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The evolution of phases during the synthesis of the organically modified catalyst support MCM-48

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Abstract

The properties of organically modified mesoporous silicates were shown to be influenced by the amount of modifier used in the synthesis reagents. Synthesis at 100 °C gave MCM-48 without the organic modifier while the addition of 10 mol% 2-cyanoethyltriethoxysilane modifier produced MCM-41 at the same temperature. Increased temperatures are required in both preparations to achieve an optimum amount of MCM-48, namely 125 °C without modifier and 150 °C with modifier while a disordered phase (resulting from the decomposition of MCM-50 during calcination) was formed at higher temperatures. The influence of synthesis time showed that the formation of MCM-48 was preceded by the appearance and subsequent collapse of a mixture of MCM-41 and MCM-50 mesophases. The MCM-48 phase then developed over time reaching an optimum after 20 h synthesis at 150 °C. Thereafter MCM-48 was replaced by a disordered material (decomposed MCM-50) and was accompanied by an increase in mean pore diameter and a large decrease in surface area. After 60–70 h, the MCM-48 phase was completely transformed to the disordered phase. These findings are rationalised on the basis that the silica charge density changes during synthesis, leading to rearrangements in mesopore phase and increased pore diameters to maintain charge matching.

Keywords: Mesoporous; MCM-48; Phase evolution; Organic modifier

1. Introduction

Zeolites are amongst the most successful microporous (pore diameter <2 nm) materials and have been used extensively in catalysis, adsorption, and ion exchange [1]. The discovery of MCM mesoporous (pore diameter 2–50 nm) silica and aluminosilica molecular sieves is one of the most promising discoveries in the field of materials synthesis [2,3]. A number of mesoporous materials have been reported, which are characterised by the mesopore structure; MCM-41 two-dimensional hexagonal, MCM-48 three-dimensional bicontinuous cubic, and MCM-50 lamellar. These materials allow larger molecules to enter the porous network and have shown potential applications as catalysts in several chemical reactions [4]. MacQuarrie demonstrated how an aminopropyl functionalised MCM type material was an effective base catalyst for the Knoevenagel reaction [5]. MCM-41 has been used successfully as a HPLC stationary phase [6] and also for the immobilisation of small enzymes in the mesopore structure [7].

MCM type materials are synthesised in the presence of a structure-directing agent surfactant in acidic/basic aqueous solution. In appropriate conditions, the surfactant forms an ordered structure e.g. hexagonal array, around which the oxide forms. Removal of the surfactant by calcination or solvent extraction results in a mesoporous material. An obvious means of determining the dependence of the characteristics of mesoporous materials on the preparation parameters used during synthesis is to vary the concentrations of silica, surfactant, water, and acid/base for specific reaction temperatures and time. The results of these investigations may be compiled into synthesis field diagrams that show the phases obtained for different parameters. Behrens et al. have varied the concentration of silica and surfactant to identify the conditions which are required to produce different phases for the SiO_2–$C_{14}TMA^+$–KOH–water–ethanol system [8]. Similar approaches have been used to establish ternary diagrams [9,10] including a recent study which identified the conditions required to form MCM-48 for a SiO_2–C_{16}TAOH/Br–H_2O preparation [11].

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The evolution of phases during MCM-41 synthesis has been well studied. Khushalani synthesised MCM-41 with different pore diameters by allowing the synthesis time to be varied between 1 and 10 days [12]. The results showed that a typical MCM-41 material with $d_{(1\,0\,0)}$ spacing of 43 Å was formed after a synthesis time of 24 h. Longer synthesis time under the same reaction conditions progressively caused an increase of the $d_{(1\,0\,0)}$ spacing of the sample until reaching a maximum of 70 Å after 10 days. Synthesis time beyond 10 days caused a loss of order accompanied by a decrease in pore volume. The effect of synthesis temperature was studied by Cheng et al. [13], who synthesised MCM-41 over a range of temperatures from 70 to 150 °C for a synthesis time of 48 h. The $d_{(1\,0\,0)}$ spacing, measured after calcination, continually increased from 35 Å at 70 °C to 43 Å at 150 °C. The maximum formation of the hexagonal phase at 150 °C was after 48–72 h while this phase was transformed into an amorphous phase after 96 h.

The transformations occurring during MCM-48 synthesis have also been explored. Wang conducted a study on the effect of temperature on the formation of MCM-48 and found that cubic structures are only formed at temperatures >95 °C [14]. MCM-41 was produced at lower temperatures. Pevzner measured the phase transitions occurring during MCM-48 phase formation using in situ X-ray spectroscopy and showed that the presence of coexisting MCM-41 and lamellar phases in the early reaction stage, are likely to be essential for the MCM-48 formation [15]. The cubic phase formed from the collapse of a preceding hexagonal phase, where a given hexagonal plane (1 0 0) evolves to form a cubic plane (2 1 1) having almost the same interplanar distance. Similar phase transformations, i.e. MCM-41 to MCM-48 to lamellar, were observed for a number of studies during MCM-48 synthesis which were attributed to changes in the electrostatic interactions between condensing silica oligomers and surfactant assemblies [11,16,17].

The modification of mesoporous materials using organic molecules has been used to improve the surface properties for e.g. base catalysis [5]. The incorporation of organic modifiers during the synthesis of mesoporous materials alters the silica-surfactant interactions and subsequently the mesopore structure of calcined materials. We have recently reported the first successful synthesis of high surface area ($850\ m^2\ g^{-1}$) organically modified MCM-48, using a 2-cyanoethyl group. This material was stable to surfactant removal by solvent extraction, and displayed enhanced mesopore characteristics relative to otherwise similarly prepared unmodified MCM-48 [18,19]. We now show how the 2-cyanoethyl group influences the structural properties of mesoporous silica and report the evolution of phases that form during the synthesis of 2-cyanoethyl modified MCM-48.

2. Experimental

In a typical synthesis, 10 g cetyltrimethylammonium bromide (CTAB, Lancaster) and 1.0 g sodium hydroxide (BDH) were dissolved in 90 g water. For unmodified preparations, 11 cm^3 tetraethyl orthosilicate (TEOS, Lancaster) were added to this solution with stirring, giving a molar ratio TEOS:CTAB:NaOH:H_2O = 1:0.55:0.5:101.4. For 10 mol% (of total silica) 2-cyanoethyltriethoxysilane (CN) modified silicates, both TEOS and 2-cyanoethyltriethoxysilane were added to the basic surfactant solution such that the molar ratio was TEOS:CN:CTAB:NaOH:H_2O = 1:0.11:0.6:0.56:111.6. After the complete addition of TEOS or TEOS + CN, the mixture was allowed to age for 30 min at 35 °C, during which time a white precipitate formed. The entire contents were then added to a PTFE lined stainless steel autoclave and heated under static conditions. The influence of synthesis time was determined by varying the reaction time at 150 °C for a preparation using 10 mol% CN modifier from 0 to 72 h. Note that since the reaction vessels are insulated by the PTFE liners, the contents for the short time experiments, <2 h, may not reach 150 °C. The reaction time is therefore presented as the duration spent in the oven at 150 °C. A temperature study was conducted by preparing both unmodified and 10 mol% CN modified silicate samples using synthesis temperatures from 100 to 175 °C for a synthesis time of 24 h. After these synthesis conditions, the autoclave was allowed to cool for 1 h to ambient temperature. A white precipitate was recovered by filtration and was added to 200 ml H_2O and heated to approximately 70 °C with stirring for 10 min to remove excess surfactant and NaOH. The solid was again recovered by filtration and washed extensively with H_2O. The surfactant and organic modifier were fully removed from all samples by calcination in flowing air at 650 °C for 6 h using a ramp rate of $2\ °C\ min^{-1}$.

Powder X-ray diffraction data was obtained by a Philips X'pert diffractometer using Ni filtered Cu Kα radiation with $\lambda = 1.54$ Å. Samples were analysed from 1.5° to 10° 2θ and d-spacings were calculated using the Bragg equation $n\lambda = 2d \sin \Theta$. Nitrogen adsorption isotherms were measured for calcined samples using a Gemini 2375 Micromeritics surface analyser. Surface areas were calculated using the B.E.T. equation and pore size distributions from the desorption data using the B.J.H. method [20,21]. All samples were pre-treated by heating in vacuum at 120 °C for 1 h. Transmission electron microscopy analysis was conducted by dispersing samples on holey C films supported on 400 mesh Cu grids. The samples were gently ground using a mortar and pestle prior to dispersion. Images were recorded using a JEOL 2010 electron microscope operated at 200 kV.

3. Results

3.1. Influence of synthesis time

The mesoporous silicas produced for different synthesis times were characterised using X-ray diffraction by means of an ex situ method. The XRD powder patterns are presented in Figs. 1 and 2, and additional data is shown in Table 1. By increasing the synthesis time, a transition occurs from a mixed MCM-41/MCM-50 mesophase to MCM-48 and finally to MCM-50. Fig. 1 shows the XRD powder patterns of uncalcined mesoporous silica synthesized for different time. X-ray analysis of the as-synthesized white powder, without any heating to 150 °C (i.e. 0 h), revealed a typical spectrum of MCM-41 with a

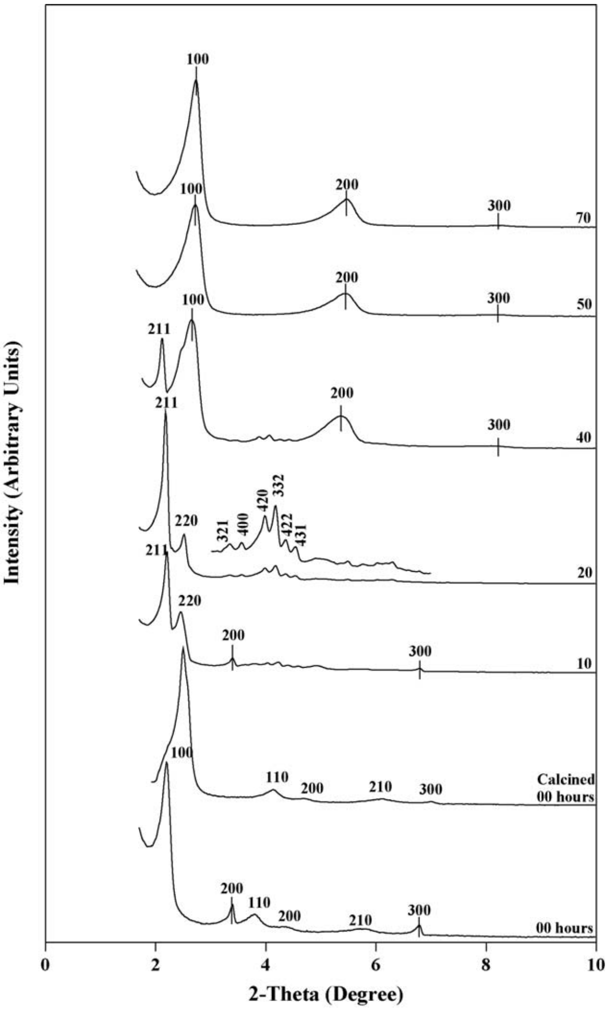

Fig. 1. XRD powder patterns of silicate (uncalcined except for sample 'calcined 00 h') synthesised using TEOS:CTAB:NaOH:H_2O = 1:0.55:0.5:101.4 for stated time at 150 °C. Reflections for MCM-50 are indicated with vertical lines.

set of four characteristic peaks. The most intense peak is (1 0 0) observed along with other MCM-41 related diffraction lines. The peaks for MCM-41 are due to the ordered hexagonal array of parallel silica tubes and can be indexed assuming a hexagonal unit cell as (1 0 0), (1 1 0), (2 0 0), and (2 1 0) at 2Θ values of 2.2°, 3.8°, 4.3° and 5.8°, respectively. The peaks at 3.4° and 6.8° 2Θ correspond to the (2 0 0) and (3 0 0) reflections, respectively, for MCM-50, which is in agreement with the results reported by Pevzner et al. [15]. From the *d*-spacings, the (1 0 0) peak is calculated to be 39 Å (2.25°) and therefore coincides with the (1 0 0) of MCM-41. The loss of the (2 0 0) and (3 0 0) peaks for the calcined sample is further evidence of the presence of MCM-50 for the room temperature preparation.

The XRD pattern revealed a clear change in the structure of the uncalcined mesoporous silica powder when synthesized for 10 h. It can be seen that the MCM-41 related (1 0 0) peak at 2Θ value of 2.2° with *d*-spacing 26 Å is now replaced by two peaks which can be indexed as (2 1 1) and (2 2 0) according to the bicontinuous cubic structure of MCM-48 [22,23]. A new set of diffraction peaks developed around $2\Theta = 4°$ can also be indexed as (3 2 1), (4 0 0), (4 2 0), (3 3 2), (4 2 2), (4 3 1), etc. for MCM-48 structure. The appearance of well-separated peaks with high intensity indicates an ordered cubic structure of MCM-48. It is interesting to note that while there is no MCM-

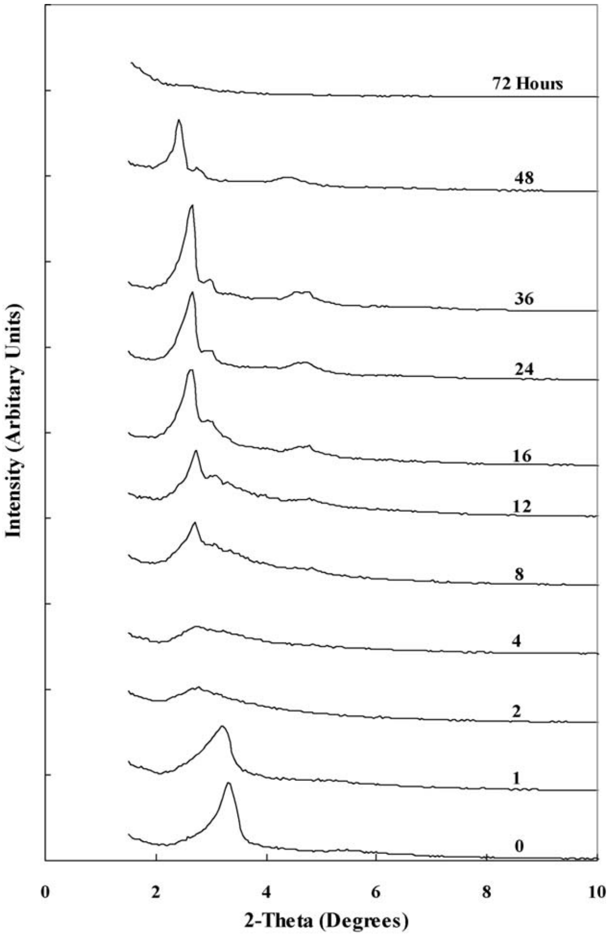

Fig. 2. XRD powder patterns of calcined and modified silicates synthesised using TEOS:CN:CTAB:NaOH:H_2O = 1:0.11:0.6:0.56:111.6 for stated time at 150 °C.

Table 1
Properties of calcined and modified silicates synthesised using TEOS:CN:CTAB:NaOH:H_2O = 1:0.11:0.6:0.56:111.6 for stated time at 150 °C

Time (h)	Phase	*d*-Spacing (Å)[a]	Pore diameter (Å)	Surface area ($m^2\,g^{-1}$)
0	MCM-41	26	<20	1650
1	MCM-41	27	<20	1600
2	MCM-48	31	26	1050
4	MCM-48	32	25	1700
8	MCM-48	32	27	1300
12	MCM-48	32	26	1400
16	MCM-48	33	26	1150
24	MCM-48	33	27	1200
36	MCM-48	33	26	1150
48	MCM-48	36	29 + 35	850
72	[b]	–	38	410

[a] Characteristic peak $d_{(1\,0\,0)}$ MCM-41 and $d_{(2\,1\,1)}$ MCM-48.

[b] Disordered pores resulting from collapse of MCM-50 after calcinations.

41 remaining after 10 h, MCM-50 is still present but has diminished in intensity.

A significant change in structure was observed when a synthesis time of 20 h was employed. It can be seen that the larger synthesis time of 20 h not only resulted in a more ordered structure of MCM-48, but also eradicated the MCM-50 phase which was present after 10 h. The characteristic peaks of the MCM-48 structure can be identified along with the enhancement of (2 1 1) peak intensity. The calculated *d*-values corresponding to different peaks of MCM-48 mesoporous silica were found to be almost identical (with a variation of approximately ±1 Å) to those reported by Schmidt et al. [22].

A mixed phase of cubic and lamellar structure, as shown in Fig. 1, corresponding to MCM-48 and MCM-50, respectively, was observed when as-recovered white powder was synthesized for 40 h at 150 °C. Compared to mesoporous material synthesized for 20 h, the intensities of the peaks related to MCM-48 pore structure are reduced and the diffraction pattern corresponding to the (1 0 0), (2 0 0) and (3 0 0) peaks of MCM-50 are detected. It is interesting to note that the diffraction peaks corresponding to MCM-50 for synthesis time ≥40 h have shifted to higher values than those for preparations of 10 and 0 h. A small shoulder on the rising edge of the (1 0 0) diffraction line seems to be the diminishing effect of the (2 2 0) peak of mesoporous silica synthesized for 20 h. MCM-50 was the only phase detected for synthesis times of 50 and 70 h.

For the materials modified by the addition of CN, Fig. 2, the calcined white powder recovered after a synthesis time of 0 h exhibited a single peak at $d = 26$ Å which is characteristic of MCM-41. This peak was also present after 1 h at 150 °C but had reduced intensity. The intensity continued to decline up to about 4 h and thereafter started to be replaced by poorly ordered MCM-48. At synthesis time greater than 8 h a well ordered MCM-48 with $d_{(2\ 1\ 1)}$ spacing centred at 32/33 Å emerged. The order of this material, measured by the intensity of the major XRD peak, reached a maximum after 36 h. Longer reaction time caused an increase in $d_{(2\ 1\ 1)}$ spacing from 33 Å for 36 h to 36 Å after 48 h. The intensities of the peaks were reduced suggesting the material is less ordered than that produced after 36 h, but the MCM-48 phase is still present. After 72 h, MCM-48 had decomposed entirely to a disordered material following the collapse of MCM-50 during calcination.

The pore size distributions measured as a function of synthesis time are presented in Fig. 3. At short reaction time, 0 and 1 h, the results suggest that the materials formed were predominantly microporous. Mesopores started to develop after 2 h with a pore diameter centred at ca. 26 Å. Longer synthesis time showed the progressive development of these mesopores with diameter centred at 26/27 Å up to 36 h. After 48 h, the main pore diameter present had increased to 29 Å, while a smaller volume of larger pores were produced with a broad pore size distribution centred at approximately 35 Å. A 72 h synthesis time produced a mesoporous material with a wide pore size distribution centred at a diameter of 38 Å. The results in Table 1 show that the materials formed after 0, 1, and 4 h synthesis time have surface areas in the range 1600–1700 $m^2\ g^{-1}$ while the sample produced after 2 h had a significantly lower value of 1050 $m^2\ g^{-1}$. The surface areas for MCM-48 are generally greater than 1100 $m^2\ g^{-1}$ and significant reductions are seen for the samples synthesised after 48 and 72 h, namely 850 and 410 $m^2\ g^{-1}$, respectively.

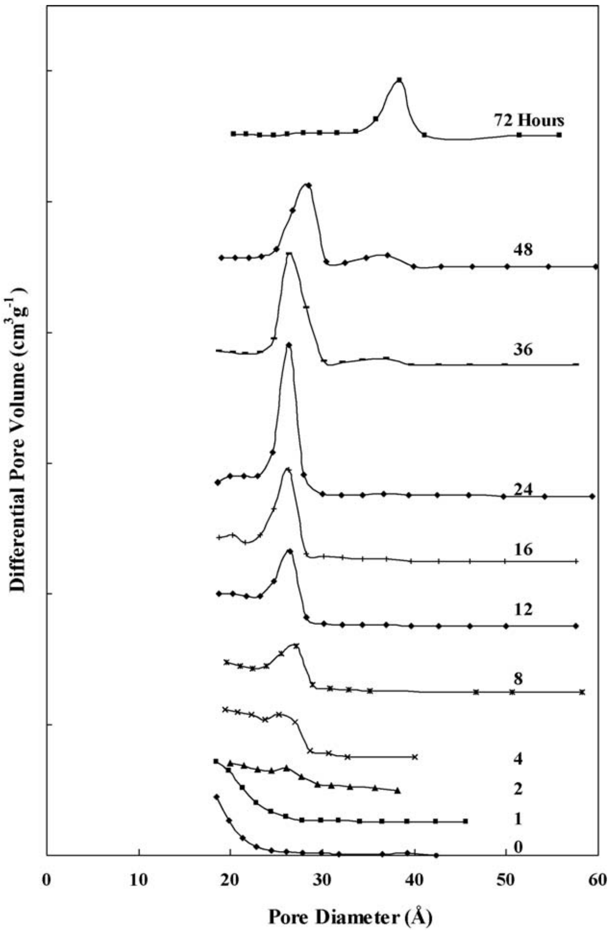

Fig. 3. BJH pore size distribution of calcined and modified silicates synthesised using TEOS:CN:CTAB:NaOH:H_2O = 1:0.11:0.6:0.56:111.6 for stated time at 150 °C.

3.2. *Influence of synthesis temperature*

The results of XRD analysis and porosity measurements of unmodified silicates and for 10 mol% CN modified preparations over a temperature range from 100 to 175 °C for 24 h are shown in Table 2. For unmodified silicates, MCM-48 with $d_{(2\ 1\ 1)}$ spacing at 30 Å was produced at 100 °C. This *d*-spacing increased to 31 Å at 125 and 150 °C. A temperature of 175 °C resulted in a material which was X-ray amorphous (MCM-50 that has decomposed). For CN modified silicates, synthesis at 100 °C gave a single reflection for MCM-41 centred at 28 Å. The silicate synthesised at 125 °C was a mixture of MCM-41, $d_{(1\ 0\ 0)}$ spacing 27 Å, and MCM-48, $d_{(2\ 1\ 1)}$ spacing 31 Å. MCM-48 was the only material detected at 150 °C and a disordered material was produced at 175 °C. The pore size distributions for unmodified silicates indicate that the pore diameter generally increased with increasing temperature, which is in good agreement with the trend shown by the XRD patterns over the same temperature range. A regular pore size

Table 2
Characteristics of unmodified mesoporous silicates synthesised using TEOS:CTAB:NaOH:H_2O = 1:0.55:0.5:101.4 and CN modified mesoporous silicates using TEOS:CN:CTAB:NaOH:H_2O = 1:0.11:0.6:0.56:111.6 at stated temperatures for 24 h

Temperature (°C)	Phase	*d*-Spacing (Å)[a]	Pore diameter (Å)	Surface area ($m^2\ g^{-1}$)
Unmodified				
100	MCM-48	30	22	1650
125	MCM-48	31	22	1550
150	MCM-48[b]	31	25 + 37	1100
175	[b]	–	38	400
10 mol% CN				
100	MCM-41	28	<20	1750
125	MCM-41 + MCM-48	27 + 31	25, Broad distribution	1300
150	MCM-48	33	27	1200
175	[b]	–	38	550

All samples were calcined.

[a] Characteristic peak $d_{(1\,0\,0)}$ MCM-41 and $d_{(2\,1\,1)}$ MCM-48.

[b] Disordered pores resulting from collapse of MCM-50 after calcinations.

distribution was recorded at temperatures of 100 and 125 °C for unmodified MCM-48: the pores were each 22 Å in diameter while the sample at 125 °C had a significantly greater volume of these pores relative to those at 100 °C (not shown). At 150 °C the majority of pores are MCM-48 with diameter 25 Å, while the diameter of the pores of the disordered material was 37 Å. A wider pore size distribution centred at 38 Å was recorded at 175 °C. For the CN modified silicates the mixed mesoporous material synthesised at 125 °C contained MCM-48 pores with diameter approximately 25 Å. The most pronounced MCM-48 phase is formed at 150 °C giving a regular pore size distribution centred at 27 Å. The surface areas of the ordered materials are generally high (1100–1750 $m^2\ g^{-1}$) and show a significant decrease for synthesis at 175 °C ($\leq$550 $m^2\ g^{-1}$).

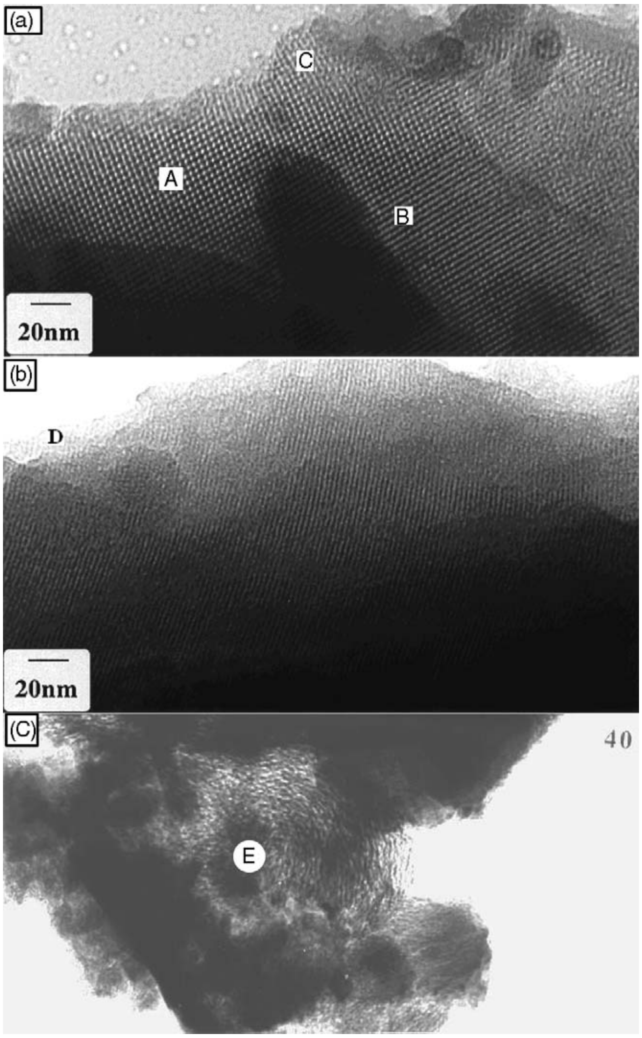

Fig. 4. TEM images for calcined and modified silicates synthesised using TEOS:CN:CTAB:NaOH:H_2O = 1:0.11:0.6:0.56:111.6 at 150 °C: (a) MCM-48 36 h; (b) MCM-41 0 h; (c) disordered 72 h.

3.3. TEM analysis

The transmission electron microscopy (TEM) images of different silica powders synthesized under various conditions are shown in Fig. 4. The TEM image of cubic MCM-48 synthesised using 10 mol% CN modifier at 150 °C for 36 h (Fig. 4a) shows a highly ordered pore arrangement in regions A and B. However, the pores are orientated at different angles in different areas. For example, in region A the pores are oriented at an angle to the plane of the image whereas in region B they are oriented parallel to the image. A localized region C, contains pores which interchange between both directions and these areas confirm the three-dimensional nature of MCM-48. The image for MCM-41 synthesised with 10 mol% CN modifier at room temperature is shown in Fig. 4b. The silica is composed of a uniform array of pores which are curved at the centre of the image. This distortion of pores has been observed for MCM-41 [24,25] and causes a sufficient reduction in the long range order of the material to eliminate reflections higher than the $d_{(1\,0\,0)}$ from the XRD powder pattern. The pores located in region D are hexagonally arranged. Fig. 4c (region E) shows the TEM image of the disordered mesoporous silicate synthesized for 72 h. This material has a ‘sponge-like’ morphology containing a range of pore dimensions, and lacks an ordered arrangement. These results agree very well with those recorded using both XRD and nitrogen adsorption porosimetry.

4. Discussion

Overall, the presence of 2-cyanoethyltriethoxysilane has a significant effect on the porous properties of calcined materials. From temperature studies, it is clear that increasing the concentration of CN modifier from 0 to 10 mol% requires a corresponding increase in the temperature needed to produce both MCM-48 and disordered materials and also allows MCM-41 to form at 100 °C. Combining the results of the synthesis time and temperature studies gives a useful comparison of the development and evolution of mesopore phases. The evolution of phases over time or temperature is MCM-41/MCM-50 → MCM-48 → MCM-50. The formation of MCM-48 phase requires elevated temperatures ($\geq$100 °C for the synthesis procedure used here) including the production of a composite MCM-41/MCM-50 as intermediate phases.

The structural transformations observed with increasing time and temperature are caused by changes in the silica charge density, which then require an adjustment to the silica surfactant mesophase to maintain charge matching. This effect has been noted by Xu et al. for the SiO_2–Na_2O–$C_{16}TABr$–H_2O [17] who attributes the transformations during MCM-48 synthesis to the fact that the silica charge density decreases with reaction time. In general, the experimental results in this communication agree well with this study and show that organically modified MCM phase evolution proceeds in a similar manner to unmodified preparations. We therefore assign the changes occurring to a decreasing charge density on the silica framework as silica condensation progresses. While the presence of the organic group has been shown to significantly influence mesopore phase, the effect of this group on the formation of the mesophase does not alter the overall phase transformations from MCM-41/50 to MCM-48 to MCM-50.

A relatively high charge density at short synthesis time allows a MCM-41/MCM-50 silica-surfactant structure, which is then converted over time to an MCM-48 mesophase and finally to MCM-50 to maintain charge matching, as the charge density decreases. Increasing reaction temperature has a similar effect on phase development i.e. MCM-41/MCM-50 to MCM-48 to MCM-50. The changes here are dictated by the increasing silica condensation rate with temperature causing similar changes in charge density as those when reaction time are increased. The addition of the 2-cyanoethyltriethoxysilane increased the onset temperature for the MCM-48 phase. This phase was observed at 100 °C without the modifier and required 125 °C and above with the modifier. This data indicates that this modifier can delay the decrease in charge density on the developing silica polymer.

5. Conclusions

The porosity characteristics of mesoporous silica are strongly influenced by synthesis time, temperature and the quantity of 2-cyanoethyltriethoxysilane modifier. A poorly ordered MCM-41/MCM-50 mesophase was formed at low synthesis time and this was progressively replaced by a mesoporous MCM-48 phase over extended reaction time. The MCM-48 phase subsequently transformed to MCM-50, which decomposed to a disordered structure on calcination and was accompanied by an increase in mean pore diameter and a significant decrease in surface area. A similar trend was observed when the synthesis temperature was increased i.e. MCM-41 → MCM-48 → disordered, with comparable variations in pore diameters and surface areas. These observations are interpreted in terms of varying charge density on the silica polymers due to the presence of organic modifier, and when synthesis time or temperature are increased, leading to materials with increasing pore diameters.

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