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Article

Crystallization of Zeolites from Organo-Silicic Colloids

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As shown recently, the networks of mesoporous high-surface-area silicates and zeolites undergo a deep depolymerization process in glycerol, near 200 °C. Within 1 h, X-ray diffraction analysis amorphous gels are obtained. However, some local ordering subsists as demonstrated by a striking similarity between the silicon and aluminum high-resolution solid-state NMR spectra before and after the reaction. The residual organization could be investigated indirectly in studying the recrystallization of these gels in the presence or absence of structure-directing agents. Were this attempt successful, the way should be opened for the synthesis of molecular sieves starting from gels obtained from naturally occurring zeolites. Here, it will be shown that an amorphous gel obtained from HZSM-5 recovers the initial long-range structure of the parent material in a few hours at 85 °C in the presence of an aqueous solution of tetrapropyl ammonium (TPA) or NH_3. The recrystallization of HY requires the presence of tetramethylammonium, but about 25% of the crystallization is obtained rapidly ($\cong$1day) at 80 °C with ammonia. Hypotheses about the preorganized structural units are presented. The value of the Si–O–Si angle in the silica cluster seems to be of paramount importance.

Introduction

In most of the procedures used for the synthesis of zeolites, the starting material (SM) is an aqueous gel with a chemical composition comparable with the composition of the target. The alumino-silicate gel is obtained by controlling the hydrolysis of a mixture of alkali silicate and aluminate or by a sol−gel procedure, operating with a mixture of silicon and aluminum alkoxides[1]. Often, but not necessarily, the synthesis is mediated through templates and is sometimes assisted by seeding.

Crystalline mesoporous silica, such as MCM-41, dissolves rapidly below 200 °C in glycerol, forming a stable gel.[2] The solubility of the organo complex in glycerol is in the percent range, that is to say, more than 10 000 times the solubility of silica in water. The long-range ordering of the silica network is lost, and the gel is X-ray amorphous. Synthetic acid faujasite HY, HZSM-5, acid Clinoptilolite, a member of the Heulandite family, can be jellified as well. The depolymerized material is a hyperbranched silicon alkoxide, the depolymerization reaction proceeding by a condensation process between a silanol group and an alcohol function of glycerol, liberating water. The water is continuously evaporated from the reacting mixture.

The similarity between the ^{29}Si NMR and ^{27}Al NMR spectra of the gel and those of the corresponding starting material suggests that a limited, local ordering persists in the gel. In particular, the observation of tetrahedral aluminum permits an estimation of the size of the smallest structural unit in the gel. For instance, in HY, there are 12.7 tetrahedral units per cubic nanometer. Because the Si/Al ratio is 12.9, there is about 1 Al/nm^3, and because both the ^{27}Al signal and the ^{29}Si signal are the same as that in bulk HY, the smallest structural unit in the gel must be about 1 nm^3. If the same argument is used, this volume is 1.24 nm^3 in a HZSM-5 gel[2].

In these nanostructural units, it may be suggested that the interatomic distances and bond angles are unchanged with respect to the SM.

If this hypothesis is correct, the recrystallization of a solid similar to the starting material from the gel should be much

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less demanding than the original synthesis: it should require a lower temperature, shorter reaction time, and so forth.

This paper shows that the recrystallization of X-ray amorphous gels is easy, supporting the existence of a residual local order in the gel. New applications toward the synthesis of porous materials containing micro- and mesopores by assembling colloidal precursors at low temperatures should follow.

Since the work by Kloetsra et al.,[3] literally hundreds of references witness a growing interest for this field. For instance,[4] evidences for multimodal porosity were presented for colloidal silicalites treated with Pluronic P123.

Previously, a structure similar to MCM-41 had been recovered from a gel derived from MCM-41 using Mokaya's high-temperature secondary crystallization procedure.[5] However, from this interesting observation, nothing can be concluded concerning the local organization in the gel because of the deep rearrangement generated by the high-temperature treatment involved in the procedure.

Nanosized molecular sieves represent a relatively new topic drawing much attention, as illustrated, for instance, by numerous communications, at the zeolite meeting in Montpellier.[6−8] The self-assembly of colloidal precursors into ordered solids is exploited for obtaining solids with a bimodal distribution of pores.

Experimental Preparations

As described previously,[2] the preparation of the precursor gel was carried out by stirring vigorously the starting material in glycerol at temperatures near 200 °C, for periods of time up to 3 h. The gel, dissolved in an excess amount of glycerol, contains all the silica present in the starting material combined with the organic residue coming from the reaction with glycerol. The gel is stable, meaning that no visible deposit is visible after weeks or even months following the reaction with glycerol. The gel composition obtained from the chemical analysis is specified by the ratio C/Si and also by the percent of silica in the gel[2].

An experiment carried out on a gel prepared by heating at 180 °C, 10 g HY (CBV, Zeolist), over 1.5 h, in 100 mL glycerol, will be detailed. To 5 mL of that solution, corresponding to about 0.5 g of the starting silicate, was added 0.07 g of TMA (tetramethylammonium) and 3 mL of H_2O (0.018 mole TMA/1 mole SiO_2). The formation of a precipitate was immediate. Aging was performed by heating the mother glycerolic suspension, at 80 °C, for 3 h, 1 day, or 2 days. Afterward, the solid residue was washed by centrifugation 3 times at 6000 rpm for a cumulated time of 40 min and dried at 80 °C for 2 h. The loss of material is negligible because about 0.5 g of the solid is retrieved.

Table 1. Preparations R54-N to R59-T, C/Si ratio = 0.99, Obtained from Gel 23, Containing 66.9% SiO_2, and Those of R61-T to R64-N, C/Si Ratio = 0.81, Obtained from Gel 25, Containing 71.2% SiO_2[a,b]

label	starting gel	aging 80°C	additive	label	starting gel	aging 80°C	additive
R54-N	23, HY	1 day	NH_3	R61-T	25, HZSM-5	1 day	TPAOH
R55-N	23, HY	2 days	NH_3	R62-T	25, HZSM-5	2 days	TPAOH
R56-N	23, HY	6 h	NH_3	R63-N	25, HZSM-5	1 day	NH_3
R57-T	23, HY	1 day	TMA	R64-N	25, HZSM-5	2 days	NH_3
R58-T	23, HY	2 days	TMA				
R59-T	23, HY	6 h	TMA				

[a] The codes are the same as those in ref 2. [b] R64-N is not distinguishable from R63-N.

The other preparations were obtained similarly, as schematized in Table 1. The hydrolysis mediated by a surfactant was compared to the hydrolysis mediated by an ammoniac solution containing 17 moles of NH_3 per liter. The weights of the recovered solid were practically the same in both cases. The solids prepared as exemplified above are labeled R#-X [R for recrystallized and X = N for ammoniac and T for tetrapropylammonium hydroxide (TPAOH) or TMA].

For studying the recrystallization of HZSM-5, the precursor gel (identical to gel 25 in ref 2) was prepared from HZSM-5 (3 g of the starting material, SM/30 mL of glycerol at 180 °C). A very rapid hydrolysis of the precursor gel was obtained by mixing 5 mL of the gel dissolved in glycerol, 1 mL of 1N TPAOH solution, and 2 mL of H_2O or 0.65 mL of a NH_3 solution and 2 mL of H_2O. The samples were aged for 1 day and 2 days at 80 °C. After washing and drying at 80 °C, four samples labeled R61-T to R64-N were analyzed.

Experimental Techniques

The X-ray diffraction analyses (XRDs) of the crystalline silicates were recorded with a D-500 SIEMENS goniometer fitted with a graphite secondary beam monochromator filtering the Cu Kα1 radiation. The wide-angle XRD was recorded between 2 and 50° with a 2θ step of 0.02° and a 1 s counting time per point. To estimate the unit cell size, the XRDs were recorded according to ASTM-D3942-90.

The ^{29}Si MAS NMR spectra were obtained at 79.492 MHz, and a spinning frequency of 7.5 kHz; a zirconia rotor, 4 mm i.d.; and 90° pulses with 20 s intervals were used. The number of transients was 250.

^{27}Al MAS spectra were recorded at 104.3 MHz with 12° pulses and 1s intervals between pulses. The spinning rate was usually 10 kHz, and the number of transients was 300.

The FT-IR spectra were obtained using a Nicolet 5SX instrument fitted with a CsI optic from a KBr window coated with the gel or from KBr pellets containing 1% of the starting materials.

The deconvolution of the NMR or FT-IR spectra was achieved by using the Origin7 software. The procedures are described in ref 2. The silica cluster nomenclature is that proposed be Engelhardt and Michel.[9]

Surface area and porosity were measured with a Quantachrome Autosorb Automated Gas Sorption system. Outgassing at 300 °C overnight was always carried out before measurement.

Thermal techniques, thermogravimetric analysis, differential thermogravimetry, and differential scanning calorimetry, were used with a Jupiter Netzsch STA 449C instrument at a constant heating rate of 10 °C/min.

Experimental Results

1. Recrystallization of HY. The XRD, IR, and NMR spectra of the solids prepared with a surfactant or with

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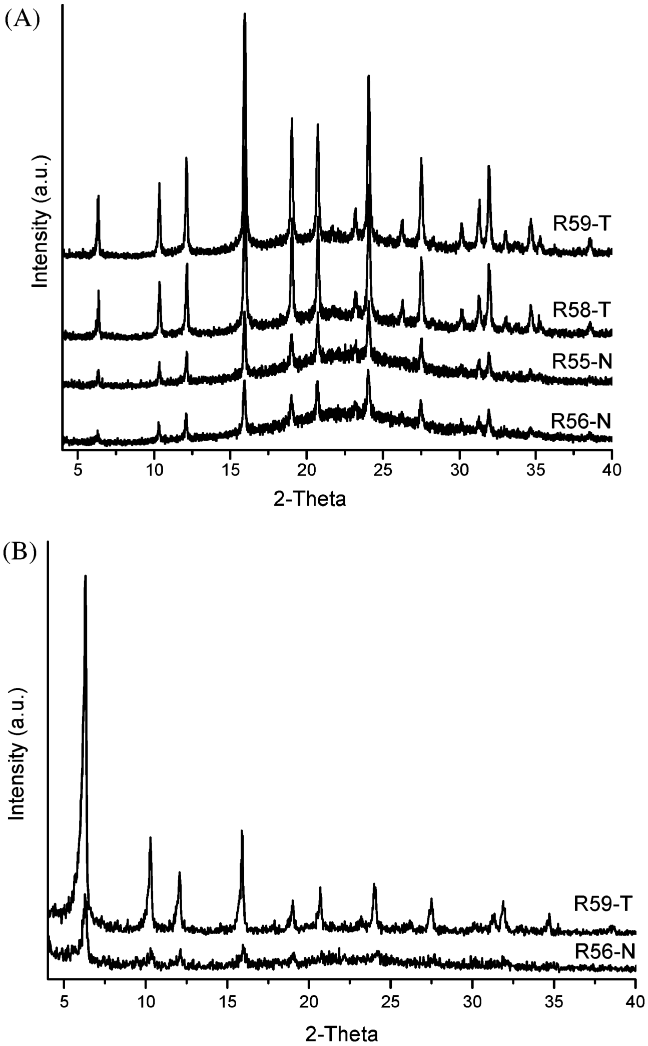

Figure 1. (A) XRD of the uncalcined, recrystallized material, R55-N to R59-T dried at 80 °C. (B) XRD of the recrystallized materials R56-N and R59-T, calcined slowly up to 550 °C. The heating rate was 100 °C/h.

ammonia will be systematically compared to those of the starting material from which the gel was obtained.[2]

The X-ray diffraction spectra of the samples obtained after hydrolysis with a surfactant and dried at 80 °C or calcined progressively up to 550 °C are displayed in Figure 1A and B. The percentage of crystallinity is appreciated as the ratio of the sum of the intensities of the diffraction lines to the total area of the halo generated by the amorphous material plus the area of the lines.

The average degree of crystallinity of the uncalcined samples obtained using ammonia was about 25%. It jumps to more than 50% in the presence of TMA. Table 2 compares the d_{hkl} spacings obtained by Parise et al.[10,11] for an ultrastable Y with composition $H_{18.9}Si_{175.7}Al_{18.9}O_{284,}$ (size a of the cubic unit cell = 24.188 Å) with those measured here for the samples dried at 80 °C.

Table 2. d_{hkl} (Å) of the Most Intense XRD Reflections Measured for the Materials Recrystallized from Gel 23 and Dried at 80 °C[a]

h,k,l	1,1,1	2,2,0	3,1,1	3,3,1	5,1,l	4,4,0	5,3,l	6,2,0	5,3,3	5,5,1	6,4,2
ref 10	13.96	8.55	7.29	5.55	4.65	4.28	4.09	3.82	3.68	3.39	3.23
R58-T	13.89	8.53	7.28	5.55	4.66	4.28	4.09	3.83	3.69	3.39	3.24
R59-T	13.96	8.55	7.29	5.56	4.66	4.28	4.09	3.83	3.69	3.39	3.24
R57-T	13.92	8.55	7.29	5.55	4.66	4.28	4.09	3.83	3.69	3.34	3.24
AVER	13.92	8.54	7.29	5.55	4.66	4.28	4.09	3.83	3.70	3.39	3.24
R54-N	13.81	8.50	7.26	5.53	4.65	4.27		3.82	3.69	3.38	3.23
R56-N	14.01	8.57	7.00	5.56	4.67	4.29		3.83	3.7	3.39	3.24
R55-N	13.94	8.55	7.3	5.56	4.67	4.28		3.84	3.7		3.24
AVER	13.92	8.53	7.29	5.55	4.66	4.28		3.82	3.69	3.37	3.24

[a] The averaged values (AVER) are shown. ref 10: $H_{18.9}Si_{175.7}Al_{18.9}O_{284}$, dealuminated USY, $(Si/Al)_{chem}$ = 9.3, lattice parameter a = 24.188 Å. A direct measurement of a in sample R-58-T gave 24.294 Å, the standard being SiO_2.

The excellent agreement observed for the recrystallized materials, R57-T, R58-T, and R59-T, prepared in the presence of TMA, and even those prepared using ammonia, indicates that a structure similar to that of ultrastable Y has been recovered.[11] The main difference between the XRD of the SM and that of the recrystallized materials, dried at 80 °C, Figure 1A, is the intensity distribution of the low-angle reflections. However, heating to 550 °C restores the intensity distribution, characteristic of dealuminated HY, in the samples treated with TMA, Figure 1B. Probably, calcination achieves the condensation of the dangling Si−OH bonds present in the hyperbranched silicon alkoxide gel. Again, when the hydrolysis of the precursor gel is carried out with ammonia, the recrystallization occurs to a lesser extent after calcination. Additionally, it should be noted that the length of the aging time does not influence noticeably the extent of recrystallization. The IR or NMR spectra confirm small range ordering.

In Figure 2A, the IR spectra of the HY starting material and gel 23 are reproduced. The contributions from the organic residue are mainly above 1200 cm^{-1}, while the framework vibrations are below. Four frequencies at 1047 ± 3, 1105 ± 10, 1156 ± 3, and 1205 ± 10 cm^{-1} were assigned to four stretching modes, ν_4, ν_3, ν_2, and ν_1, respectively, of the silicon tetrahedron. It was suggested[2] that the intensity of ν_4 could be a trustable measurement of the silanols or O−C substitutions. Both kinds of substitutions result indeed in an increase of the Si−O distance. A critical examination of the spectral region near 1050 cm^{-1} confirms the decrease of the intensity with respect to that in the initial gel, as expected if a condensation reaction occurs.

Considering the dealumination and aging patterns in fluid cracking catalysts, Hernandez-Beltrán et al.[12] have observed that the intensity of the so-called D6R vibration near 615 cm^{-1} increases as the Si/Al ratio increases or, alternatively, as the unit cell parameter a decreases.

In Figure 2B, it can be seen that the IR spectrum of R57-T reproduces in minute detail the spectrum of the starting HY. The NH_3 hydrolysis product shows the same general features but without the degree of resolution achieved for the pre-

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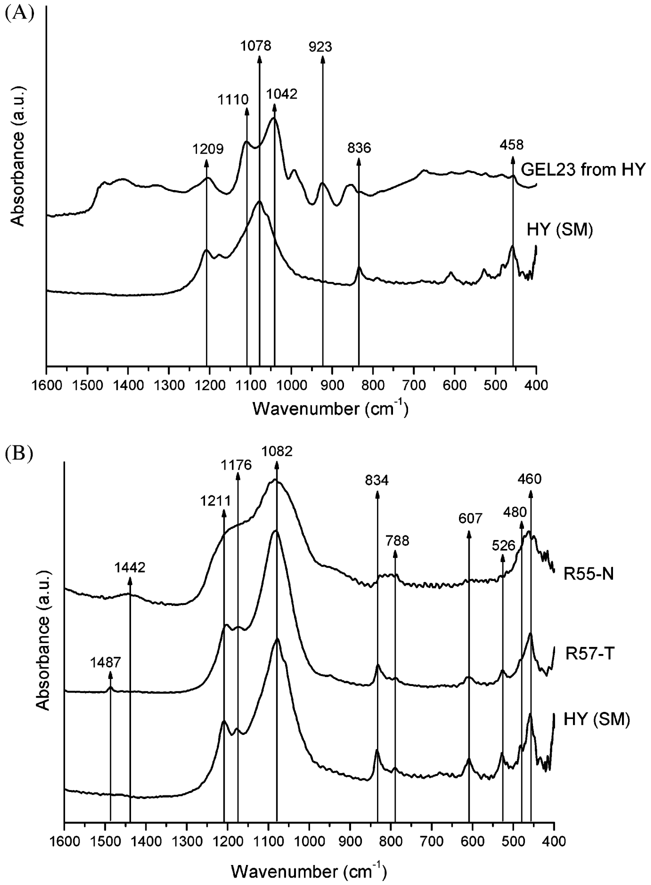

Figure 2. (A) IR spectra of gel 23 and the starting material HY. (B) IR spectra of uncalcined R55-N and R57-T and that of the starting material.

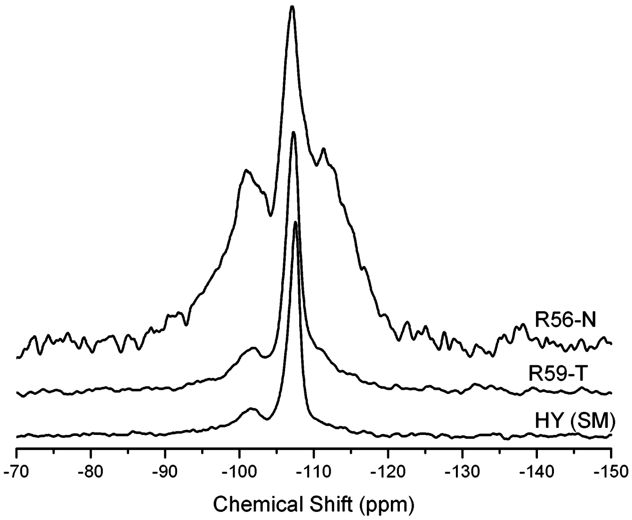

Figure 3. Comparison between the ^{29}Si MAS NMR spectra R56-N and R59-T and that of HY.

paration in the presence of TMA. In particular, the D6R band (at 607 cm^{-1}) is better defined in R57-T than in R55−N.

Another aspect of the gel transformation resulting from hydrolysis is revealed by the ^{29}Si and ^{27}Al MAS NMR spectra shown in Figures 3 and 4. The main results are summarized in Table 3. In the presence of a surfactant, the Q^4 and Q^3 silicon lines are very much the same in position and intensity as those in the starting HY or in the precursor gel 23^2.

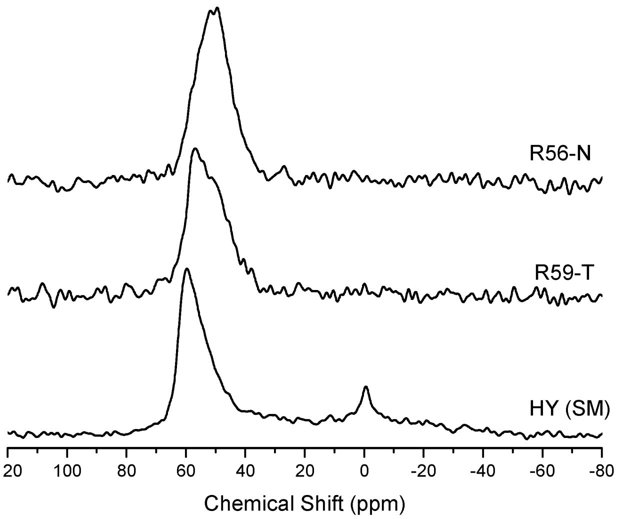

Figure 4. Comparison of the R56-N and R59-T ^{27}Al MAS NMR spectra with that of HY.

Table 3. NMR Parameters of the Starting Material, HY, and That of Samples R56-N and R59-T[a]

label	%Cry XRD	Q^4 [b]	intensity (%)	Q^4 (ppm)	fwhm (ppm)	Q^3 (ppm)	fwhm (ppm)	Si/Al	Al^{IV} (ppm)
HY	100			−107.5	1.8	−101.6	4.0	18.4	60
R59-T	50,1	−110.6	10.0%	−107.5	2.3	−102.2	5.3	23.2	56.4
R56-N	22,4	−112	66.6%	−107.0		−101.0		17.3	50.8

[a] The ^{29}Si chemical shifts of the Q^4 cluster in the amorphous gel 53 and those in the crystallized lattices HY and R59-T are identical. The manufacturer Si/Al ratio is 15. [b] Q^4 assigned to the residual amorphous material, see text.

At about −111 ppm, a new shoulder is observed. Its integrated area represents only 10% of the intensity of the sum of the intensity at −107 and −102 ppm. In the presence of ammonia, a stronger contribution is located at −112 ppm in R56-N. Because, according to the XRD in Figure 1A, the contribution of the amorphous fraction is larger in this sample, we suggest that the ^{29}Si lines at −111 or −112 ppm are attributable to a Q^4 cluster different from that in the zeolite (chemical shift at −107 ppm).

The Si/Al ratios obtained from the intensity of the line assigned to the Q^3 clusters are larger in the recrystallized samples than in HY.[9] For the SM HY used here, the NMR measurements, assuming there is no contribution of silanols, gives a Si/Al ratio equal to 18.4 instead of the 15 given by the manufacturer. Any SiOH contribution should decrease the apparent Si/Al ratio. Because the opposite is observed, there is probably a moderate loss of aluminum in the two successive transformations, namely, the depolymerization of HY and recrystallization. The disappearance of the line at about 0 ppm in the ^{27}Al spectra in Figure 4 supports this hypothesis. From the deconvolution of the ^{29}Si MAS NMR spectra in Figure 3, we got a Si/Al ratio between 17 and 23.

The textural parameters obtained from the low-temperature adsorption isotherms, in Figure 5A and B, and the Barret−Joyner−Halenda (BJH) procedure[13] are summarized in Table 4. They are in very good agreement with the structural

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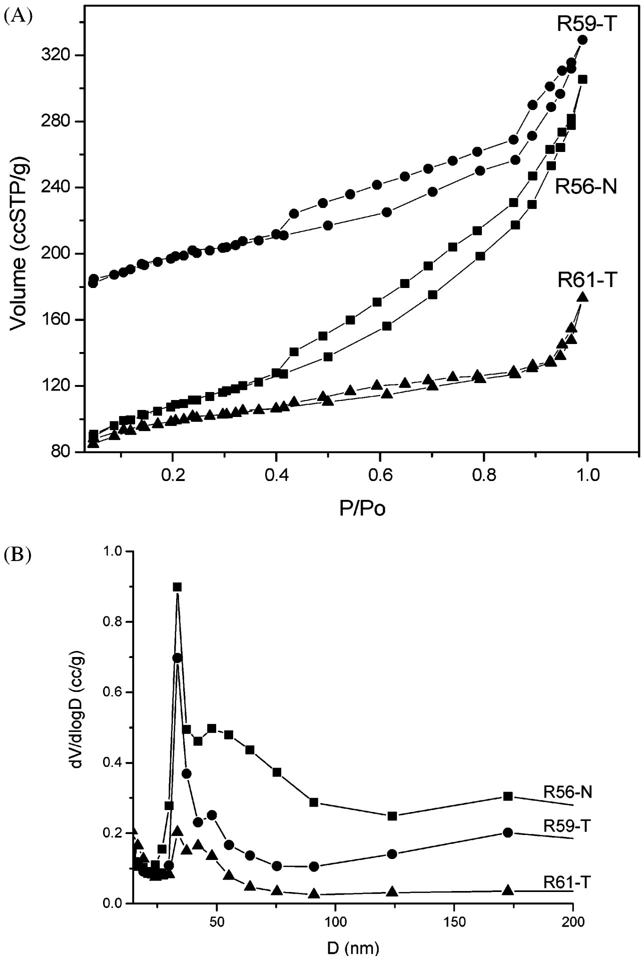

Figure 5. (A) N_2 adsorption−desorption isotherms of recrystallized zeolites outgassed at 300 °C. (B) Pore size distributions, BJH method applied to the desorption branch[13] of recrystallized zeolites outgassed at 300 °C.

Table 4. Textural Parameters Obtained from Low-Temperature N_2 Adsorption−Desorption Isotherms on Samples R56-N, R59-T, and R61-T, Calcined up to 550 °C, the Heating Rate Being 100°C/h[a]

parameters	R56-N	R59-T	R61-T
t-plot micropore *A*, m^2/g	144.8	421.8	254.2
t-plot external *A*, m^2/g	224.4	179.7	140.1
t-plot micropore *V*, cc/g	0.078	0.226	0.136
total pore *V*, cc/g	0.484	0.509	0.314
% micropore/pore volume	16	44	43
BET, m^2/g	369.2	601.6	394.3
HK micropore width, nm	0.141	0.138	0.136

[a] *A*: specific surface area. *V*: total volume of the pores.

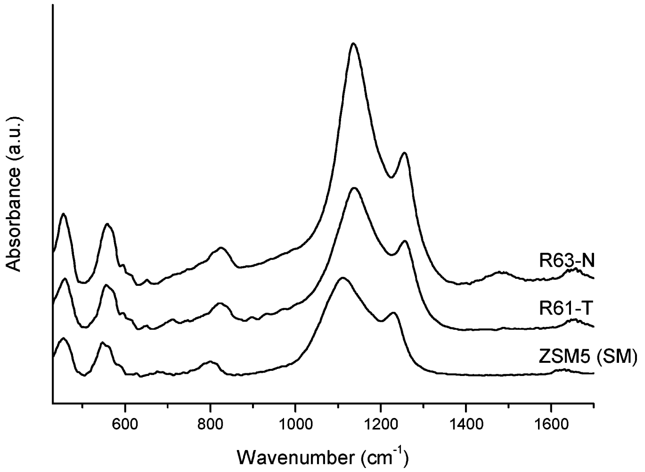

Figure 6. IR spectra of R61-T, R63-N, and the starting material HZSM-5.

data if we assume that R59-T is made from HY crystallites organized within mesopores at the intervention of TMA, whereas R56-N consists of a mixture of some crystallized HY and amorphous particles aggregated upon precipitation. The t-plot micropore volume and surface area are about 3 times larger in R59-T than in R56-N. In the pore size distributions in Figure 5B, maxima at 5 and 24 nm, both in the mesopore domain, are observed.

The "micropore" surface area represents the major contribution to the whole area in R59-T. The opposite observation holds for R56-N.

As far as the chemical shift of the ^{29}Si Q^4 NMR line is concerned, it is well-documented that it correlates strongly with α, the average Si−O−Si angle. The following empirical equation applies, with a linear correlation coefficient of 0.998, to silica polymorphs:[9]

$$\delta\ (\text{ppm}) = -55.821\ \text{s} \times \alpha - 176.65 \qquad \alpha = \forall\text{Si}-\text{O}-\text{Si}$$

The range of the Q^4 chemical shifts, shown in Table 3, correspond to the angular range from 143 to 149°, the larger values being those assigned to the amorphous material in admixture with the crystalline fraction in samples R59-T and R56-N.

2. Recrystallization of ZSM-5. The treatment applied to the HY gel has been repeated on gel 25 obtained from HZSM-5,[2] except that TMA was replaced by TPAOH, as shown in Table 1. Two solids were prepared, namely, R61-T and R62-T, aged 1 day or 2 days, respectively, at 80 °C in the mother solution, and washed by centrifugation. Another set of two samples was prepared using the NH_3 solution as the hydrolyzing agent. The experimental results are shown in Figures 6−8: the essential features of the ZSM-5 network are retrieved.

A comparison of the XRDs of the samples dried at 80 °C, Figure 7A, with those calcined at 550 °C, Figure 7B, shows the benefit brought about by the elimination of the dangling OH bonds on the intensity of the diffraction lines below 10°, as also observed for the recrystallized HY.

The IR spectra (Figure 6) as well as the XRD do not show marked differences between the samples prepared, using either the surfactant or the ammonia solution, in opposition to the observations reported for the HY recrystallization. The average degree of crystallization estimated from the XRD is 81 ± 0.2% (Figure 7A). In agreement with earlier observations, the length of the aging time, at 80 °C, is not important at the day scale. The silicon NMR spectra of Figure 8 show a perfect superimposition of the spectra of R61-T and R63-N, in agreement with the corresponding XRD in Figure 7 and the claim that the ZSM-5 recrystallization does not require a surfactant. When dealing with ZSM-5 ^{29}Si NMR, the most well-known difficulty is in assigning the lines due to two Q^4 clusters differing in the Si−O−Si angle. Their respective intensities are, therefore, uncertain, but this does not affect the value of the Si/Al ratio.

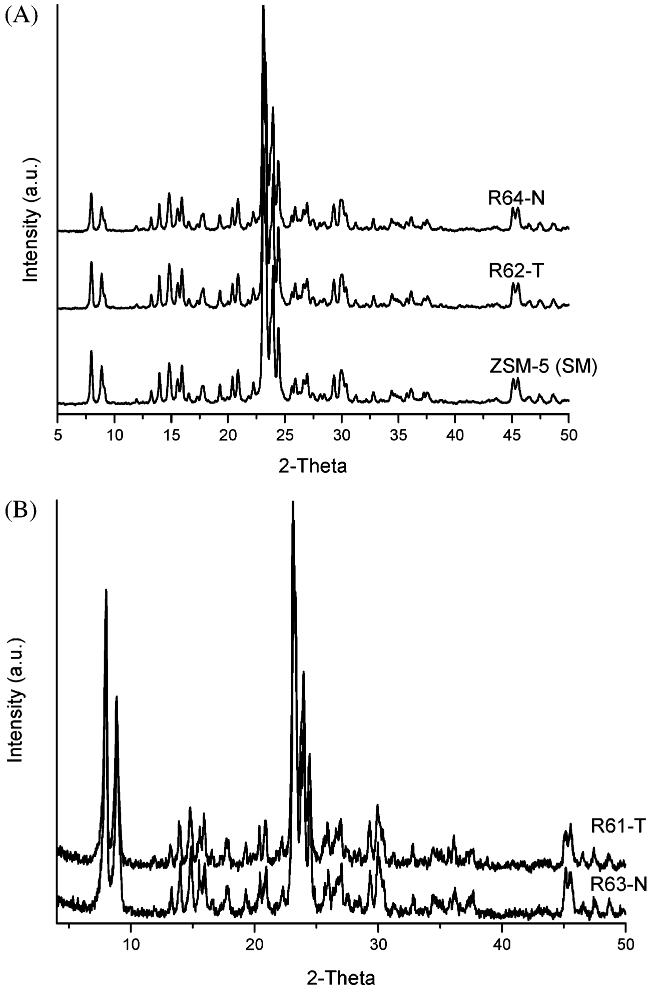

Figure 7. (A) XRD of the recrystallized R63-N and R61-T material, dried at 80 °C, and that of the SM, HZSM-5. (B) XRD of the same materials, calcined slowly up to 550 °C. The heating rate was 100 °C/h.

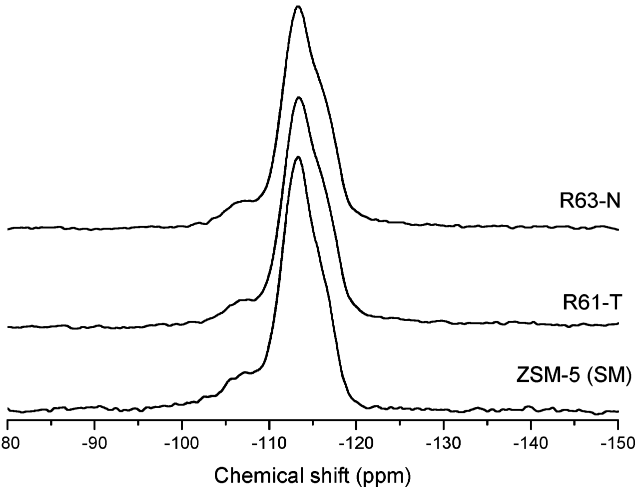

Figure 8. Quasi-identity of the ^{29}Si MAS NMR spectra of recrystallized materials R61-T and R63-N and that of HZSM-5.

The line at −108 ppm, assigned to a Q^3 cluster in ZSM-5, is weaker than that in the SM, but the loss of intensity was already noticeable in gel 25 as described earlier,[2] and it was interpreted by a loss of aluminum. The constancy of the chemical shifts in the recrystallized samples and that in the SM samples and the observation of two nonequivalent Q^4 tetrahedral silicon lines, independent of their intensity (Figure 8), are important features for understanding the recrystallization mechanism (Table 5), as will be shown in further studies. The ^{27}Al MAS NMR spectra (not shown) consist of a single resonance of tetrahedral aluminum at 54 ± 0.3 ppm.

Table 5. NMR Parameters of the Starting Material, HZSM-5, and That of Samples R61-T and R63-N and ^{29}Si Chemical Shifts of the Q^4 and Q^3 Clusters[a]

	Q^4 (ppm)	*W* (ppm)	Q^4 (ppm)	*W* (ppm)	Q^3 (ppm)	*W* (ppm)	Si/Al NMR
HZSM-5	−116.4	3.3	−113.1	3.7	−108.7	8.9	19
intensity %	22.1		56.8		21.0		
R61-T and R63-N	−115.8	4.6	−112.9	3.5	−108.0	6.7	33.5
intensity %	42.5		45.5		11.9		

[a] The manufacturer Si/Al ratio is 25 for HZSM-5.

In the recrystallized R61-T, the t-plot micropore area, in m^2/g, represents 81% of the total area, Table 4, in agreement with the high degree of crystallinity. There is also some mesoporosity, as shown by a weak maximum near 25 nm in the distribution of the porous volume in Figure 5B.

In conclusion, ZSM-5 can be recovered from the amorphous gel by simple precipitation with NH_3 or TPAOH, with the aging conditions playing a minor role. This aspect will receive careful consideration in the future.

Discussion

The very fast recrystallization of the gels obtained from HY and ZSM-5 is a strong argument in favor of the existence of a structural preorganization in these gels. In the case of HY, the TMA surfactant noticeably favors the crystallization, while TPAOH is not necessary for retrieving ZSM-5 from the gel.

Chemically, the gels are polyalkoxides characterized by a C/Si ratio close to 1. Physically, it has been suggested that they are composed of nano-units with a volume of about 1 nm^3. These small organized units play, most probably, the important role of seeds in the crystallization process. The main difference between the two starting gels is observed in the effect of the hydrolyzing agent.

A more perfect recrystallization process is observed by hydrolyzing the gel obtained from HY with an aqueous solution of the surfactant and water at 80 °C, as opposed to that obtained with an ammonia solution. Hydrolysis prepares SiOH groups that will ultimately interact with the surfactant micelles.

With ammonia, the random precipitation does lead to the formation of a long-range ordered solid in the case of the ZSM-5 structure and does not in the case of faujasite.

The main question is, thus, about the structural elements subsisting in the gel. It is appropriate to recall some results of earlier investigations on amorphous silicas, combining electron radial distribution[14] and IR.[15,16] The silicon tetrahedron characteristic geometry was independent of the synthesis procedure. The tetrahedral angle O−Si−O is almost

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(15) Fripiat, J. J.; Leonard, A.; Barake, N. *Bull. Soc. Chim. Fr.* **1963**, 122.
(16) Ratnasamy, P.; Leonard, A. J. *Catal. Rev.* **1972**, *6* (2), 293.

constant. The amorphous character results, in the first place, from the distribution of the Si−O−Si angles. In silica gels, it varies between 146 and 176°, while it is 180° in *β* cristobalite and 143° in α quartz.

Because of the constancy of the values of the ^{29}Si chemical shifts in the chain of transformations "crystallized solid → gel → recrystallized material", the main structural parameter surviving these transformations is probably the Si−O−Si angle. The angular misfits would be at the origin of the amorphization. The existence of unbounded oxygen, in silanol, or in Si−O−C bonds, the carbon belonging to a glycerol fragment, could, of course, generate such misfits. Up-to-date techniques, such as neutron diffraction, should shed light on the gel structures.

The fundamental question on the mechanism of the agglomeration of fragments within a long-range ordering also demands further studies.

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