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Crystallization and Spontaneous Phase Transformation of MTN-Type Zeolite with Tetragonal Symmetry

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MTN-type zeolite with tetragonal symmetry was hydrothermally synthesized in a reactant system of Na_2O–SiO_2–NaF–H_2O using *N*-ethyl-hexamethylenetetraammonium bromide as the template. A spontaneous phase transformation of the as-synthesized zeolite at ambient temperature from tetragonal to cubic symmetry was investigated with polarized light microscopy, X-ray powder diffraction, ^{29}Si magic angle spinning nuclear magnetic resonance, and differential scanning calorimetry. The results of the investigations indicate that the as-synthesized tetragonal MTN zeolite is a metastable phase. © 2002 Elsevier Science (USA)

Key Words: **MTN zeolite; spontaneous phase transformation; *N*-ethyl-hexamethylenetetraammonium bromide.**

INTRODUCTION

MTN-type zeolite, also known as ZSM-39 (1), CF-4 (2), dodecasil-3C (3), and holdstite (4), has long been considered as one member of the clathrasils. A unit cell of the zeolite Si–O framework is constructed by eight [$5^{12}6^4$] and eight [5^{12}] cages. The [$5^{12}6^4$] cage, the larger one containing guest molecules, is composed of 5- and 6-oxygen-membered rings, which are too small to let the encaged ions and/or molecules pass through freely. This leads to its almost uselessness in adsorption, separation, and catalysis, although this kind of zeolite has potential as an advanced nonlinear optical material, especially that with tetragonal symmetry (5).

MTN-type zeolites of tetragonal structure have been synthesized using methylamine (2), pyridine (5), and tetrahydrofuran (THF) (6) as the structure directing agent associated with glycerin (2), HF solution (5), and ethylenediamine (6), respectively, whereas cubic MTN zeolites have been obtained using tetramethyl- or tetraethylammonium hydroxide (1, 7), pyrrolidine or propylamine (8), 2-aminopropane or 2-amino-2-methylpropane (9), and tetramethylethylenediamine (TMEDA) (10) as the template.

Many papers have been published dealing with the phase transformation of zeolites and zeolite-like analogues. The high-resolution ^{29}Si MAS NMR spectra show that siliceous MFI-type zeolite (silicalite-I) changes from monoclinic symmetry to orthorhombic induced by adsorbing *p*-xylene (11). A cubic–tetragonal symmetry transition of siliceous FAU zeolite upon the loading of ethylamine into the framework was investigated via XRD, ^{29}Si MAS NMR, and FT-IR (12). Similarly, the clathrasil family also suffers serious handicaps as advanced materials due to the problem of its phase stability. It is also well known that the framework symmetry of MTN-type zeolite is quite flexible. In general, the cell of MTN-type zeolite has an ideal cubic structure, for which there are three types of Si sites, T_1, T_2 and T_3, identified by three lines with the intensity ratio of 8:32:96 expected in the ^{29}Si MAS NMR spectrum, whereas some samples show a well-resolved triplet for the T_3 site after calcination or dealumination indicating a lower symmetry structure (13–17). A reversible, thermally induced phase transition in clathrasil dodecasil-3C (MTN) with tetragonal symmetry has been reported (5, 6, 18). Synchrotron powder diffraction analysis results indicated that as the temperature was lowered there were four space groups of MTN-type zeolite: *Fd*3*m* (cubic symmetry), *I*4/*amd* (tetragonal symmetry), *Imma* (orthorhombic symmetry), and *C*2/*m* (monoclinic symmetry) (18). The tetragonal structure began to transfer into cubic symmetry when the temperature was elevated to about 75°C, and transferred into an orthorhombic structure upon cooling to -5°C. As the temperature was lowered to nearly -20°C the orthorhombic structure started to change. The ultra-high-resolution ^{29}Si MAS NMR spectra of MTN-type zeolite exhibited the differences of these phase structures (18).

The symmetry transformation from tetragonal to cubic for MTN-type molecular sieves is found not only in a thermally induced process but also in a spontaneous process

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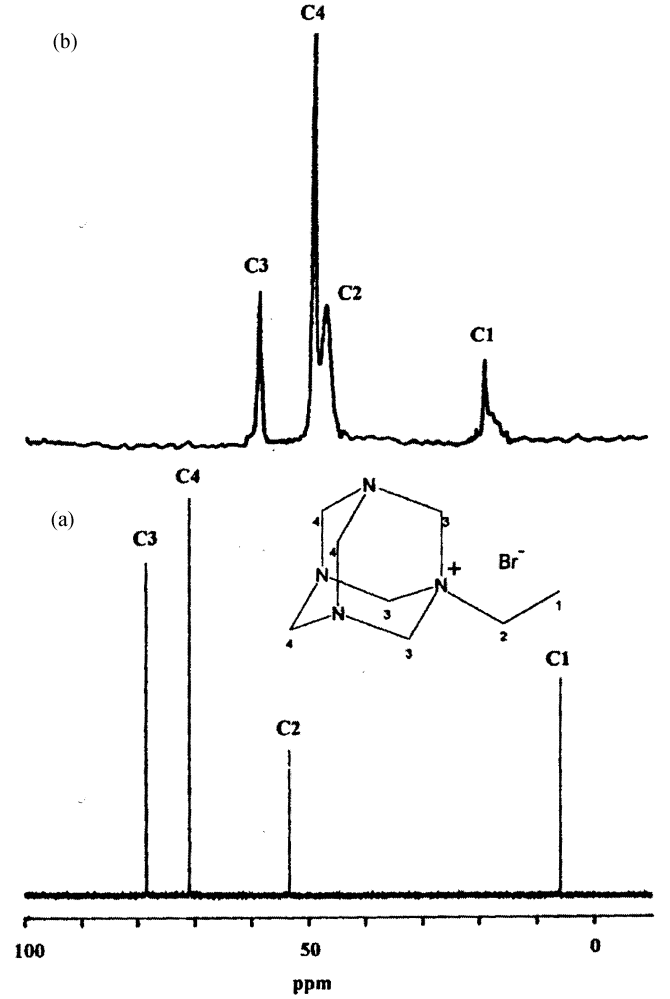

FIG. 1. (A) ^{13}C NMR (500 MHz, D_2O) spectrum of $EtHMTA^+Br^-$, and (B) ^{13}C CP MAS NMR spectrum of $EtHMTA^+$ encaged in as-synthesized EtHMTA-CF-4. Structure of $EtHMTA^+Br^-$ and position number are also shown.

which takes place at ambient temperature as we have observed. In this work, *N*-ethyl-hexamethylenetetraammonium bromide ($EtHMTA^+Br^-$, whose structure is given in Fig. 1), a derivative of hexa-methylenetetraamine, is first used for synthesizing single crystals of MTN-type zeolite with tetragonal symmetry. A spontaneous process of symmetry transformation is investigated in detail by powder X-ray diffraction (XRD), polarized light microscope, ^{29}Si magic angle spinning nuclear magnetic resonance (MAS NMR), and differential scanning calorimetry (DSC).

EXPERIMENTAL

Synthesis of Structure-Directing Agent (SDA)

N-Ethyl-hexamethylenetetraammonium bromide ($EtHMTA^+Br^-$), the structure-directing agent for synthesizing tetragonal MTN zeolite, was prepared as follows: hexamethylenetetraamine (70 g, 0.5 mol) was dissolved in chloroform (500 ml), followed by dropwise addition of ethylbromide (37.3 ml, 0.5 mol). The whole mixture was stirred at reflux at 40°C for 24–48 h until a great deal of white precipitate appeared. The product was filtered, washed with chloroform, and dried in air at 60°C. The synthesis was quite reproducible among several experiments and the yields of well-crystallized products ranged from 80% to 90%.

Preparation of MTN-Type Molecular Sieve with Tetragonal Symmetry

The MTN-type molecular sieve sample used in this study was hydrothermally synthesized from a reactant system of EtHMTA–Na_2O–SiO_2–NaF–H_2O. Tetraethylorthosilicate (TEOS) of reagent grade was used as the silica source. In a typical preparation, $EtHMTA^+Br^-$ (13.695 g), distilled water (32.3 g), and an aqueous solution of NaOH (10%, 4.40 g) were mixed with stirring in a plastic vessel. TEOS (11.62 g) was then added and the mixture was stirred at ambient temperature for 8–12 h allowing evaporation of ethanol to form a transparent clear solution. An aqueous solution of NaF (10%, 9.24 g) and 80 mg of CF-4 crystal seeds synthesized in a methylamine–glycerin–SiO_2–H_2O system (2) were then added into the clear solution. A homogeneous sol of the reactant was formed after vigorous stirring for 0.5 h with the molar composition of 1.0 EHMTA $^+Br^-$:0.1 Na_2O:0.4 NaF:1.0 SiO_2:45 H_2O. The sol was sealed in Teflon-lined stainless-steel autoclaves of 40 ml and reacted under autogeneous pressure at 200°C for 2–4 days. The product was filtered, washed with distilled water, and dried in air at room temperature.

Characterization

The crystal morphology and interference color were observed using an AO Micro Star optical microscope with crossed Nicols and a gypsum plate inserted. XRD patterns of the sample were recorded by a Rigaku D-MAX/Π A X-ray powder diffractometer with Cu$K\alpha$ radiation ($\lambda = 0.15418$ nm) in the 2θ range of 5–40° at a scanning speed of 8°(2θ)/min, and in the 2θ range of 28–40° at a scanning speed of 2° (2θ)/min.

The DSC spectrum was collected on a Setaram Differential Scanning Calorimetry 92 spectrometer. About a 20-mg sample of as-synthesized MTN molecular sieves was used for a measurement. The temperature was elevated from − 70°C to 200°C at a rate of 10°C/min in a nitrogen atmosphere.

^{29}Si MAS NMR spectra were recorded at room temperature using a Bruker MSL-300 spectrometer. The ^{29}Si resonance frequency used was 59.627 MHz, and the rotor was spun at 4.0 kHz. The radio frequency field was 37.0 kHz,

TABLE 1
Examples for Synthesis of MTN-Type Zeolite

No.	Silica source	Molar ratio of the reactant SiO_2	R^+Br^-[a]	Na_2O	H^+	F^-	H_2O	Initiation of reaction	T(°C)	t(days)	Product
1	WG[b]	1.0	1.0	0	0.95	0	40	Spontaneously	180	25	Amorphous
2	WG[b]	1.0	1.0	0	0.95	0	40	Spontaneously	200	20	Amorphous and ZSM-39
3	WG[b]	1.0	1.0	0	0.95	0.4	40	Spontaneously	180	20	Amorphous
4	WG[b]	1.0	1.0	0	0.95	0.4	40	Spontaneously	200	20	α-Quartz and amorphous
5	WG[b]	1.0	1.0	0	0.95	0.4	40	Seeds of CF-4	200	7	A[c]
6	TEOS	1.0	1.0	0	0	0.4	40	Seeds of CF-4	180	12	A[c]
7	TEOS	1.0	1.0	0	0	0.4	40	Seeds of CF-4	200	17	Cristobalite
8	TEOS	1.0	1.0	0.1	0	0.4	45	Seeds of CF-4	160	10	A[c]
9	TEOS	1.0	1.0	0.1	0	0.4	45	Seeds of CF-4	180	6	A[c]
10	TEOS	1.0	1.0	0.1	0	0.4	45	Seeds of CF-4	200	2	A[c]

[a] R^+ = *N*-ethyl-hexamethylene tetraammonium cation. [b] WG = sodium silicate aqueous solution (SiO_2 wt% = 24.83, Na_2O wt% = 7.22). [c] A = Et HMTA-CF-4.

corresponding to a $\pi/3$ pulse width of 4.5 μs, the reversing angle was 60°, and the recycle time was 10 s. Q_8M_8 (trimethylsilyl ester of cubic octameric silicate) was used as a second reference for the ^{29}Si chemical shift. The ^{13}C-resonance frequency was 75.468 MHz, and the rotor was spun at 4.0 kHz. The radio frequency field was 50 kHz, corresponding to a $\pi/2$ pulse width of 5.0 μs, the reversing angle was 60°, and the recycle time was 3 s. For each measurement 2000–6000 spectra were accumulated. Adamantane was used as a second reference for the ^{13}C chemical shift.

RESULTS AND DISCUSSION

^{13}C MAS NMR Spectra

The ^{13}C NMR (500 MHz, D_2O) spectrum shown in Fig. 1A indicates four resonance peaks for $EtHMTA^+Br^-$ at 5.86, 53.41, 70.93, and 78.52 ppm, corresponding to C_1, C_2, C_4, and C_3, respectively. This fact proves that the product of $EtHMTA^+Br^-$ synthesized using the method described in the Experimental section is a pure phase without impurities.

Figure 1B shows the ^{13}C MAS NMR spectrum of $EtHMTA^+$ trapped in $[5^{12}\,6^4]$ cages of the as-synthesized zeolite. Four peaks of ^{13}C resonance indicate that the template of $EtHMTA^+$ keeps intact in the cage. On the other hand, an obvious movement of the resonance positions in comparison with those of the $EtHMTA^+\ Br^-$ dissolved in D_2O evidences a strong interaction between the framework of the zeolite and the template.

Crystallization of MTN-Type Molecular Sieve with Tetragonal Symmetry

The molar composition of the reactant and the reaction conditions for preparing single crystals of MTN molecular sieves with tetragonal symmetry are listed in Table 1. When a sodium silicate aqueous solution (24.83 wt% SiO_2, 7.22 wt% Na_2O) was used as the silica source, a certain amount of H_2SO_4 (10%) was added to neutralize the excess

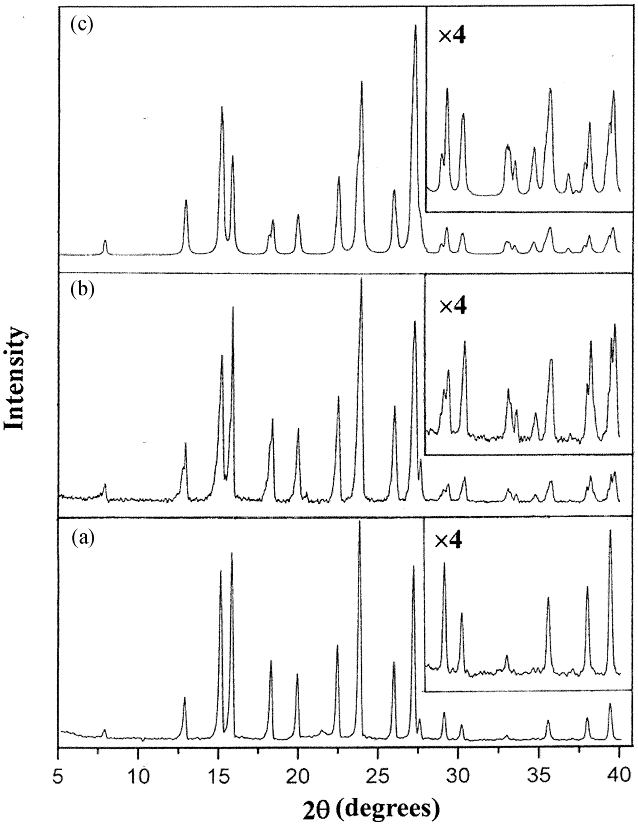

FIG. 2. XRD patterns of (A) as-synthesized EtHMTA-ZSM-39 and (B) EtHMTA-CF-4, and (C) the simulated one of pyridine dodecasil-3C (5) of tetragonal structure with Powder Cell program (19). XRD peaks in the 2θ range of 28°–40° with intensities 4 times the origin are shown in inset sections.

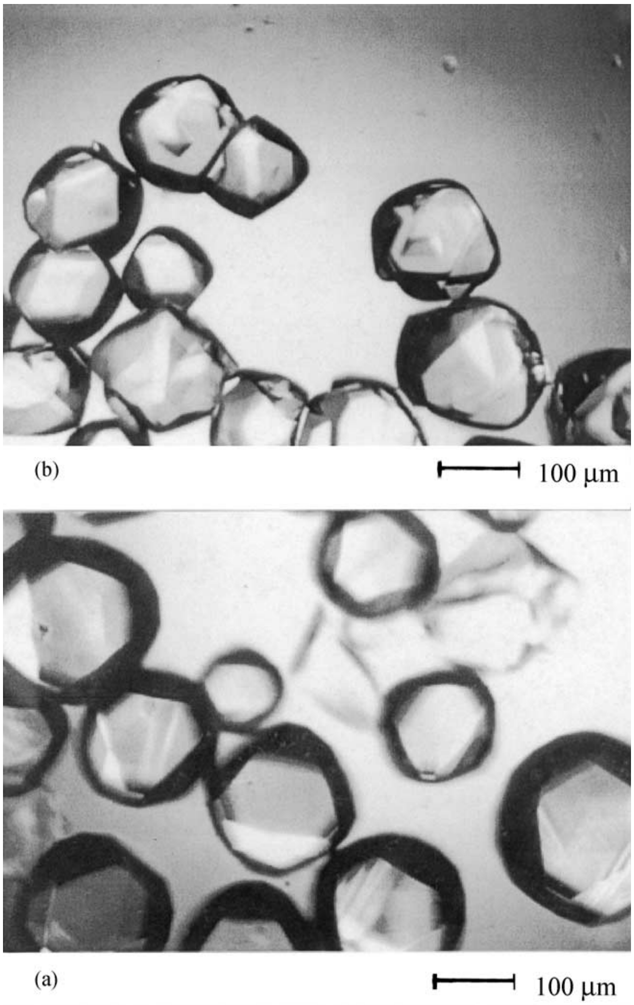

FIG. 3. Optical microscope photographs under polar light of (A) as-synthesized EtHMTA-CF-4 and (B) EtHMTA-CF-4 30 days later.

Na_2O. At higher reaction temperature (200°C) the cubic structure of MTN zeolite named EtHMTA-ZSM-39 (whose XRD pattern is shown in Fig. 2A) crystallized from the reactant in the absence of NaF. While in the presence of NaF, MTN-type zeolite with tetragonal symmetry named EtHMTA-CF-4 was obtained at the same reactant temperature. Thus, it can be inferred that the presence of NaF in the reactant plays an important role in the crystallization of tetragonal structure. Moreover, it is found that the gel can be kept a long time without nucleation of any zeolite phase without seeding in the reactant. The speed of nucleation of the starting reactant gel depended on the crystal seeds added. When TEOS was used as the silica source to replace sodium silicate aqueous solution, a small amount of NaOH (10%) was added to control the basicity of the reactant for improving the crystallization process of tetragonal MTN zeolite. Additionally, crystallization is also dependent on the reaction temperature. The EtHMTA-CF-4 phase was obtained only in the temperature range of 160–200°C. Single crystals of pure EtHMTA-CF-4 crystallized in 2 to 4 days at 200°C with the preferred reactant composition listed in Table 1, No. 10. Figures 2B and 3A exhibit the XRD pattern and the morphology of the crystals, respectively.

The XRD patterns of the as-synthesized ZSM-39 phase and the CF-4 phase and a simulated pattern of dodecasil-3C with tetragonal symmetry (5) are shown in Fig. 2. The cubic phase and the tetragonal phase show an obvious difference in the position and the number of diffraction peaks in the 2θ range of 28–40° shown in the inset of Fig. 2. Both observed and calculated XRD data of MTN-type zeolites with cubic and tetragonal symmetry are listed in Tables 2 and 3, respectively, to identify the variety of MTN frameworks of

TABLE 2
X-ray Powder Diffraction Data of MTN-Type Zeolite with Tetragonal Symmetry

h	k	l	$2\theta(°)$,[a] observed	d(Å),[a] observed	d(Å),[b] calculated	I/I_0(%),[a] observed
1	0	1	7.880	11.210	11.202	7.1
1	1	2	12.816	6.902	6.874	13.8
2	0	0	12.938	6.837	6.831	25.6
1	0	3	15.100	5.862	5.886	31.4
2	1	1	15.239	5.809	5.832	61.6
2	0	2	15.886	5.574	5.601	86.5
0	0	4	18.240	4.860	4.892	24.6
2	2	0	18.389	4.821	4.830	36.9
2	1	3	20.092	4.416	4.459	31.5
3	1	0	20.527	4.323	4.320	4.7
3	1	2	22.513	3.946	3.952	47.6
3	0	3	23.898	3.720	3.734	56.3
3	2	1	23.921	3.717	3.720	100
2	2	4	26.022	3.421	3.437	42.3
3	2	3	27.273	3.267	3.276	75.3
4	0	2	27.780	3.209	3.225	17.2
1	1	6	28.863	3.091	3.090	6.6
3	3	2	29.121	3.064	3.071	12.1
3	0	5	30.150	2.962	2.968	8.0
3	2	5	32.870	2.723	2.722	6.8
5	0	1	32.970	2.715	2.706	6.6
4	3	1	32.970	2.715	2.706	6.6
5	1	0	33.330	2.686	2.679	3.8
4	2	4	34.545	2.594	2.591	2.8
2	1	7	35.192	2.548	2.542	3.2
4	1	5	35.383	2.536	2.528	6.5
4	3	3	35.497	2.527	2.520	7.0
5	0	3	35.497	2.527	2.520	7.0
3	0	7	37.755	2.381	2.382	5.0
5	2	3	37.972	2.368	2.364	9.8
3	3	6	39.275	2.292	2.291	9.3
6	0	0	39.458	2.282	2.277	11.6

[a] 2θ, d, and I/I_0 values are observed from as-synthesized EtHMTA-CF-4 with tetragonal symmetry. [b] d values are calculated from Py-D3C of tetragonal symmetry (5) with a unit cell of $a = b = 13.6620$ Å, $c = 19.5669$ Å, $V = 3652.17$ Å^3.

TABLE 3
X-Ray Diffraction Data of MTN-Type Zeolite with Cubic Symmetry

h	k	l	$2\theta(°)$,[a] observed	d(Å),[a] observed	d(Å),[b] calculated	I/I_0(%),[a] observed
1	1	1	7.890	11.196	11.208	4
2	2	0	12.910	6.852	6.864	9
3	1	1	15.140	5.847	5.853	38
2	2	2	15.820	5.597	5.604	95
4	0	0	18.290	4.847	4.853	16
3	3	1	19.950	4.447	4.453	17
4	2	2	22.450	3.957	3.962	30
3	3	3	23.830	3.731	3.736	100
5	1	1	23.830	3.731	3.736	
4	4	0	25.980	3.427	3.432	20
5	3	1	27.190	3.277	3.281	51
4	4	2	27.580	3.232	3.235	6
6	0	0	27.580	3.232	3.235	
6	2	0	29.110	3.065	3.069	7
5	3	3	30.200	2.957	2.960	5
6	2	2	30.560	2.923	2.926	
5	5	1	32.970	2.715	2.718	2
7	1	1	32.970	2.715	2.718	
5	5	3	35.540	2.524	2.527	6
7	3	1	35.540	2.524	2.527	
8	0	0	37.070	2.423	2.427	1
7	3	3	37.960	2.368	2.372	8
6	4	4	38.250	2.351	2.354	
8	2	0	38.250	2.351	2.354	1
6	6	0	39.410	2.284	2.288	9
8	2	2	39.410	2.284	2.288	

[a] 2θ, d, and I/I_0 values are observed from the phase of EtHMTA-ZSM-39 with cubic symmetry. [b] d values are calculated from ZSM-39 (1) of cubic symmetry with a unit cell of $a = 19.41$ Å, $V = 7312.7$ Å^3.

as-synthesized ZSM-39 and CF-4. A perfect agreement of observed and calculated XRD data confirms that CF-4 and ZSM-39 prepared in the starting gel system are pure phases of MTN-type zeolite with tetragonal and cubic symmetry, respectively.

Observation on Polarized Light Microscope

In general, a strong interference color caused by birefringence can be observed on the single crystals up to a certain size (e.g., 50 μm) with various symmetry except cubic using polarized light microscope. Figure 3A shows a photograph of EtHMTA-CF-4 crystals with strong interference colors which was taken on the microscope. Moreover, we have found that the strong interference colors vanished gradually at ambient temperature as time went on, and 30 days later they disappeared completely as shown in Fig. 3B. This phenomenon implies the possibility of a symmetry transformation from tetragonal to cubic during the process.

XRD Patterns

XRD patterns of the as-synthesized CF-4 phase in the angle range of 28–40° recorded at ambient temperature and at various times after the phase was obtained are shown in Fig. 4. The gradual loss of the doublet for the peaks at 29.1°, 32.9°, 37.9°, and 39.4° took place respectively, which corresponds to the changes of interference colors of the single crystals.

The variation of the position and the number of peaks in a selected scanning range are not obvious at the beginning of the phase transformation process. During the first 10 days, there is a slight change of the doublet for the peaks at about 29.1°, 32.9°, 37.9°, and 39.4°, (2θ), respectively, while in the last 15 days, the double peaks combine quickly. Thirty days later the XRD pattern of EtHMTA-CF-4 phase in the angle range of 28–40° is the same as that of the EtHMTA-ZSM-39 phase. The Miller indexes for each peak of tetragonal and cubic structure are listed in Tables 2 and 3, respectively. The Miller indexes corresponding to the peaks in the XRD pattern of EtHMTA-CF-4 at 28.863°, 32.870°, 37.755°, and 39.275° are (116), (325), (307), and (336), respectively. During the process, both the (325) peak at 32.87° and the (307) peak at 37.76° move to higher angle and combine with peaks at 32.97° and 37.96°, respectively, while the (116) peak at 28.863° and the (332) peak at 29.121, the (336) peak at 39.275°, and the (600) peak at 39.458° overlapped with each other at 29.11° and 39.41°, respectively. The result of the investigation on XRD patterns proves the existence of the phase transformation of as-synthesized EtHMTA-CF-4 from tetragonal to cubic symmetry at ambient temperature.

DSC Investigation

DSC curves of as-synthesized EtHMTA-CF-4 established the existence of three phases in the temperature range of − 71°C to 200°C. Two weak transition peaks (Fig. 5) were observed at − 31°C and 71°C for EtHMTA-CF-4 prepared using TEOS as the silica source. A transformation (see Fig. 5A) starts at 67°C and ends at 74°C. Another phase transformation commences at − 32.5°C, and finishes at − 29.5°C. This phase transformation, which is observed on the as-synthesized EtHMTA-CF-4 single crystals with XRD and optical polarized light microscopy, takes place in the temperature range of 0–30°C which is not located in the phase transition temperature range shown on DSC curves. Thus, it can be concluded that the phase transformation process of EtHMTA-CF-4 is not due to the changes of the temperature at 71°C shown on DSC curve for a tetragonal–cubic transformation, that is, not a thermally induced phase transformation process as reported before (18). Therefore, the phase transformation is a spontaneous process.

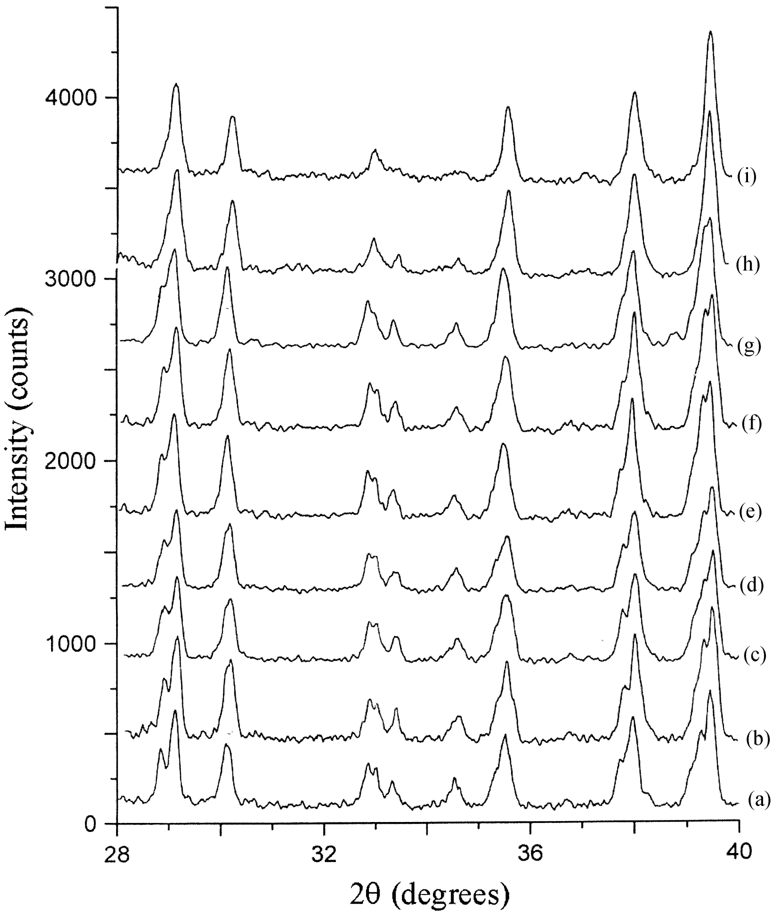

FIG. 4. XRD patterns of as-synthesized EtHMTA-CF-4 recorded at different times, after (a) 0 days, (b) 2 days, (c) 5 days, (d) 10 days, (e) 15 days, (f) 20 days, (g) 25 days, and (h) 30 days. XRD pattern of (i) EtHMTA-ZSM-39.

The phase transformation behavior of as-synthesized EtHMTA-CF-4 was different from that reported for the MTN-type zeolite synthesized using the template of pyridine (5), tetrahydrofuran/N_2, or tetrahydrofuran/Xe (6). J. S. Tse *et al.* reported that distinct guest molecules interact differently with the host lattice cages, which tends to cause different distortions from ideal symmetry (18). The configuration of $EtHMTA^+$ as the template is obviously different from that of the templates used for synthesizing MTN zeolite reported. It seems that the interaction between the framework and EtHMTA is different from that between the host cage and the templates reported (5, 6), which leads to a metastability of the phase of the as-synthesized EtHMTA-CF-4 at ambient temperature.

^{29}Si MAS NMR

The ^{29}Si MAS NMR spectra recorded at different stages of the phase transformation process are shown in Fig. 6. The spectrum of as-synthesized sample of EtHMTA-CF-4 shows five lines with an intensity ratio of 1:4:4:4:4, which is consistent with the spectrum of MTN-type molecular sieves with tetragonal symmetry (5, 6, 18). It deviates from the cubic symmetry by the loss of the threefold [1,1,1] symmetry axis. As time goes on, there is a clear change in the triplet peak of the T_3 site. Two peaks at -117.0 and -119.6 ppm become weaker gradually and combine with the peak at -118.0 ppm 30 days later. Meanwhile, the spectrum of EtHMTA-CF-4 at this time shows three resonances of intensity ratio of 1:4:12 as is expected for a perfect cubic lattice, confirming the deduction from the observation by polarized light microscopy and XRD.

The ^{29}Si MAS NMR spectra reflect a transformation from the tetragonal structure to the cubic symmetry. This phenomenon is bound to occur if the Si–O bond lengths are too short to accommodate the lattice structure exactly, causing a strain and subsequent distortion from the ideal symmetry (1). Thus, the phase structure with a lower symmetry is so unstable that it would change to the ideal symmetry by lattice expansion as time goes on.

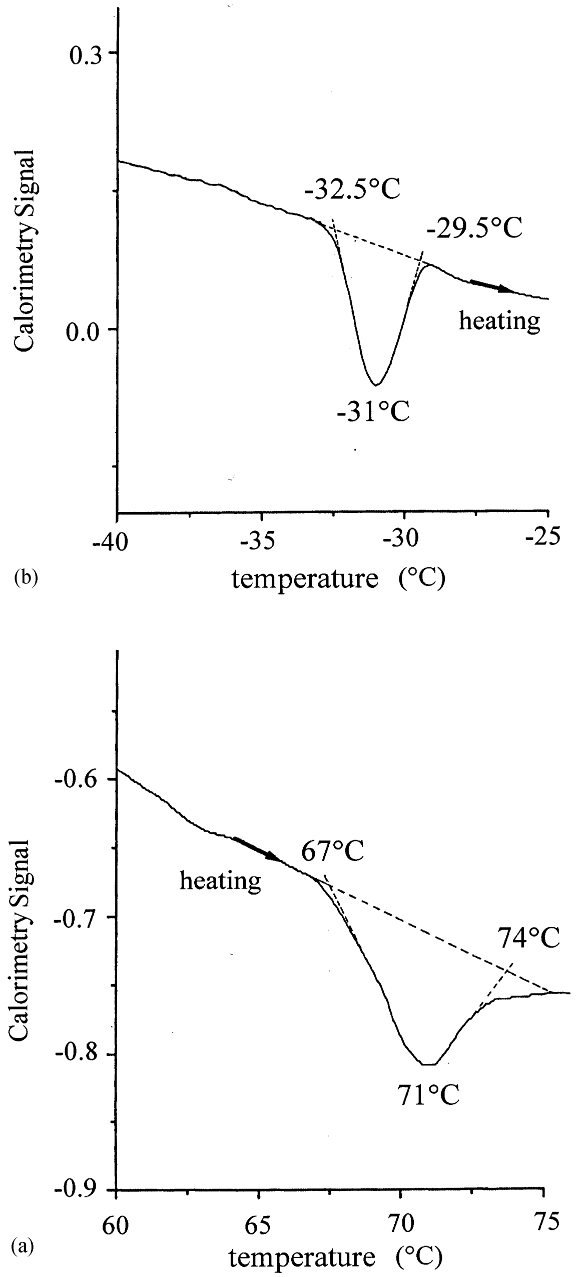

FIG. 5. Differential scanning calorimetry curves for EtHMTA-CF-4.

CONCLUSION

Tetragonal MTN molecular sieves can be hydrothermally synthesized in the reactant system of EtHMTA–Na_2O–SiO_2–NaF–H_2O, in which TEOS was used as the silica source. Observations by polarized light microscopy, XRD, ^{29}Si MAS NMR, and DSC prove the spontaneous transformation from tetragonal to cubic symmetry at ambient temperature for the as-synthesized MTN-type zeolite using $EtHMTA^+Br^-$ as the template.

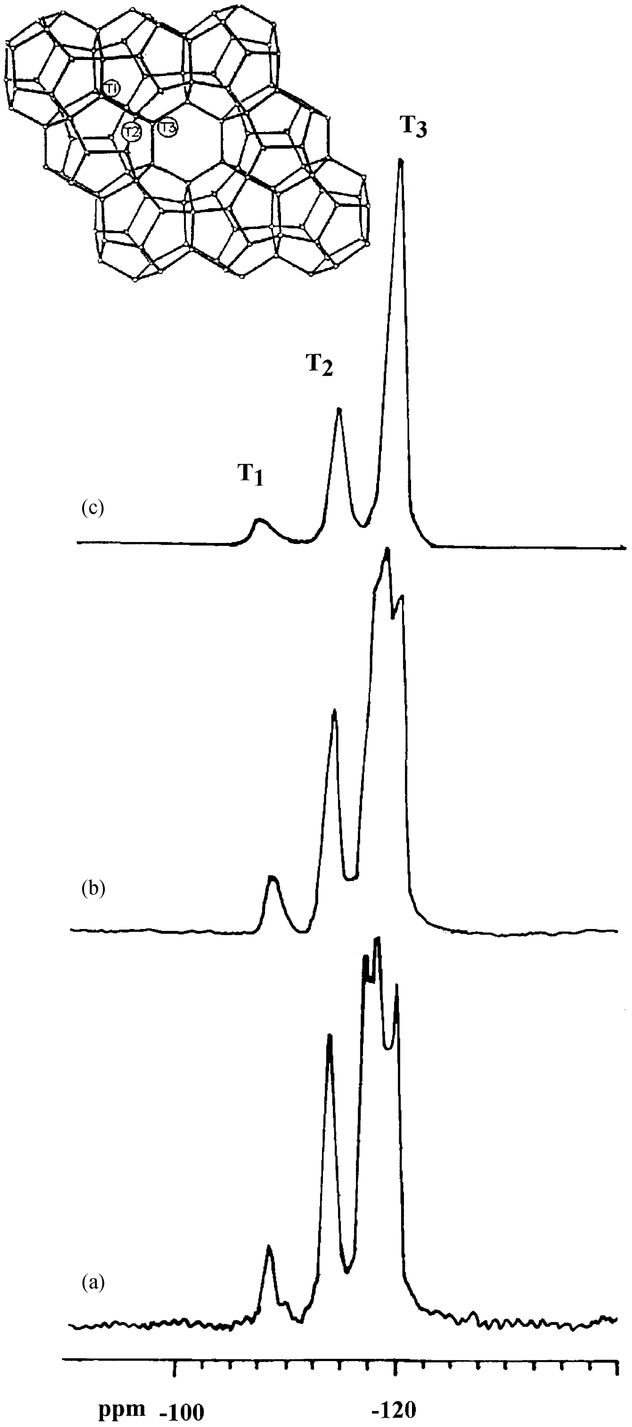

FIG. 6. Solid state ^{29}Si MAS NMR spectra of (A) as-synthesized EtHMTA-CF-4, (B) 15 days later phase of EtHMTA-CF-4, and (C) 30 days later phase of EtHMTA-CF-4. The topological structures of ZSM-39 are also shown (20).

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