.

3. Results and Discussion

X-ray Powder Diffraction. The X-ray diffractograms of the SKS-5 samples as a function of hydration are shown in Figure 3. For the as-received SKS-5 sample, the XRD pattern reveals some lines including four intense lines at 2θ of 18.00° , 23.09° , 23.58° , and 27.00° , which is consistent with the literature.^{2,3} These four lines are used as fingerprints to monitor the crystal structure of the samples during the hydration process. Clearly, the crystal structure of α - $\text{Na}_2\text{Si}_2\text{O}_5$ is almost unchanged in the 10 days hydrated sample. Even for the 3 months hydrated sample, most of the α - $\text{Na}_2\text{Si}_2\text{O}_5$ structure remains with the appearance of some minor lines in the XRD pattern. But the XRD pattern changes completely after the exposure time extends to 6 months, indicating that a phase transformation from α - $\text{Na}_2\text{Si}_2\text{O}_5$ to a new crystal structure may probably occur. In the X-ray diffractograms, a line at 2θ of 9.37° first appears in the XRD pattern of the 3 months hydrated sample and becomes

TABLE 1: Relative Contents (%) of Various Silanols and Water in Hydrated SKS-5 Samples Determined by ¹H NMR and Thermogravimetry^a

sample	isolated silanols (0–3 ppm)	oriented water (6.7 ppm)	silanols I (14.0 ppm)	silanols II (18.7 ppm)	ratio Si–OH/H ₂ O ^b	total water content ^c (%, wt/wt)
10 days	19.7	71.5	8.8		1:1.3	4.0
3 months	5.1	76.7	18.2		1:1.7	11.3
6 months	1.7	60.9	19.0	18.4	1:0.8	23.1

^a All the data except for the total water contents were obtained by ¹H NMR. The error for the relative integrated intensities of proton-containing species in each hydrated sample is estimated to be within ±5%. ^b The molar ratios of the total Si–OH:molecular H₂O with considering that each molecular-H₂O contains two protons. ^c Determined by thermogravimetry, including the hydrogen-bonded water and water molecules converted to silanols.

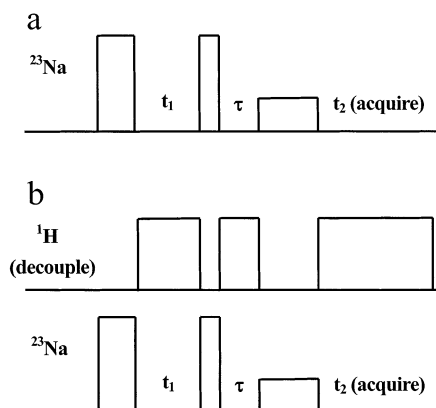


Figure 2. Pulse programs used for two-dimensional ²³Na MQMAS experiments: (a) three-pulse sequence without ¹H decoupling (used for as-received sample); (b) three-pulse sequence with ¹H high power decoupling (used for hydrated samples).

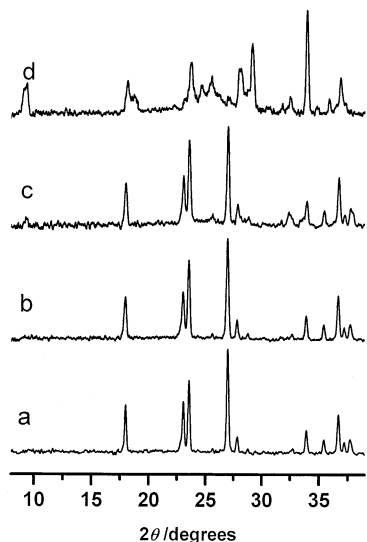


Figure 3. XRD powder patterns of the series SKS-5 samples as a function of hydration time: (a) as received; (b) 10 days; (c) 3 months; (d) 6 months.

intense in that of the 6 months hydrated sample. The appearance of this line suggests an increase of the interlayer space in the corresponding hydrated samples, assuming the layer structure still remains. Further increasing the hydration time causes no obvious change in the corresponding XRD pattern.

The information about the new crystal structure in the 6 months hydrated sample should be very useful for understanding the details of the hydration process of SKS-5. For this reason, a careful comparison of the XRD pattern in Figure 3d with the ICDD (International Center for Diffraction Data) XRD data of the various inorganic materials is performed. Although many new lines appear in the XRD pattern of the 6 months hydrated

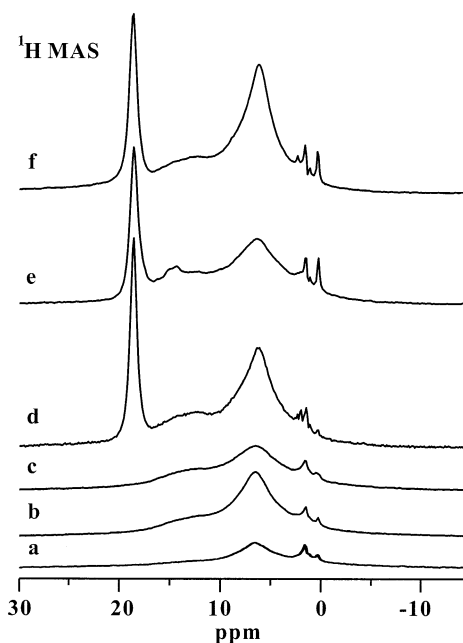


Figure 4. ¹H spin-echo NMR spectra of the series SKS-5 samples as a function of hydration: (a) 10 days hydrated; (b) 3 months hydrated; (c) 3 months hydrated and then dehydrated; (d) 6 months hydrated; (e) 6 months hydrated and then dehydrated; (f) 6 months hydrated, then dehydrated, and then rehydrated.

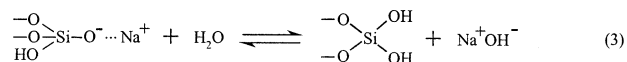
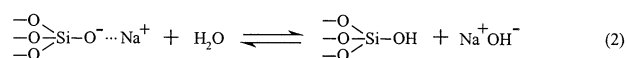
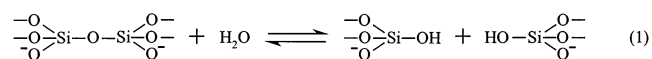
sample, only a small part of them (at 2θ of 9.37°, 18.19°, 18.73°, 23.77°, 25.57°, 28.14°, and 29.15°) fit well with those of a known crystal Na₂Si₄O₉. Fitting the XRD pattern (by Lorentz line shape) in Figure 3d indicates that the Na₂Si₄O₉ only amounts to 9% of the new phase. Obviously, the new phase is not a pure phase and its crystal structure is still unclear. An attempt to obtain the unit cell of the new crystal structure in the 6 months hydrated sample fails due to the lower intensities and resolutions of the lines with large 2θ values, which are usually selected to refine crystal structure.

¹H MAS NMR. ¹H MAS spectra of the series SKS-5 samples as a function of hydration are shown in Figure 4. Because the as-received SKS-5 exists in an anhydrous form, no proton-containing species can be detected by ¹H MAS NMR in this sample. For the 10 days hydrated sample (the water up-take is ca. 4%), four peaks (two sharp peaks at 0–3 ppm, a broad peak at 6.7 ppm and a broad shoulder at 14.0 ppm) appear in the ¹H MAS spectrum (Figure 4a). According to the data of ¹H chemical shifts in layered silicates,^{14–16} the sharp resonances at 0–3 ppm in the ¹H MAS spectra can be assigned to isolated silanols and/or free water, the broad resonance at 6.7 ppm arises from hydrogen-bonded water (oriented water) and the broad resonance centered at 14.0 ppm is due to hydrogen-bonded silanols with proton bonded to oxygen atom in adjacent layer. The broad line-width of the resonance at 14.0 ppm implies that

there is a large chemical shift distribution for the hydrogen-bonded silanol.

After the sample was exposed in the atmosphere for 3 months (11.3% water up-take), the intensities of the two broad resonances increase significantly while those of the two sharp peaks remain almost unchanged, indicating an increase of the hydrogen-bonded water and the hydrogen-bonded silanols in the 3 months hydrated sample. It is surprising that an unexpected strong signal at 18.7 ppm is present in the ^1H MAS spectrum of the 6 months hydrated sample (23.1% water up-take). Until now, ^1H chemical shifts larger than 18.0 ppm in solid materials were observed only in a few cases such as KH dicrotonate (hydrogen-bonded anions).^{16,17} In hydrous silicate glasses, Kohn et al. observed a ^1H signal at 17 ppm and assigned it to a very strong hydrogen-bonding interaction between $\text{Si}-\text{OH}$ and $^-\text{O}-\text{Si}$, possibly with both groups (OH and O^-) attached to the same silicon atom.⁶ The correlation between the $\text{O}\cdots\text{H}$ distance in a hydrogen-bonded complex ($\text{O}-\text{H}\cdots\text{O}$) and the proton chemical shift in various materials suggests a very short $\text{O}\cdots\text{H}$ distance of ~ 130 pm be present for the ^1H signal at 18.7 ppm.¹⁶ Thus, the signal at 18.7 ppm is likely due to a similar hydrogen-bonding silanol as proposed by Kohn et al., but with a much stronger hydrogen-bonding interaction between $\text{Si}-\text{OH}$ and $^-\text{O}-\text{Si}$. Further exposing the sample for more than 6 months, no obvious change could be observed in the ^1H MAS spectrum. In the following text, the silanols corresponding to the resonances at 14.0 and 18.7 ppm in the ^1H NMR spectra were denoted as "silanol I" and "silanol II", respectively.

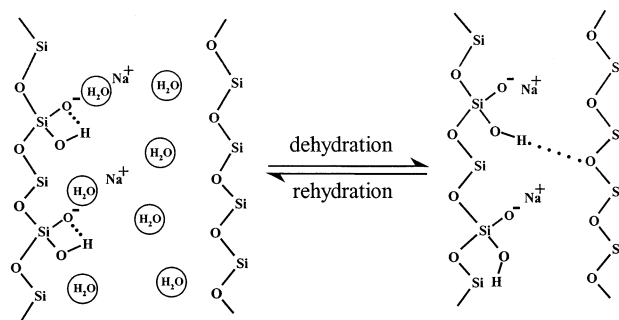
Since SKS-5 has the same crystal structure as $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$, no proton can be expected to exist in this material. However, three kinds of silanol groups (isolated silanol, silanol I, and silanol II) were observed in the ^1H MAS spectra of the hydrated samples. This should be the result of a partial hydrolysis of the SKS-5 framework. Because both the bridging oxygen and nonbridging oxygen are present in SKS-5, the following hydrolysis reactions may proceed during the hydration process:



Obviously, reactions 2 and 3 should generate sodium hydroxide. As will be seen in the following text, we could only detect sodium hydroxide by ^{23}Na MAS NMR for the 6 months hydrated sample. Therefore, reaction 1 that hydrolyzes the $\text{Si}-\text{O}-\text{Si}$ linkages should be predominant during the whole hydration process and reactions 2 and 3 may only proceed for the 6 months hydrated sample.

By means of dehydration–rehydration treatment, the natures of the hydrogen-bearing species were clearly clarified. After the 3 months hydrated sample was dehydrated at room temperature, it can be seen from Figure 4c that the resonance at 6.7 ppm is largely reduced while the resonance at 14.0 ppm remains almost unchanged. This demonstrates again that the former results from hydrogen-bonded water and the latter results from a stable proton-containing species, probably the hydrogen-bonded silanol with the proton atom bonded to the oxygen atom in the adjacent layer. In addition, the line-widths of the two

peaks at 0–3 ppm are slightly broadened, but the difference between the integrated intensities of these two peaks before and after dehydration is negligible, indicating that the peaks at 0–3 ppm arise from the isolated silanols rather than free water. After dehydrating the 6 months hydrated sample, the signal at 18.7 ppm decreases and new signals at ca. 15.2 ppm appear. The signals at ca. 15.2 ppm may be also associated with the structure similar to that of silanol I. A scheme that reflects the influence of dehydration–rehydration treatment on the 6 months hydrated sample is illustrated as follows:



In this scheme, the sodium ion will be tightly associated with the nonbridging oxygen after some adsorbed water molecules are removed and the interaction between the hydrogen-bonding proton and the nonbridging oxygen is weakened, resulting in part of silanol II converted to silanol I or even isolated silanol. After rehydration treatment, sodium ion is surrounded by the absorbed water molecules and the distance between the sodium ion and the nonbridging oxygen increases, leading to a strong interaction between the hydrogen-bonding proton and the nonbridging oxygen and thus a transformation from silanol I to silanol II.

Table 1 shows the relative contents of the three kinds of silanols and hydrogen-bonded water obtained from the ^1H MAS NMR spectra. We can find that most of the silanols formed at the beginning of the hydration process are isolated silanols. With increasing the hydration time, the relative content of isolated silanols is significantly reduced and more and more hydrogen-bonded silanols are formed. The ratios of the total $\text{Si}-\text{OH}$ to molecular- H_2O are 1:1.3, 1:1.7, and 1:0.8 for the 10 days, 3 months, and 6 months hydrated samples, respectively, implying first a decrease and then an increase of hydrolysis reaction. Because the ^1H MAS spectrum remains unchanged when the exposure time exceeds 6 months, no further hydrolysis of the silicate network occurs. Most likely, the hydrogen-bonding network (including hydrogen-bonded silanol I and silanol II or even hydrogen-bonded water) formed during the hydration process strengthens the stability of the new phase.

^{29}Si NMR. There is only one sharp peak at -94.5 ppm with a line-width of 37 Hz (without line-broadening) in the ^{29}Si MAS spectrum of the as-received sample (Figure 5a), which is in line with the work of Heidemann et al.¹⁸ The absence of other peaks indicates that the as-received sample is a very pure $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ crystallite. After exposing SKS-5 to the atmosphere for 10 days, the intensity of the signal at -94.5 ppm is slightly reduced and some minor peaks at -90 to -120 ppm appear in the corresponding ^{29}Si MAS spectrum (Figure 5b). By spectral simulation, we can estimate that about 13% of SKS-5 has already converted to the new phase (Table 2) though the XRD data show almost no change in this sample. When the exposure time is extended to 3 months, the intensities of these new peaks increase at the expense of the intensity of the -94.5 ppm peak (Figure 5c). The conversion of SKS-5 is about 40% for this

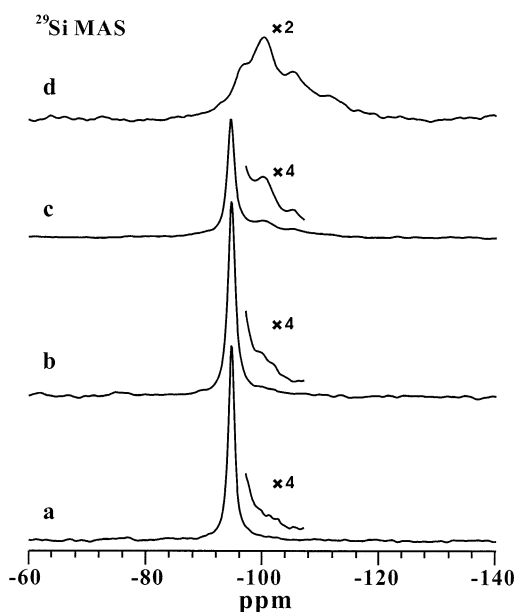


Figure 5. ²⁹Si MAS spectra of the series SKS-5 samples as a function of hydration time: (a) as-received; (b) 10 days; (c) 3 months; (d) 6 months.

TABLE 2: ²⁹Si NMR Data of the Series Samples of SKS-5 as a Function of Hydration

sample	peak	relative content ^a	conversion (%)
as received	-94.5 ppm	100	0
10 days	-94.5 ppm	87 ^b	13 ^b
	—	—	—
3 months	-90.8 ppm	1	40
	-94.5 ppm	60	
	-96.2 ppm	7	
	-100.0 ppm	22	
	-105.2 ppm	7	
	-111.0 ppm	3	
6 months	-90.8 ppm	1	100
	-96.2 ppm	14	
	-100.0 ppm	53	
	-105.2 ppm	16	
	-111.0 ppm	16	

^a Normalized to a total spectral area of 100. The error for the relative integrated intensities is estimated to be within $\pm 10\%$. ^b The conversion is estimated from intensity variation of the signal at -94.5 ppm in the 10 days hydrated sample with respect to the as-received SKS-5 sample.

sample. After 6 months hydration, the signal at -94.5 ppm disappears completely and five peaks at -90.8, -96.2, -100.0, -105.2, and -111.0 ppm can be resolved (Figure 5d). The ²⁹Si MAS spectra of the series of hydrated samples suggest that a complete phase transformation takes place during the period from 3 to 6 months hydration, which is in accordance with the previous XRD results. However, ²⁹Si MAS NMR provides a more quantitative description of the transformation during the hydration process. After the conversion is accomplished, the ²⁹Si MAS spectrum remains almost unchanged (not shown), indicating that the new phase is very stable upon further hydration.

It is interesting that only three peaks at -96.2, -100.0, and -105.2 ppm are present in the ¹H → ²⁹Si CP/MAS spectra of the series samples (Figure 6). The appearance of the three signals for the 10 days hydrated sample implies that the layered disilicate SKS-5 is very sensitive to absorbed water and the structural transformation from α-Na₂Si₂O₅ to the new phase has

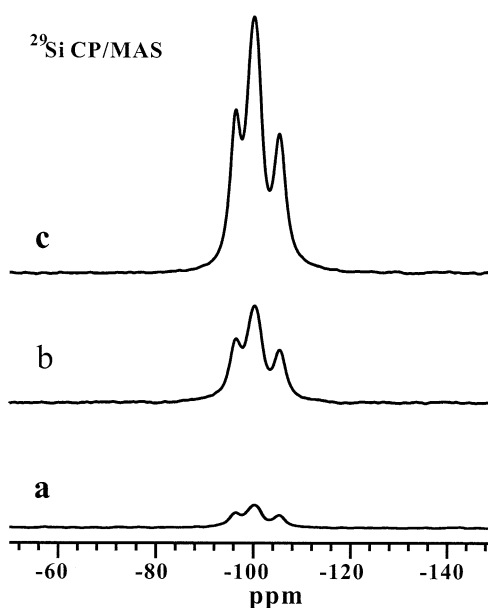
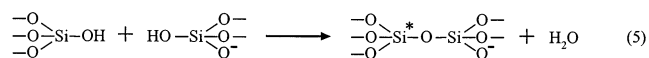
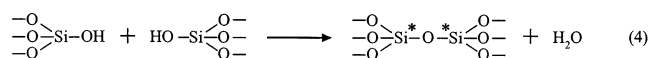


Figure 6. ¹H → ²⁹Si CP/MAS spectra of the sodium disilicate SKS-5 samples as a function of hydration time: (a) 10 days; (b) 3 months; (c) 6 months.

already occurred during the initial hydration period. During the whole hydration process, the ²⁹Si chemical shifts and the relative intensities of the three silicon sites remain unchanged, indicating that the hydrolysis of the silicate network proceeds in a very similar manner. In addition, the absence of the two resonances at -90.8 and -111.0 ppm in all of the ¹H → ²⁹Si CP/MAS spectra, which are present in the corresponding ²⁹Si MAS spectra, suggests that the two signals result from silicon atoms that do not couple to a proton. According to their chemical shifts, the former can be attributed to a Q² group and the latter is probably due to the Q⁴ group [Si(OSi)₄] formed by the following condensation reactions (the asterisks denote Q⁴ groups):



In both reactions, the reactants should originate from the products of reactions 1 and 2. It should be noted that the hydrolysis of SKS-5 framework through 1–3 reactions can only produce (SiO)₂Si(OH)O⁻Na⁺ and (SiO)₂Si(OH)₂ as Q² groups. However, both of them are associated with a proton. Therefore, we tentatively assign the -90.8 ppm signal to the Q³ group [(SiO)₃SiO⁻Na⁺] that is not close to a proton. The larger chemical shift of the silicon site is likely due to a slight deviation of bond angles or bond lengths from those of the equivalent silicon site in SKS-5.

The three signals at -96.2, -100.0, and -105.2 ppm in the ¹H → ²⁹Si CP/MAS spectra of the hydrated samples, according to their chemical shifts, can be assigned to Q² [(SiO)₂Si(OH)O⁻Na⁺] groups which are generated by the reaction 1 or Q³ groups [(SiO)₃SiO⁻Na⁺] close to neighboring hydroxyl groups. In the 6 months hydrated sample, part of the three resonances may also arise from Q³ [(SiO)₃Si(OH)] or Q² [(SiO)₂Si(OH)₂] groups formed by reactions 2 and 3, which was verified by the appearance of sodium hydroxide (see the later ²³Na NMR section). However, the concentration of these groups should be

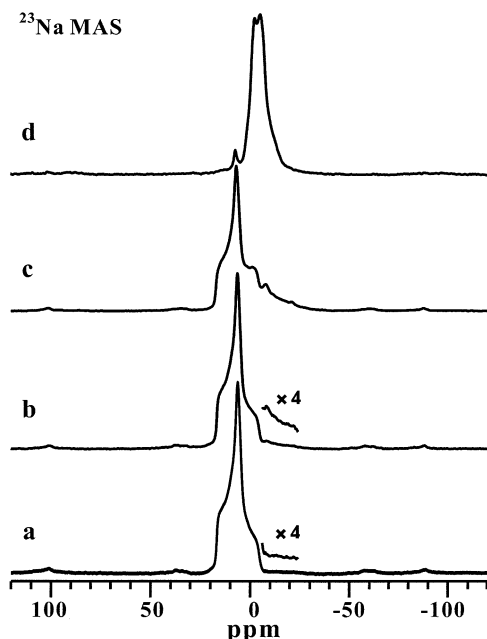


Figure 7. The ^{23}Na MAS spectra of the sodium disilicate SKS-5 samples as a function of hydration time: (a) as-received; (b) 10 days; (c) 3 months; (d) 6 months.

very low because of the low content of sodium hydroxide (about 5%) detected by the ^{23}Na MAS NMR in the 6 months hydrated sample. On the basis of the ^{29}Si NMR experiments, it can be concluded that the hydrolysis of the silicate network proceeds mainly through reaction 1 (by breaking the Si—O—Si linkages) and partially through the reactions 2 and 3 to form Q^3 $[(\text{SiO})_3\text{Si}(\text{OH})]$ and Q^2 $[(\text{SiO})_2\text{Si}(\text{OH})_2]$ groups.

^{23}Na NMR. Figure 7 shows the ^{23}Na MAS spectra of the series SKS-5 samples as a function of hydration. For the as-received sample, only a typical second-order quadrupolar line shape was observed in the ^{23}Na MAS spectrum, which can be attributed to the equivalent 5-coordinated sodium site in the $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ crystal structure. As the sample was exposed in the atmosphere for 10 days, small peaks at 5 to -17 ppm appear in the ^{23}Na MAS spectrum. The intensities of these peaks increase with increasing hydration time. Extending the hydration time to 6 months, the ^{23}Na signal from the $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ structure disappears completely, accompanying by significant change of line shapes. In addition, a small peak at 7.3 ppm (about 5% of the total sodium signals) is present in the ^{23}Na MAS spectrum of the 6 months hydrated sample, which can be attributed to sodium hydroxide.¹⁹ The appearance of this sodium species generated by reaction 2 or 3 is likely due to an increase of the interlayer space and high content of absorbed water in this hydrated sample, which cause the sodium ion far away from the nonbridging oxygen atom and surrounded by water molecules. No difference can be found in the ^{23}Na MAS spectrum when the as-received sample was exposed to the atmosphere for more than 6 months.

Although the ^{23}Na nucleus is sensitive to the local coordination environment and is usually used as a probe to investigate structural information in solid materials, the inability of magic-angle spinning to completely average out the effects of second-order quadrupolar interactions leads to residual line-broadening in ^{23}Na MAS spectra. Thus, little information can be obtained because of the serious line-broadening and the superposition of various resonances. However, the residual second-order quadrupolar interactions can be averaged by the MQMAS method that combines the MAS technique and spin manipula-

tions.^{9,10} In the two-dimensional (2D) MQMAS spectrum, the projection into the F_1 dimension gives rise to a spectrum in which the anisotropic effect has been removed. Meanwhile, the NMR parameters of quadrupolar nuclei such as quadrupolar coupling constant (C_Q) and asymmetry factor η , can be extracted by simulating the slice projection of the 2D MQMAS spectrum in the F_2 dimension.

Figure 8 shows the ^{23}Na 2D MQMAS spectra of the series samples. Four sodium sites can be resolved in the different hydration periods. In the 2D MQMAS spectrum of the as-received SKS-5, only one signal (site 1) can be observed and it is unambiguously attributed to the 5-coordinated sodium site in the $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ crystallite. After exposing SKS-5 in the atmosphere for 10 days, another weak signal (site 2) is present in the corresponding 2D spectrum. With extending the exposure time to 3 months, the signal intensity of site 2 increases and a new signal appears (site 3). For the 6 months hydrated sample, the signal of site 1 disappears completely. Meanwhile, a new signal of site 4 is present and the intensities of the signals of site 2 and site 3 are largely increased. In these MQMAS spectra, the signal at 7.3 ppm in the ^{23}Na MAS spectrum is not observed, probably due to the low amount (5%) of sodium hydroxide and the fast relaxation of this sodium nucleus during the multiple-quantum evolution period. The line shapes for each sodium site extracted from slices in the F_2 dimension of the 2D MQMAS spectra were shown in Figure 9. For site 1, site 2, and site 4, typical second-order quadrupolar line shapes are observed while a very sharp Gaussian line shape is present for the site 3. The NMR parameters of the first three sodium sites are obtained by fitting the corresponding slices in the 2D MQMAS spectra while that of site 3 is obtained directly from the 2D MQMAS spectrum by the following equations^{20,21} (all the results are list in Table 3):

$$\delta_{\text{iso}} = \frac{10}{27} \langle \delta_{F_2} \rangle + \frac{17}{27} \langle \delta_{F_1} \rangle \quad (6)$$

$$P_Q = \sqrt{\frac{680\nu_Q^2 \times 10^6}{27} (\langle \delta_{F_1} \rangle - \langle \delta_{F_2} \rangle)} \quad (7)$$

where δ_{iso} is the isotopic chemical shift, P_Q is quadrupolar product ($P_Q = C_Q(1 + \eta^2/3)^{1/2}$ and C_Q is the quadrupolar coupling constant), ν_Q is quadrupolar frequency, $\langle \delta_{F_2} \rangle$ and $\langle \delta_{F_1} \rangle$ are the position (ppm in unit) of the signal in the F_2 and F_1 dimension of the corresponding 2D MQMAS spectrum, respectively.

The ^{23}Na MQMAS results agree well with the data from ^1H and ^{29}Si NMR experiments. For the 10 days hydrated sample, the appearance of site 2 in the ^{23}Na MQMAS spectrum corresponds to the structural change (as shown by ^{29}Si NMR) and the appearance of silanol I (as shown by ^1H NMR). Similarly, the appearance of site 4 in the ^{23}Na MQMAS spectrum of the 6 months hydrated sample is associated with the appearance of silanol II in the ^1H MAS spectra. In addition, in the 6 months hydrated sample, the disappearance of site 1 in ^{23}Na MQMAS spectrum also consists with the disappearance of the -94.5 ppm signal (of the $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$) in the ^{29}Si MAS spectrum, implying a complete transformation from $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ to the new phase.

Generally, NMR parameters such as quadrupolar coupling constant (C_Q), asymmetry factor η , and especially the isotropic chemical shift δ_{iso} can provide unique, quantitative information about the local coordination environment of quadrupolar nuclei, and are correlated to bond distance and size of cations.^{22–24} On

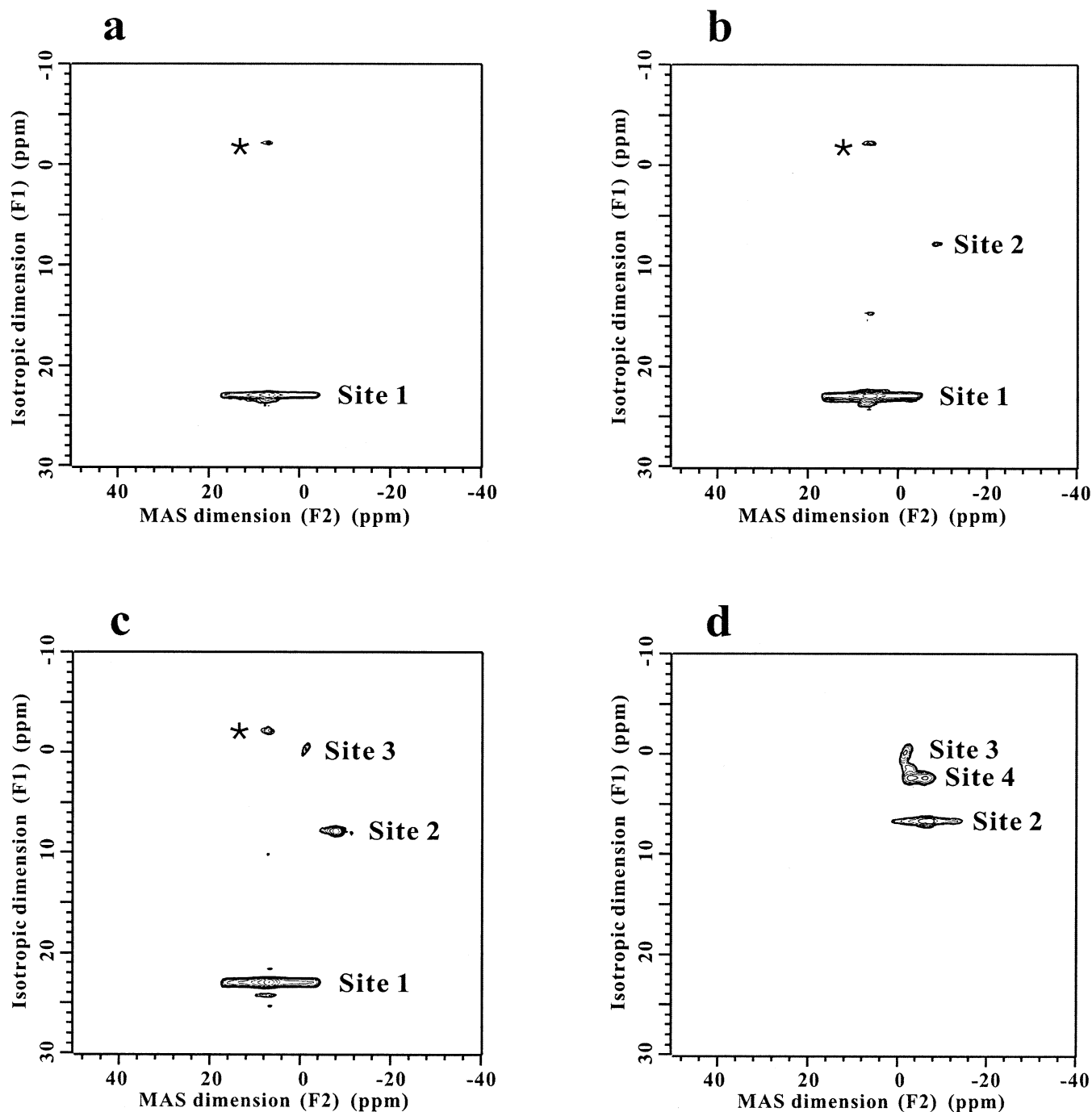


Figure 8. ^{23}Na two-dimensional MQMAS spectra of the sodium disilicate SKS-5 samples as a function of hydration time: (a) as received; (b) 10 days; (c) 3 months; (d) 6 months. The asterisks in the spectra denote spinning sidebands.

the basis of isotropic chemical shift δ_{iso} (see Table 3), the local environments of the four sodium sites can be determined. Obviously, site 1 with a δ_{iso} of 17 ppm is due to 5-coordinated sodium ion in $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ crystal structure and the other three sites with a δ_{iso} of ca. 0 ppm can be assigned to the 6-coordinated sodium ion. Concretely, site 3 corresponds to 6-coordinated sodium ion associated with water molecules, resulting in a more symmetrical environment around the sodium ion and a small C_Q .⁵ Both site 2 and site 4 are 6-coordinated sodium ions, in which the coordination oxygen atoms should include those of the hydrogen-bonded silanols. However, the coordination oxygen atoms in the hydrogen-bonded silanols may be different for these two sodium sites. For site 2, they should be the oxygen atoms of silanol I; but for site 4, the oxygen atoms of silanol II are involved.

4. Conclusion

The present investigation demonstrates that solid state NMR is a powerful tool for clarifying the interaction between water molecules and the SKS-5 framework, and it actually provides a more detailed description about the hydration process of SKS-5 with respect to XRD technique. The water molecule plays an important role in influencing the stability of SKS-5, and the crystal structure of this material is gradually converted from $\alpha\text{-Na}_2\text{Si}_2\text{O}_5$ to a new phase during the hydration process. The hydration of SKS-5 begins with the formation of hydrogen-bonded water with the silicate framework, and then the appearance of a small amount of isolated silanols and hydrogen-bonded silanol I as a result of the hydrolysis of SKS-5 framework. When the hydration time is extended to 6 months,

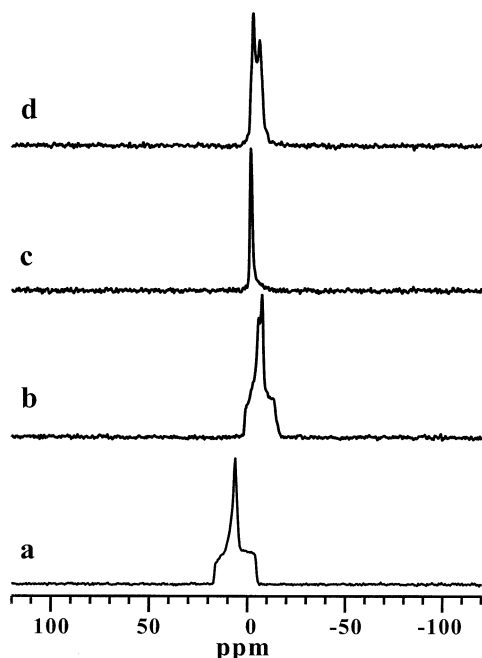


Figure 9. Slice projections along the F_2 dimension for different sodium sites extracted from the corresponding 2D MQMAS spectra: (a) site 1, (b) site 2, (c) site 3, and (d) site 4.

TABLE 3: ^{23}Na NMR Parameters for the Different Sodium Sites in the Series SKS-5 Samples as a Function of Hydration^a

site	$\delta_{\text{iso}}/\text{ppm}$	C_Q/MHz	η
site 1	17.0 ± 1.0	1.8 ± 0.1	1.0 ± 0.1
site 2	1.6 ± 1.0	1.6 ± 0.1	0.8 ± 0.1
site 3 ^b	-0.9 ± 1.0	0.5 ± 0.1^c	
site 4	-0.3 ± 1.0	1.1 ± 0.1	0.1 ± 0.1

^a δ_{iso} is isotropic chemical shift, C_Q is the quadrupolar coupling constant and η is the asymmetry factor. ^b The NMR parameters of site 3 was obtained directly from the corresponding 2D MQMAS spectrum with eqs 6 and 7 shown in the text. ^c This parameter is the quadrupolar product $C_Q(1 + \eta^2/3)^{1/2}$.

the conversion from SKS-5 to the new phase is accomplished and a new kind of hydrogen-bonded silanols II appears. Most likely, the hydrogen-bonding network formed during the hydration process strengthens the stability of the new phase. The silicon sites in the new phase are very complicated and confirmed to be mainly the Q^2 $[(\text{SiO})_2\text{Si}(\text{OH})\text{O}^-\text{Na}^+]$ and Q^3 $[(\text{SiO})_3\text{SiO}^-\text{Na}^+]$ groups by ^{29}Si MAS and $^1\text{H} \rightarrow ^{29}\text{Si}$ CP/MAS experiments. In addition, a small amount of Q^3 $[(\text{SiO})_3\text{Si}(\text{OH})]$ and Q^2 $[(\text{SiO})_2\text{Si}(\text{OH})_2]$ groups are also present in the new crystal structure. Five sodium sites with different local environments can be resolved by ^{23}Na MAS and ^{23}Na MQMAS

experiments. It is probably due to the hydrolysis of the SKS-5 framework and the variations of the sodium coordination that cause the structural conversion during the hydration process. In a similar manner, the function of water molecules in the other layered silicates such as SKS-6 ($\delta\text{-Na}_2\text{Si}_2\text{O}_5$) and SKS-7 ($\beta\text{-Na}_2\text{Si}_2\text{O}_5$) can also be well recognized by multinuclear solid-state NMR spectroscopies.

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