Structural Order in MCM-41 controlled by Shifting Silicate Polymerization Equilibrium

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Powder X-ray diffraction, ^{29}Si and ^{129}Xe NMR spectroscopy of MCM-41 show that the long-range structural order and textural uniformity of the mesoporous molecular sieve are markedly improved due to a shift in the reaction equilibrium when acetic acid is repeatedly added during the conversion of sodium silicate and $NMe_3(C_{16}H_{33})Cl$ to a MCM-41 phase.

Recently, the discovery of a new family of mesoporous molecular sieves designated as MCM-41 has been reported by researchers at the Mobil Corporation.[1,2] The MCM-41 material possesses a uniform hexagonal array of cylindrical pores embedded within a silica-based matrix. The material is synthesized through a hydrothermal reaction of silicate gel in the presence of a surfactant. The pore diameter can be tailored within the range of 1.6–10 nm by the choice of the surfactant molecular size. The large pore size of MCM-41, compared with that of zeolite pores, has led to a great focusing of potential applications of the materials for the adsorption, separation and catalytic conversion of large molecules.

The quality of powder X-ray diffraction (XRD) patterns and magic angle spinning ^{29}Si NMR spectra reported in the literature for MCM-41 vary widely.[1–11] In general, line widths of the XRD patterns and ^{29}Si NMR spectra increase upon calcination, indicating a loss of long-range structural order. This appears to be more serious for pure silica MCM-41 than for the Al-substituted form. Variability in the long-range structural order greatly inhibits not only the interpretation of spectroscopic or other characterization studies of these novel materials, but also restricts practical applications requiring structural integrity. Hence, we report a method to control long-range structural order of MCM-41 very precisely.

The following MCM-41 synthesis procedure has been developed in the present work. A sodium silicate solution of Na/Si = 0.5 (2.4 mass% Na_2O, 9.2 mass% SiO_2 and 88.4 mass% H_2O) was prepared by combining 1 mol dm^{-3} aqueous NaOH solution with Ludox HS40 (39.5 mass% SiO_2, 0.4 mass% Na_2O and 60.1 mass% H_2O, Du Pont) and heating the resulting gel mixture with stirring. This solution was slowly added to a hexadecyltrimethylammonium chloride (HTACl) solution (24.9 mass% HTACl, 0.4 mass% NH_3 and 74.7 mass% H_2O) with vigorous stirring at room temperature, to give a mixture of SiO_2/HTA = 6. The current work has also confirmed that MCM-41 is obtained with SiO_2/HTA ratios ranging from 0.5 to 12:1. An aqueous solution of sodium aluminate may subsequently be added dropwise with vigorous stirring in order to synthesize Al-MCM-41 with Si/Al $\geqslant$ 15.

The HTA–silicate mixture was heated in a polypropylene bottle, without stirring, to 373 K for 24 h. The mixture was then cooled to room temp. The pH was then adjusted to approximately 11 by dropwise addition of acetic acid with vigorous stirring. The reaction mixture was heated again to 373 K for 24 h. This procedure for pH adjustment and subsequent heating was repeated twice (*i.e.* carried out three times in all). The precipitated product, MCM-41 containing HTA was filtered, washed with doubly distilled water and dried in an oven at 370 K. The product was calcined in air for 2 h at 773 K using a muffle furnace.

Some MCM-41 samples were synthesized by the above method, while others were synthesized by eliminating the step for pH adjustment to 11. Cu-Kα XRD patterns of the MCM-41 samples were obtained at room temp. using a Rigaku D/MAX-III (3 kW) instrument. Typical XRD patterns are displayed in Fig. 1. All the MCM-41 samples obtained before calcination exhibited XRD patterns with a very intense (100) diffraction peak and three weak (110), (200) and (210) peaks, which are characteristic of the MCM-41 phase with a unit-cell dimension

of a = 4.8 ± 0.2 nm.[1,2] The XRD line width of the as-synthesized samples was not significantly affected by pH adjustment during the synthesis. Conversely, the XRD line width and intensity for calcined sample were affected very markedly by the pH adjustment procedure. The (110), (200) and (210) diffraction lines were well resolved in the case of MCM-41 samples synthesized following the pH adjustment procedure, while the same XRD lines were severely broadened for samples synthesized without the pH adjustment. Upon calcination, the XRD lines in Fig. 1(*a*) and 1(*b*) shifted to higher 2θ values indicating a significant lattice contraction; the d_{100} spacings indicated 25 and 12% lattice contractions, respectively. This is in agreement with previous studies reporting 20–25% lattice contractions.[7] Contrarily, lattice contraction did not occur for highly ordered samples synthesized by repeated pH adjustment [Fig. 1(*c*), (*d*)]. For the sample in Fig. 1(*d*) a transmission electron micrograph showed highly ordered hexagonal mesopores, similar to previous studies while the BET area of this high quality MCM-41 was 927 m^{2}g^{-1}.

The effect of acetic acid addition to the MCM-41 synthesis mixture was found to be reversible by the addition of NaOH and heating to 373 K for 24 h. Furthermore, the product MCM-41 phase was proved to be stable over 30 d under these reaction conditions. The reversibility of the synthesis reaction and the long-term product stability under the reaction conditions indicate that the MCM-41 phase is in equilibrium with the reactants. Thus, addition of acetic acid to the reaction mixture shifts the equilibrium towards formation of MCM-41. The
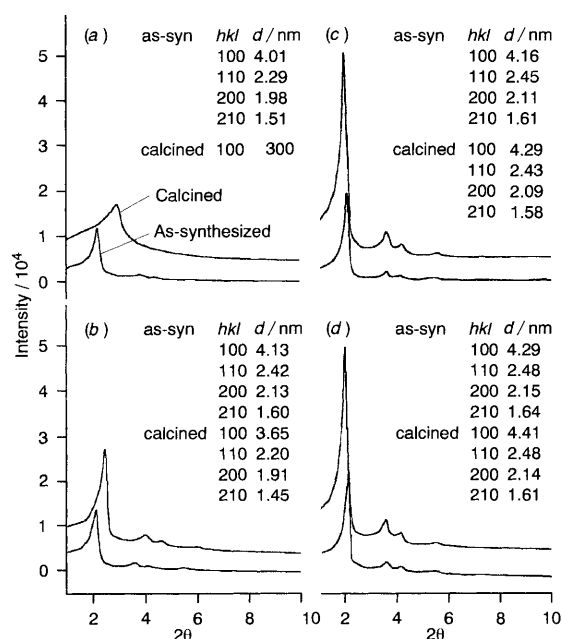

Fig 1 XRD patterns of MCM-41 obtained using a Cu-Kα X-ray source: (*a*) synthesized without pH adjustment, (*b*) synthesized with pH readjustment to 11 using acetic acid, (*c*) synthesized by repeating the pH adjustment procedure twice, and (*d*) three times. The as-synthesized samples were previously washed with distilled water and dried in oven at 370 K, and the calcination was performed in air at 773 K.

MCM-41 yield, based on the SiO_2 recovery, increased from 62 to 83, 88 and 90% as the procedure for pH adjustment and subsequent heating was repeated twice (*i.e.* carried out three times in all). However, if the acid was added too quickly during the reaction, or the same amount of acetic acid was added at once to the initial reaction mixture, the XRD pattern was found to be poor. Thus, the equilibrium between the MCM-41 phase and the reactants was maintained within a very narrow and shallow local energy minimum.

Fig. 2 shows [129]Xe NMR spectra (Bruker AM 300) of xenon gas adsorbed on calcined Al-MCM-41 (Si/Al = 50, calcined at 813 K for 10 h) at 53.3 kPa at 296 K. The [129]Xe NMR spectrum of Al-MCM-41 synthesized with pH adjustment contains a narrow single Lorentzian line appearing at δ 71 ± 1. Whilst the line width obtained from Al-MCM-41 samples synthesized without pH adjustment increased due to heterogeneous NMR line broadening. [129]Xe NMR spectra of pure silica MCM-41 showed similar results, but the NMR lines were narrower than those for Al-MCM-41. Heterogeneous line shapes indicate a lack of sample uniformity;[12] the narrow NMR line at δ 71 is believed to come from xenon adsorbed within the MCM-41 pore whilst the side peak can be attributed to xenon adsorbed within disintegrated sample zones.

Fig. 3 shows MAS ^{29}Si NMR spectra of MCM-41 samples (Bruker AM 300, 5 s relaxation delay). The ^{29}Si NMR spectra
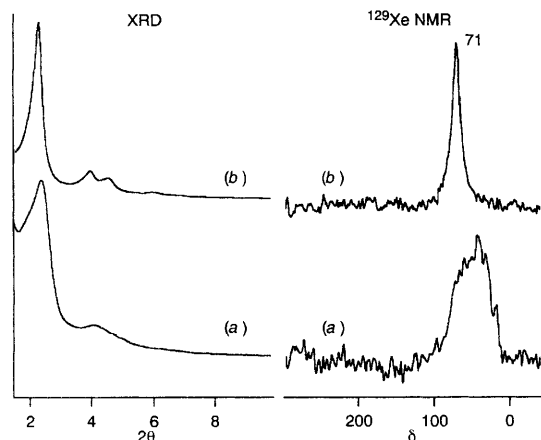

Fig. 2 XRD patterns and [129]Xe NMR spectra of calcined Al-MCM-41 (Si/Al = 50, calcined at 813 K) obtained under 53.3 kPa at 296 K: (*a*) synthesized without pH adjustment, and (*b*) synthesized by repeating the pH adjustment procedure twice
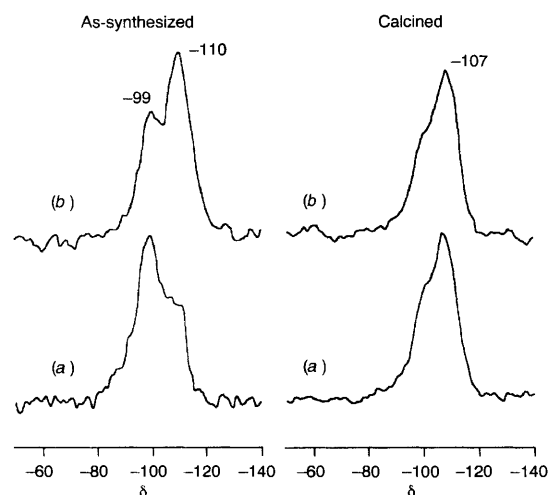

Fig. 3 MAS ^{29}Si NMR spectra of MCM-41 samples: (*a*) synthesized without pH adjustment, and (*b*) synthesized by repeating the pH adjustment procedure twice

indicate that pH adjustment during synthesis leads to a significant increase in the intensity ratio between $Si(-OSi-)_4$ and $Si(-OSi-)_3OH$ tetrahedral silicon atoms (Q_4/Q_3) for samples before calcination, while the Q_4/Q_3 silicon ratio for calcined samples is not affected by the pH adjustment. The NMR spectra indicate that condensation of hydroxyl groups during calcination seldom occurs with MCM-41 samples synthesized with acetic acid. However, the Q_4/Q_3 silicon NMR peak resolution is not significantly improved by the pH adjustment. Thus, ordering in the local atomic structure of calcined MCM-41 samples is not significantly improved by the pH adjustment.

In conclusion, the formation of MCM-41 from sodium silicate and HTACl in aqueous solution is very sensitive to pH with MCM-41 and NaOH in equilibrium with the reactants. Neutralization of the product NaOH with acetic acid to pH *ca.* 11 shifts the reaction equilibrium toward the formation of MCM-41. The present synthesis method using repeated addition of acetic acid gives much higher quality MCM-41 than procedures using a pH adjustment at the beginning of reaction.[13] Contrary to previous studies on MCM-41, our high quality samples synthesized by the present procedure showed no significant changes in silanol group content and lattice spacing upon calcination at 773 K. The XRD pattern and BET surface area of the pure-silica MCM-41 samples did not change significantly after heating for 2 h at 1173 K in dry air. The materials were stable up to 973 K under hydrothermal heating in humid air containing 20 Torr H_2O. We have also synthesized an Al-MCM-41 sample, applying the technique of repeated pH adjustment to 11 and using a gel composition of SiO_2: 0.067 Al_2O_3 : 0.167 HTACl : 0.033 $NMe_3(C_{12}H_{25})Br$: 0.033 NPr_4Br : 0.025 $(NH_4)_2O$: 0.273 Na_2O : 50 H_2O. The Al-MCM-41 sample was calcined at 813 K and then ion exchanged with Y^+. Similar experiments for the Al-MCM-41 sample have likewise indicated that the thermal and hydrothermal stability extend up to 1173 and 1073 K, respectively. Moreover, the ^{27}Al NMR spectrum obtained after heating for 2 h at 1173 K in humid air still showed a tetrahedral aluminum peak centred at δ 53, with an intensity 4 times stronger than the octahedral aluminum peak centred near δ 0.

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