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Facile synthesis of the cubic mesoporous material MCM-48. Detailed study of accompanying phase transformations

Wieslaw J. Roth

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Abstract The synthesis of cubic mesoporous material MCM-48 has been simplified and can be accomplished via facile hydrothermal synthesis using convenient commercial reagents. The cubic structure evolves from the initially formed hexagonal MCM-41 and undergoes slow conversion to the lamellar MCM-50 precursor. The system was sampled at 1 hr intervals and the intermediate products characterized by elemental analysis, X-ray powder diffraction and adsorption. The results are discussed from the standpoint of possible mechanisms of MCM-48 generation.

Keywords MCM-48 facile synthesis · MCM-48 phase conversions · MCM-41 · M41 family

1 Introduction

Following discovery of the M41S family of mesoporous materials (Kresge et al. 1992) it was found that such materials were formed readily in the presence of surfactants under variety of conditions (Vartuli et al. 1994; Monnier et al. 1993; Roth and Vartuli 2005). However, synthesis of high quality stable products with well defined structures like the hexagonal MCM-41 and cubic MCM-48 required more demanding conditions and sometimes special reagents (Roth and Vartuli 2005). MCM-41 was quickly available through convenient preparation methods but it took over 5 years to identify reliable and comparably facile synthesis procedure for MCM-48 (Liu et al. 2001; Sayari 2000; Roth 2000). The cubic phase was also intriguing and puzzling from the standpoint of formation mechanism. While MCM-41 assembly via rod-like micelles represented a viable pathway, the packing of short elongated surfactant aggregates to convert corresponding channels (in MCM-48) into regular and intricate 3-D assemblies was more problematic. It became evident that the cooperative self-assembly (Monnier et al. 1993), which lacks specificity of micelle packing mechanism, must be accepted as the best description available.

As a large pore material with well defined 3-D channel system, MCM-48 offered a significant potential, possibly superior to MCM-41, as a catalyst and adsorbent (Alfredsson and Anderson 1996; Anderson 1997; Kaneda et al. 2002). Its testing and characterization were delayed because of sample availability due to synthesis reliability problems. MCM-48 was initially obtained using surfactant in the hydroxide form and silicon alkoxide, tetraethylorthosilicate, TEOS, with controlled hydrolysis of the latter (Vartuli et al. 1994). Both reagents were the primary targets for possible replacement because of cost, hazard and/or availability and because the overall approach was hardly suitable for routine preparations and scale-up. Thus, preparation of MCM-48 with sources such as solubilized, colloidal or solid silica and commercial surfactant salts were considered of high priority. The improvements in MCM-48 synthesis were gradual (Roth 2000) until around 2000 several reports described reproducible synthesis of MCM-48 using common reagents and standard synthesis conditions (Liu et al. 2001; Sayari 2000; Roth 2000). Recently a fast and efficient synthesis of MCM-48 with TEOS has been reported (Boote et al. 2007).

W.J. Roth (✉)
Corporate Strategic Research, ExxonMobil Research and Engineering, Annandale, NJ 08801, USA
e-mail: wieslaw.j.roth@exxonmobil.com

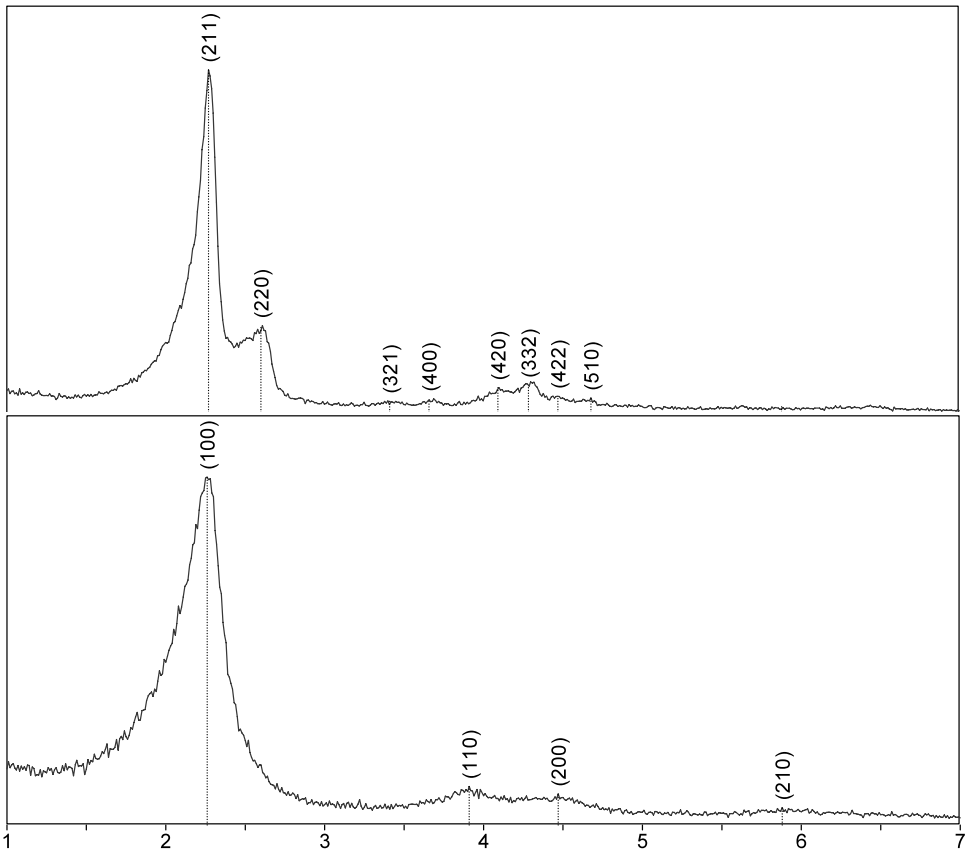

Fig. 1 Indexed XRD patterns of MCM-48 (*upper*) and MCM-41 (*lower*) in the studied system

We observed MCM-48 formation in a simple synthesis mixture comprising silica solid, surfactant chloride (cetyltrimethylammonium chloride, CTMA-Cl) and tetramethylammonium hydroxide (TMA-OH) as mineralizer (Roth and Vartuli 2001). All three are convenient commercial reagents. This mixture afforded high quality MCM-41 when the Si/surfactant ratio was around 5–6 while at Si/surfactant ∼4 MCM-48 was favored. With regard to MCM-41 the synthesis method (Roth 1998; Roth and Vartuli 2001) was referred to as 'rational' because the CTMA-TMA-OH ratio was 1:1 and effectively acting as surfactant hydroxide, CTMA-OH. Furthermore it entailed almost quantitative incorporation of the surfactant in the solid mesoporous phase making the appearance of stoichiometric interaction between silica and surfactant, i.e. the mesoporous phase could be formally considered as a CTMA-silicate. The reduction of silica amount in the mixture favored formation of MCM-48. Around 3.5/1 molar ratio Si/surfactant essentially pure MCM-48 was obtained (Roth 2000). We provide detailed description of the synthesis and accompanying phase changes, and discuss observations and new insights concerning possible mechanisms of these transformations.

2 Results and discussion

The primary tool for identification of mesoporous materials in the bulk is X-ray powder diffraction. The XRD patterns are in most cases dominated by a low angle line and therefore structure recognition and phase assignment must rely on smaller peaks at higher 2-theta. MCM-48 can be unequivocally recognized based on its characteristic XRD profile that can be indexed as a body-centered cubic space group, Ia3d. The differentiation from MCM-41, see Fig. 1, and other mesoporous phases can be made visually based on the (220) reflection emerging on the high angle side of the principal low angle peak (see additional discussion in connection with observations in this work). The first dominant peak in MCM-48 is in the same position as in the hexagonal phase, MCM-41, forming first in the synthesis mixture, which hints a strong structural connection between the two. This was analyzed and discussed in detail earlier for another system (Landry et al. 2001).

A second XRD/structural peculiarity is the coincidental position of the second, (220) peak of MCM-48 and the first reflection of the lamellar phase that slowly emerges after MCM-48 formation and apparently at its expense. In practice this delays detection of the onset of lamellar phase,

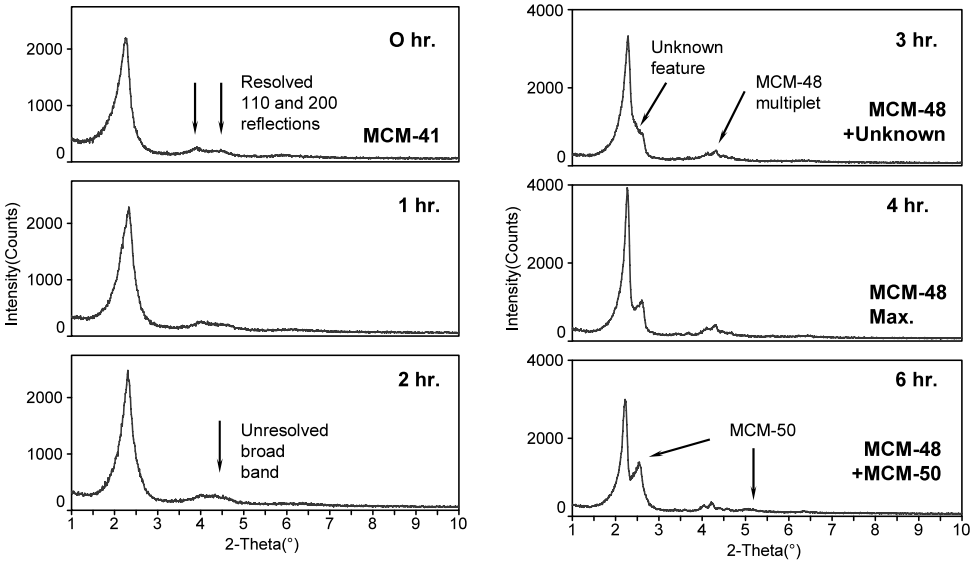

Fig. 2 XRD patterns of uncalcined solids isolated form the MCM-48 synthesis mixture at different times

which is best diagnosed post synthesis based on nitrogen adsorption/desorption isotherm (Kruk et al. 2002).

2.1 MCM-48 synthesis

As alluded to in the preceding discussion and as illustrated in Fig. 2, the MCM-48 synthesis involved continuous transformation of the surfactant-silica solid phase. The preparation started from digesting the mixture of solid silica and tetramethylammonium hydroxide in water for about 1 hr at 100°C followed by cooling and addition of the surfactant solution of CTMA-Cl in water. The molar composition was 3:1:1 while the silica content was about 7 wt.%. The reaction was carried out at 160°C for total of 6 hrs. Small samples were withdrawn without interruption at 1 hr intervals and the isolated solids were characterized by XRD, elemental analysis and nitrogen adsorption after calcination to remove the organic template.

2.2 Monitoring synthesis progress and phase changes by X-ray diffraction

As can be seen in Fig. 2, the hexagonal MCM-41 is the first distinct product forming in the system upon heat-up to reaction temperature so that, at 0 hr., a reasonably resolved XRD pattern (MCM-41) can be observed for the as-synthesized template containing product. Porosity is also quite substantial (see Table 1) but the structure is not firmly established and deteriorates considerably upon calcination as shown by poor quality XRD's (Fig. 3).

The first sign of MCM-48 formation in as-synthesized sample is seen (Fig. 2) at three hours. It is associated with the appearance of a shoulder on the high angle side of the first principal peak, hinting a relationship to the cubic phase.

Table 1 Properties of the solid products isolated form the synthesis mixture at different times during MCM-48 preparation

Product properties	Time, hrs. 0	1	2	3	4	5	6
Si/N molar ratio	3.8	4.1	4.1	4.3	4.5	4.5	4.5
BET, m^2/g	604	999	1480	1177	1180	1196	946
Mesopore capacity, STP, cm^3/g	200	380	550	500	540	540	430
Pore volume, cm^3/g	0.41	0.61	0.94	0.845	0.9	0.91	0.79

XRD's of calcined samples suggested MCM-48 appearance even at 2 hrs. In the as synthesized product the new feature at 3 hrs. must be considered an unknown one since the profile is unresolved with monotonically decreasing intensity. Only upon calcination does a distinct 'MCM-48' doublet emerge.

The MCM-48 structure continues to evolve and improve, as also revealed through adsorption characteristics discussed below, reaching highest XRD intensity at around 4–5 hours time. After that the lamellar MCM-50 precursor begins to form. It is detected in XRD as the dominant first peak in the pattern starts losing intensity while the second increases. The corresponding structural change is not discernible initially but is best diagnosed post synthesis through nitrogen isotherms.

2.3 Changes in textural properties and composition during synthesis

Mesoporous products are evident in the mixture from the outset as indicated by considerable pore volume, BET and strong low angle line in XRD at 0 hr. The mesoporous phase, clearly forming upon heat up, has initially poor pore system

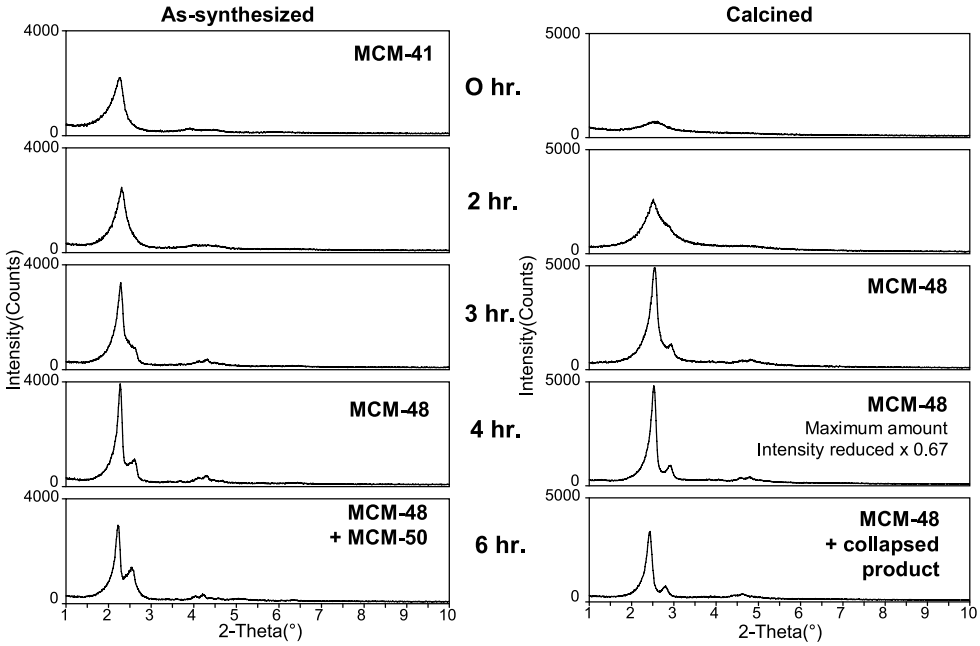

Fig. 3 Comparison of XRD patterns of as-synthesized and calcined solids isolated form the MCM-48 synthesis mixture at different times

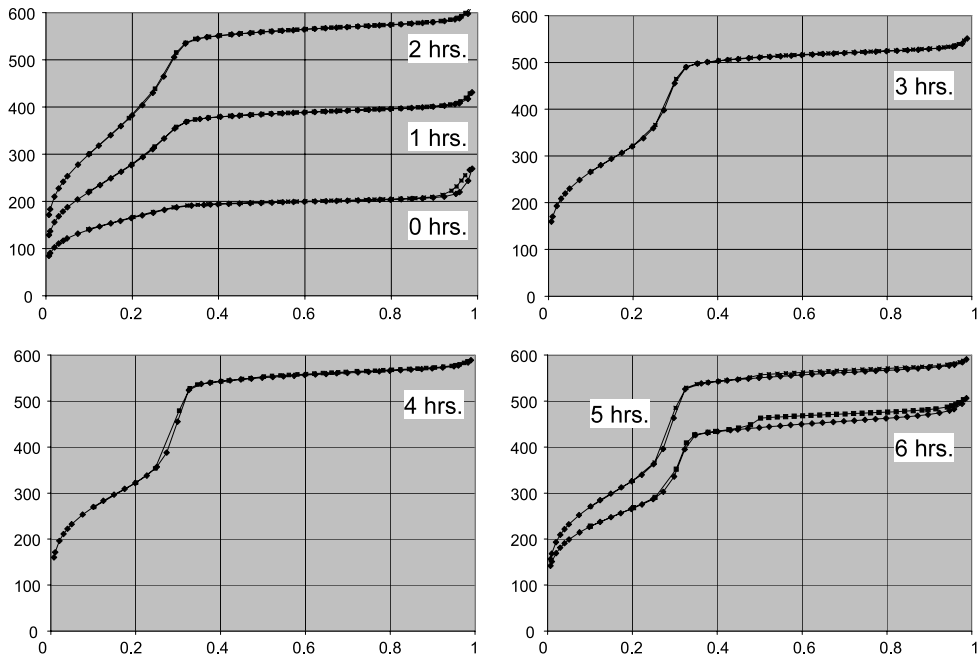

Fig. 4 Nitrogen adsorption/desorption isotherms for the products collected at different times during the synthesis

quality as revealed by the corresponding nitrogen adsorption/desorption plot (isotherm) shown in Fig. 4. A steady increase in stable pore volume is observed, reaching plateau within 2–3 hrs. The observed variations in pore volume and BET in the period 2–4 hrs. may be not due to real differences but reflect experimental error, e.g. from sample collection or treatment (calcination). After 2 hrs synthesis the capillary condensation part of the plot is becoming more steep, suggesting improving uniformity of the pores and by implication firming up of the MCM-48 structure and its maximum content. The apparent optimum at about 5 hrs. is followed by onset of the lamellar phase formation shown by the lowering of the horizontal part of nitrogen isotherm and appearance of the hysteresis attributable to MCM-50 precursor (Kruk et al. 2002). Simultaneously with the changes in XRD and especially the nitrogen isotherm the ratio Si/surfactant of the solid, which is analyzed at room temperature shows gradual increase towards 4.5:1 value. This implies either increased binding of silica (reducing overall 'solubility') or release of surfactant into the solution. For a better appraisal of the situation the analysis would have to involve the system at synthesis temperature, which presents obvious technical chal-

lenges but if carried out may supply valuable insight. The increased incorporation of silica is consistent with formation of a more stable, dense product and should be viewed as the most likely option.

2.4 Mechanism of MCM-48 formation

The structural changes observed during synthesis can be the result of dissolution/recrystallization or internal restructuring of the pre-formed solid. The former seems more traditional and therefore easier to accept without evidence, placing the burden of proof on the latter apparently more attractive option. This latter option was examined in detail for an analogous but slightly different system, with TEOS as the silica source (Landry et al. 2001). A detailed mechanism for structural rearrangement was proposed lending viability to this process. The key points in support of the internal restructuring mechanism are the aforementioned matching d-spacing values of principal reflections of the MCM-41, MCM-48 and MCM-50 precursor forming in the system. This may be viewed as compelling evidence but only from static, i.e. structural, point of view. It clearly needs to be expanded into the dynamic phenomena and include evidence and proposals with regard to species migration in and out of the structure, wall restructuring and build up, etc. The internal transformation of mesoporous phases, cubic SBA-1 to hexagonal SBA-3 upon drying has been reported (Liu et al. 2002) lending credibility to this pathway in general. Further study of this area may become more vigorous if one can envision different consequences of this process with perceived benefits from internal restructuring.

2.5 Activated MCM-48

Structurally well defined MCM-48 is known to form predominantly in high silica systems. Inclusion of alumina usually interferes with MCM-48 formation, which is reflected in lower quality XRD patterns (Xia and Mokaya 2003). The problem of MCM-48 can be solved by post-synthesis activation, which is quite effective both with and without precalcination (Roth 2000). This leaves open the challenge if MCM-48 can be formed in more complex systems, in particular in the presence of Al. We recently obtained evidence that using a co-template, like tetraalkylammonium cation, is conducive to formation of MCM-48 even in the presence of Al. This will be the subject of future publication.

3 Experimental

The synthesis was performed under hydrothermal conditions (160°C) using precipitated silica (90% solids), 29% cetyltrimethylammonium chloride (CTMA-Cl) and 25% tetramethylammonium hydroxide (TMA-OH) solutions. Initially the mixture of TMA-OH, water and silica, weight ratio 2:5.82:1.1 was reacted for about 1 hr at 100°C followed by cooling and addition of 6.08 parts of CTMA-Cl solution. The molar composition silica:TMA-OH:CTMA-Cl was 3:1:1 while the silica content was about 7 wt.% of the entire mixture. X-ray powder diffraction patterns were recorded on a Scintag diffractometer while nitrogen isotherms were determined on Micromeritics ASAP 2000 apparatus. Chemical analyses were performed in-house using ICP-AES.

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