

# Phase Transformation of MCM-41 in the Mother Liquid at Moderate Temperature

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A new crystalline phase (via amorphous intermediate), NCUZ-1, was obtained when MCM-41 (Si/Al = 9) was under prolonged heating in the mother liquid (which contains NaAlO<sub>2</sub>, [N(CH<sub>3</sub>)<sub>4</sub>]<sub>2</sub>SiO<sub>3</sub>, SiO<sub>2</sub>, and surfactant C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>OH(aq) at 105°C for more than two weeks. The largest *d* spacing of NCUZ-1 calculated from X-ray diffraction data is approx. 6 Å, indicating that the long-range order of the mesopores in MCM-41 was not present in NCUZ-1. Nitrogen absorption studies showed that NCUZ-1 contains both mesopores and micropores. The volume ratio of the mesopore to micropore is approx. 10 to 1 and the BET surface area is 400 m<sup>2</sup>/g. The TEM micrograph of NCUZ-1 revealed a homogenous phase with distorted mesopores. The <sup>13</sup>C NMR spectrum of NCUZ-1 before calcination is similar to that of uncalcined MCM-41, indicating that the organic templates in both phases have a similar structure. In the phase transformation process, the counteranion (OH<sup>-</sup>) of the surfactant template played an important role. It increased the solubility of the aluminosilicate wall; the breaking and reforming the Si–O and Al–O bonds make the phase transformation possible, although the process is very slow. When C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>Cl, instead of C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>OH, was used as a template, no NCUZ-1 phase was obtained under the same reaction conditions. TEM micrograph, nitrogen absorption isothermal, and <sup>13</sup>C NMR spectra of NCUZ-1 suggested that the mesopores were present in the NCUZ-1 phase, although there is no long-range order of these mesopores. © 2001 Academic Press

**Key Words:** MCM-41; phase transformation; NCUZ-1; mesoporous, microporous.

## I. INTRODUCTION

Understanding how molecules and ions can preferentially organize themselves under certain conditions to form extended crystalline solid structures is a well-established goal in modern inorganic chemistry. The templating strategy for the preparation of high-crystalline zeolites is well known and the crystallization of zeolites enables us to understand

more about the self-assembly mechanism of macromolecule architecture. Following the discovery of ordered mesoporous (pore diameter from 20 to 500 Å) aluminosilicate M41S materials by the group at Mobil Corp. (1), a considerable effort in expanding this new family of micelle-templated structures (MTS) has been invested. It includes the testing of different synthesis pathways based on different structure-directing agents or reaction mechanisms (2). One of the unique members, MCM-41, has stimulated intensive studies, due to the fantastic hexagonal arrangement of unidimensional mesopores. Several creative preparation methods with various recipes have been reported (3) and the rationalized formation mechanisms were proposed (4, 5). Monnier *et al.* (5) and Steel *et al.* (6) had observed a lamellar-to-hexagonal phase transition in the formation of MCM-41. Nevertheless, Chen *et al.* (7) observed the transformation of hexagonal structure to the lamellar phase after reaction for 40 h at 150°C, and hexagonal to ZSM-5 phase after 3 days crystallization at 170°C (due to the decomposition of the surfactant template). A rich variety of morphologies (such as ball, tubular, fibrous, thin sheet, hollow spherical) was also obtained via novel synthetic strategies (8). These results revealed that the synthesis conditions as well as the reactants play a key role in the formation of those mesostructures. Furthermore, the postsynthesis hydrothermal treatments (9) have also been discussed. Gallis and Landry (10) described the use of temperature modification to transform MCM-41 into MCM-48. The process takes less than a day and produces the MCM-48 phase, which is sufficiently polymerized to be stable to calcination. Ozin and coworkers (11) have found that the swollen processes, including the lattice parameters and the pore size, could be achieved by using a postsynthesis approach. They reported that when a conventional synthesis of MCM-41 materials (carried out at 343 K) was followed by a hydrothermal treatment of the samples at 423 K in their mother liquid for a period of 1–10 days, a gradual pore size expansion up to approx. 7 nm took place. In this article, we investigate the phase change of MCM-41 during prolonged heating in the mother liquid.

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The variation of the micelle template and ordering of the mesopores are reported. The parameters that determined the long-term stability of MCM-41 in its mother liquid at moderate temperature will be discussed.

## II. EXPERIMENTAL

**Chemicals.**  $\text{NaAlO}_2$  and silica were purchased from a commercial resource and used without further purification. As much as 0.5 M of  $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{OH}$  solution was purchased from Pfaltz and Bauer and 10% tetramethylammonium silicate was from Sachem (Austin, TX).

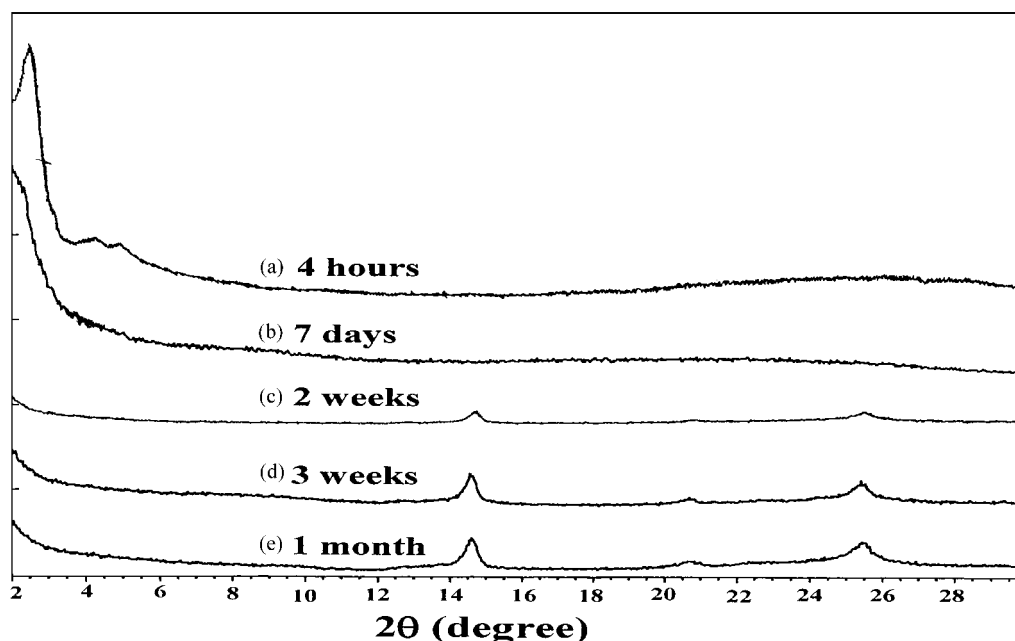
**Preparation.** The recipe we used for the preparation of MCM-41 was based on the literature report [3a]. The amount of 0.083 g of  $\text{NaAlO}_2$  was dissolved in 3.9 g of 0.5 M of  $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{OH}$  solution. To it, 1.0 g of 10% tetramethylammonium silicate was added, followed by 0.5 g of silica. The mixture was stirred thoroughly overnight then loaded into an autoclave, and heated at  $105^\circ\text{C}$  for a certain period of time. The autoclave was taken out of the oven and quenched with cold water. The white powder was isolated by filtration, washed with warm water, and dried in air. The structure of the products was identified by X-ray powder diffraction patterns.

**Physicochemical studies.** Fourier transform infrared (FTIR) spectra were recorded as pressed KBr pellets using a Bio-Rad 155 FTIR spectrometer. X-ray powder diffraction studies were carried out with a Scitag Xgen-4000 X-ray diffractometer using  $\text{CuK}\alpha$  radiation at 45 kV and 40 mA.

Thermogravimetric analysis (TGA) was performed with a Perkin-Elmer TGA-7 thermal analysis system using dry nitrogen as carrier gas at a flow rate of 30 psi pressure. The TGA experiments were conducted from room temperature to  $900^\circ\text{C}$  with a linear heating rate of  $5^\circ\text{C}/\text{min}$ .  $^{13}\text{C}$ ,  $^{29}\text{Si}$ , and  $^{27}\text{Al}$  solid state NMR were taken with a Bruker DSX-400 WB NMR spectrometer at room temperature. Nitrogen absorption measurements were conducted on a Micromeritics ASAP-2000 accelerated surface area and porosimetry system using nitrogen as a probe gas. The sample was dehydrated under high vacuum at  $100^\circ\text{C}$  for 4 h and  $400^\circ\text{C}$  for 5 h before measurement. Scanning electron microscopy (SEM) studies were performed with a Hitachi S-800 at 15 kV. The samples for SEM imaging were mounted on metal stubs with a conducting tape and a thin layer of Au was coated to avoid charging. Transmission electron microscopy (TEM) was performed with a JEOL-2000, FXII microscope at 120 kV. The sample was dispersed in water, then deposited on a wholly-carbon film-coated Cu grid for imaging.

## III. RESULTS AND DISCUSSION

*The phase transformation of MCM-41 in the mother liquid.* When the reaction mixture was heated at  $105^\circ\text{C}$  in the autoclave, the MCM-41 phase was formed in the mother liquid within 2 h. The crystallinity of MCM-41 increased as the reaction time increased up to a couple of days then decreased again. The product is an amorphous powder when the reaction mixture was heated for 7 days. However,



**FIG. 1.** The X-ray diffraction patterns of materials obtained at different heating time: (a) MCM-41, (b) the amorphous phase, (c)–(e) NCUZ-1 isolated after reacting for 2 weeks, 3 weeks, and one month respectively.

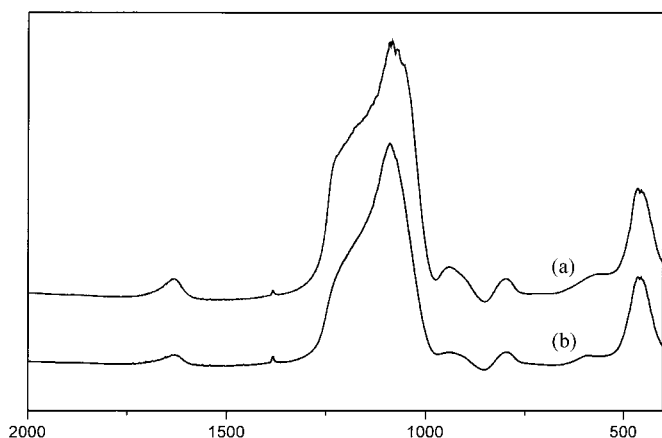


FIG. 2. IR spectra of (a) MCM-41 and (b) NCUZ-1.

when the reaction mixture was heated for longer than two weeks, another crystalline phase appeared and the crystallinity of the new phase increased as the reaction time increased, as shown in Fig. 1. NCUZ-1 and MCM-41 have similar IR (Fig. 2) spectra, and the thermal stability of both materials was up to 900°C.

*The structure of NCUZ-1.* The pore structure of NCUZ-1 is quite different from that of MCM-41 as evidenced by several spectroscopic data. The TEM micrograph of NCUZ-1 showed that there are various types of pores, including the hexagonal mesopore and other distorted pores, mixed together in a single piece of structure fragment, as shown in Fig. 3. Although the pore structure of NCUZ-1 is irregular, no phase separation was observed in the TEM

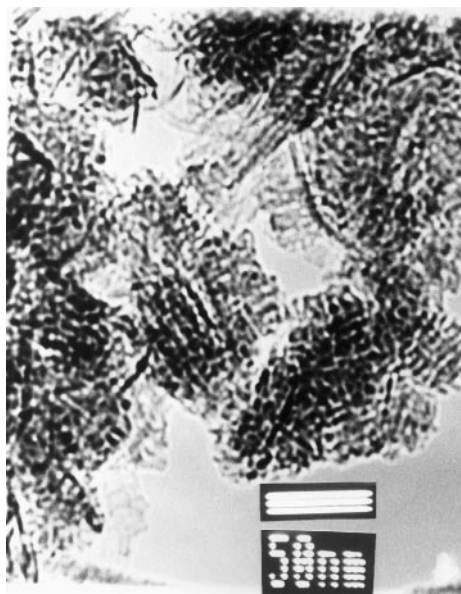


FIG. 3. The TEM micrograph of calcined NCUZ-1 (as (e) in Fig. 1).

micrograph. The nitrogen absorption isothermal of NCUZ-1 (Fig. 4) showed the mixing of the type I (microporous) and type IV (mesoporous) absorption behavior with the BET surface area of 400 m<sup>2</sup>/g. There are two BJH pore sizes centered at 25 and 5.9 Å with a volume ratio of 10 to 1, consist with the TEM observation. The TEM micrograph and nitrogen absorption isothermal data suggested that there are some mesopores still existing in the NCUZ-1 phase but the pores do not have a long-range order. In other words the domain size of the regular arranged mesopore is too small to be detected by the X-ray diffraction studies. That is why the low-angle diffraction peaks, which correspond to the order of the mesopores in MCM-41, are absent in the XRD pattern of NCUZ-1. To further prove the existence of the mesopore structure in the NCUZ-1 phase, the solid state <sup>13</sup>C NMR spectrum of uncalcined NCUZ-1 was taken. It showed that the <sup>13</sup>C NMR of NCUZ-1 before calcination was similar to that of MCM-41 as shown in Fig. 5. This indicates that the micelle surfactant template was also present in the NCUZ-1. It is known (7) that MCM-41 undergoes a structure transformation to zeolitic (ZSM-5) or lamellar-type materials, in particular, at high pH solution. However, no known aluminosilicate or silica phase matches exactly with the NCUZ-1 phase and it is also impossible to solve the structure of NCUZ-1 by the few weak diffraction peaks. Nevertheless, the nitrogen absorption isothermal data suggest that NCUZ-1 is an aluminosilicate compound with defined pore size and acceptable surface area.

*The possible mechanism of the phase transformation of MCM-41.* As mentioned in the above paragraph, the <sup>13</sup>C NMR spectra of NCUZ-1 and MCM-41 (before calcination) are very similar to each other. This indicates that the chemical structure of the micelle surfactant template, [C<sub>16</sub>H<sub>33</sub>N(CH<sub>3</sub>)<sub>3</sub>]<sub>n</sub><sup>+</sup>, in NCUZ-1 is similar to that in the MCM-41. In other words, the rod-type micelle template was not totally destroyed in NCUZ-1. Nitrogen absorption isothermal data of NCUZ-1 has also confirmed the presence of mesopores in addition to the newly forming micropores. However, the mesopores in the aluminosilicate framework are randomly arranged, which explains why no diffraction peak of the regular mesopores was observed. The <sup>27</sup>Al NMR spectrum of the NCUZ-1 phases is similar to that of MCM-41, see Fig. 6. Most of the Al atoms were tetrahedron coordinated, with only trace amounts of octahedron-coordinated Al sites, suggesting that most of the Al atoms were on the framework. The <sup>29</sup>Si NMR spectra of MCM-41, the amorphous phase, and NCUZ-1 all contained Si(3Al), Si(2Al), Si(1Al), and Si(0Al) peaks. The presence of four types of <sup>29</sup>Si NMR peaks further confirmed that most of the Al atoms were present in the framework in each phase.

Nitrogen absorption studies showed that the volume ratio of mesopore/micropore decreased as the crystallinity of

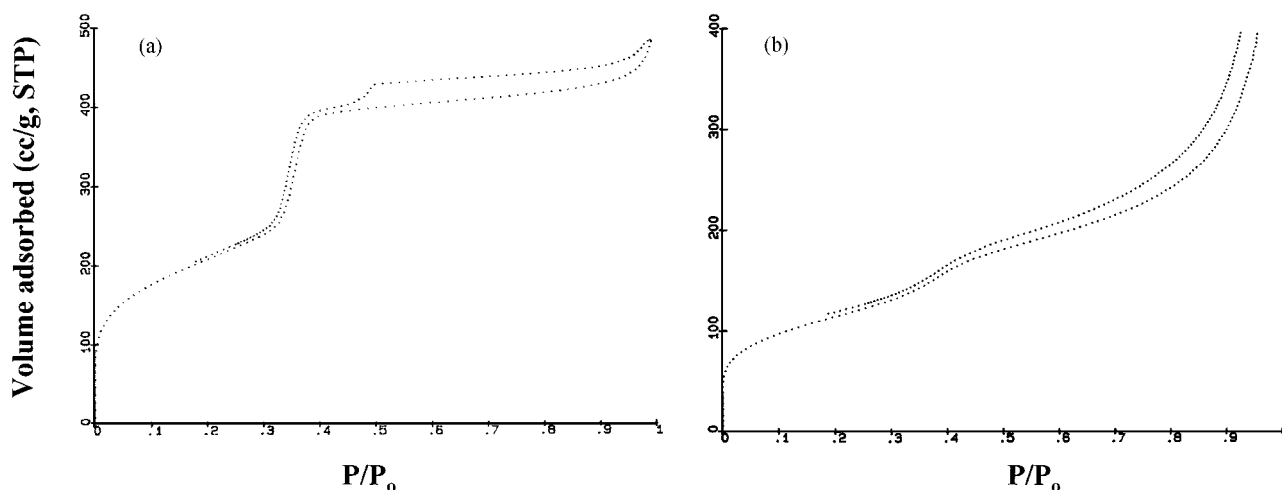


FIG. 4. The nitrogen adsorption isothermal curves of (a) MCM-41 and (b) NCUZ-1 (as (e) in Fig. 1).

NCUZ-1 increased. This indicates that the crystallization of the new phase NCUZ-1 and the destruction of the regular arrangement of the mesopores occurred simultaneously. No phase separation of NCUZ-1 was observed in the TEM and SEM studies. It has been reported (12) that the TEM images of platinum wires deposited inside the MCM-41 pores demonstrated that there is no connection between the me-

sopores and the pores parallel and curved to some extent. The curvature of the pore (as well as the aluminosilicate wall around it) may be why the aluminosilicate wall of MCM-41 was not crystalline. When the MCM-41 phase was heated in the mother liquid for longer time, the Si-O (or Al-O) bond-breaking and bond-forming processes continued. The aluminosilicate walls rearranged (or connected with each other) slowly into a new ordered structure, which at the same time destroyed the mesopores. In this stage of the process where the long-range order of the mesopores was destroyed and the domain size of the ordered aluminosilicate was not high enough to be detected by X-ray diffraction studies, the amorphous material was formed. As the domain size of the ordered aluminosilicate increased, new diffraction peaks from the ordered aluminosilicate appeared. It is worth noting here that NCUZ-1 can be regarded as an intermediate between MCM-41 and some kind of zeolitic phase, such as sodalite. Although NCUZ-1 does not have a good crystallinity, it is a very stable material (stable in MCM-41 mother liquid for up to two months and at temperature up to 900°C) with both mesopores and micropores.

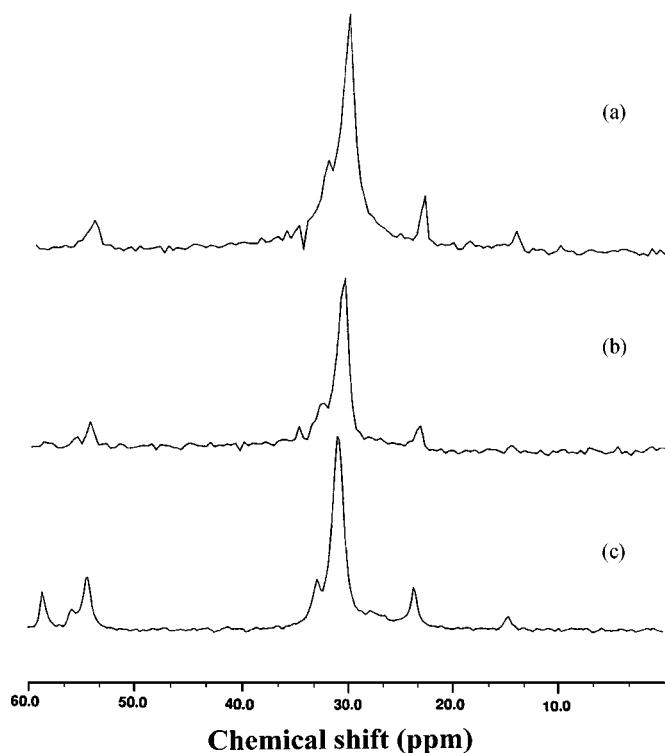


FIG. 5.  $^{13}\text{C}$  NMR spectra of (a) MCM-41, (b) the amorphous phase, and (c) NCUZ-1 (as (e) in Fig. 1) before calcination.

*The effect of  $\text{OH}^-$  ions on the phase transformation of MCM-41.* It is interesting to know what is the role the counteranion of the surfactant template plays in the crystallization and phase transformation of MCM-41 in the mother liquid at moderate temperature. The mechanism of building a MCM-41 framework around the surfactant template is not totally understood. The Mobil group [1] proposed the liquid crystal templating mechanism; however the Stucky [5] group believed that the multidentate binding-preferred polymerization and charge matching of silicate are crucial for the formation of the mesoporous phase. Hence the effect of the basicity of the reaction media was not emphasized. However, it has been known that the pH value

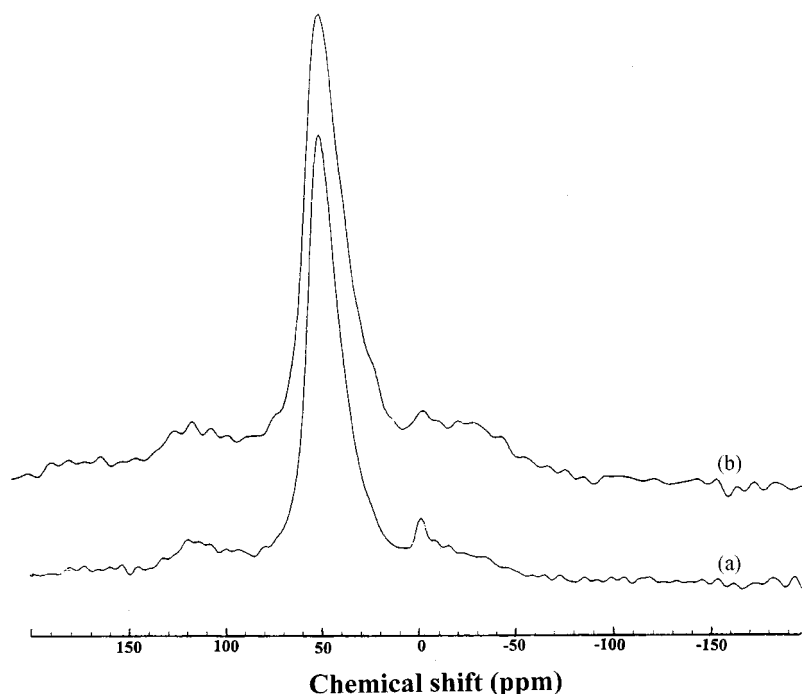


FIG. 6.  $^{27}\text{Al}$  NMR spectra of (a) MCM-41 and (b) NCUZ-1 (as (e) in Fig. 1) after calcination.

of the reaction media will affect the crystallization of zeolite due to the mineral effect. In our recipe, pure  $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{OH}$  instead of  $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{OH}/\text{Cl}$  (which was used by the Mobil group) was used as a surfactant template. In a controlled experiment, when the  $\text{C}_{16}\text{H}_{33}\text{N}(\text{CH}_3)_3\text{Cl}$  was used as a template, no phase transition occurred after the MCM-41 was heated under the same reaction conditions for 2 months. This result indicates that the  $\text{OH}^-$  ions might play an important role in the stability of the metastable MCM-41 phase under hydrothermal reaction conditions. The Si-O bond was strong but acidic; the  $\text{OH}^-$  ions were the strong base that can break the Si-O bonds. Therefore, the aluminosilicate wall of MCM-41 could rearrange (or connect with each other) via bond-breaking and bond-forming processes to form other ordered domains in the basic reaction medium, although the rate of this rearrangement is very slow.

#### IV. CONCLUSIONS

In conclusion, we have synthesized a new crystalline aluminosilicate phase, NCUZ-1, by heating MCM-41 prolongly in its mother liquid at a moderate temperature. The rate of the transformation of MCM-41 to the NCUZ-1 phase is very slow and the existence of strong base  $\text{OH}^-$  ions is necessary. The mechanism of the phase transformation is believed to be through the formation of ordered aluminosilicate domains via Si-O (or Al-O) bond-breaking and bond-forming processes and at the same time destroys

the regular arrangement of the hexagonal mesopores of MCM-41.

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