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Heteropolyacids aided rapid and convenient syntheses of highly ordered MCM-41 and MCM-48: exploring the accelerated process by ^{29}Si MAS NMR and powder X-ray diffraction studies†

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A rapid and convenient route is described for the synthesis of mesoporous MCM-41 and MCM-48 materials using heteropolyacids as novel promoters, and a probable mechanism for the rapid nucleation is proposed based on HSAB theory.

The discovery of ordered mesoporous materials[1] and the explosive research in this area have opened new vistas in materials science.[2,3] The two most important members of the mesoporous family are MCM-41 and MCM-48; while the former comprises an array of hexagonal '*honeycomb*' structures, the latter possesses a cubic '*gyroid*' one. Though synthesis of MCM-41 is facile, that of MCM-48 is intricate because of the '*swinging*' presence of its cubic phase lying amidst hexagonal and lamellar ones; hence, not many reports on reliable, low template content, cost effective synthesis of MCM-48 have been published.[4–7] An approach to reduce synthesis time of porous materials using inorganic anions as promoters has been reported earlier,[8] however, the synthesis of MCM-41 and MCM-48 using catalytic amounts of promoters whilst maintaining the ordered structures is a daunting task. It is in this context that we have endeavored to use heteropolyacids as a new class of promoters for the synthesis of mesoporous materials.

We report here for the first time a novel, convenient (avoiding addition of any co-surfactant[5] or acid, *e.g.*, H_2SO_4[7]) as well as rapid synthesis route for MCM-41 and MCM-48 by using very low template concentration (Si/template ≈ 5) and catalytic amounts of heteropolyacids (HPAs, $H_3PMo_{12}O_{40}\cdot 24H_2O$, $H_3PW_{12}O_{40}\cdot 24H_2O$) and the oxometalate species ($Na_2MoO_4\cdot 2H_2O$, $Na_2WO_4\cdot 2H_2O$, $NaH_2PO_4\cdot 2H_2O$) as promoters.

Promoter mediated MCM-41 and MCM-48 syntheses have been performed with an initial gel composition of SiO_2–0.32NaOH–0.2CTABr–125H_2O–0.0033P (CTABr = cetyltrimethylammonium bromide, P = promoter) and SiO_2–0.4NaOH–0.21CTABr–120H_2O–0.0033P, respectively. In a typical synthesis, 3 g of fumed silica was added to a solution of x g NaOH [x = 0.64 (for MCM-41), 0.8 (for MCM-48)] in 25 mL H_2O and stirred for 1 h. To this mixture, drop-wise addition of a solution of y g CTABr [y = 3.64 (for MCM-41), 3.82 (for MCM-48)] in 50 mL H_2O was followed by an addition of required amount of promoter in z mL of H_2O [z = 37 (for MCM-41), 33 (for MCM-48)]; the final gel was stirred for 90 min. The samples were autoclaved at 100 °C for 4 h (for MCM-41) and at 150 °C for 12 h (for MCM-48). The as-synthesized mesoporous samples were air-calcined at 540 °C. To study the effect of promoters in the nucleation process, syntheses were carried out at different time intervals and the samples were characterized using powder XRD and ^{29}Si MAS NMR. The effect of promoter concentration was studied in the synthesis of MCM-41 employing variable Si : P ratios from 25 to 600 in the gel for 4 h. The best ordered patterns of MCM-41 (from XRD) were obtained at Si : P ratio of 300 that was chosen as the standard throughout this work (see Fig. S1 of ESI†).

Atomic absorption spectroscopic (AAS) analyses of the HPA mediated syntheses of mesoporous samples revealed absence of Mo or W in their frameworks. Powder XRD patterns of calcined MCM-41 and MCM-48 (Fig. 1A and B), synthesized using promoters showed excellent well-resolved XRD patterns in the 2θ region of 1.5 to 6°. The improved surface area and unit cell dimensions of the materials (Table 1) showed increased porosity, when HPAs were used in the syntheses.

TEM images and the diffraction patterns of the promoter mediated MCM-41 and MCM-48 samples exposed excellent hexagonal (*p6mm*) and cubic (*Ia3d*) mesophases respectively (Fig. 2A and B). Especially, the TEM images of MCM-48 resembled plate-like morphology and were completely devoid of any intra-particle defects, which usually account for secondary mesoporosity.[7] SEM images of the samples revealed hexagonal (also spheroidal) and cuboidal particles of MCM-41 and MCM-48 respectively (Fig. 2C and D), further supporting the XRD and TEM results.

^{29}Si MAS NMR experiments on MCM-41 and MCM-48 (Fig. 3) synthesized in presence and absence of $H_3PW_{12}O_{40}$ (PTA) at different time intervals were carried out to determine the degree of polymerization and concentration of the silanol groups. The two major peaks, Q^3 (δ ~ −100 ppm) and Q^4 (δ ~ −110 ppm) measure the concentration of ^{29}Si of the type (SiO)$_3$≡Si–OH and (SiO)$_3$≡Si–O–Si≡, respectively.[6,9,10] It was observed that the % Q^4 species increased with time at the expense of Q^3 and Q^2 species. In contrast to the spectra obtained without using PTA, the more condensed and ordered arrays of MCM-41 and MCM-48 were obtained at 4 h and 12 h respectively when PTA was used, as evident from the respective $Q^3 : Q^4$ ratios. Similar $Q^3 : Q^4$ ratios in the synthesis of MCM-48 with and without promoters (3 h and 36 h respectively) imply

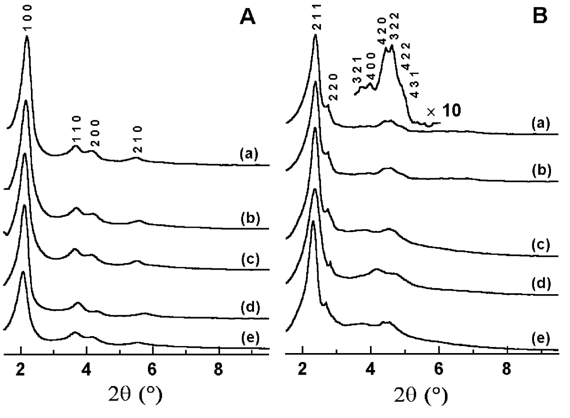

Fig. 1 Powder XRD patterns† of (A) calcined MCM-41 samples synthesized at 100 °C using (a) $H_3PW_{12}O_{40}$ (4 h), (b) $H_3PMo_{12}O_{40}$ (4 h), (c) Na_2WO_4 (8 h), (d) Na_2MoO_4 (8 h), and (e) without promoter (16 h); (B) calcined MCM-48 samples synthesized at 150 °C using $H_3PW_{12}O_{40}$ at (a) 12 h, (b) 15 h, (c) 18 h, (d) 24 h, and (e) without promoter for 36 h.

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† Electronic supplementary information (ESI) available: powder XRD patterns and instrumentation details. See http://www.rsc.org/suppdata/cc/b2/b206482k/

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Table 1 Physical characteristics of MCM-41 and MCM-48 samples synthesized with or without promoters

Material	Promoter	Synthesis time/h	d_{hkl}/Å	a_0/Å[b]	Surface area†/m² g⁻¹	(Q^3/Q^4)[c]
MCM-41	none	16	42.37 (100)	48.92	1024	1.22 (0.32)
MCM-41	MA/WA	8	41.73 (100)	48.18	1162	nd
MCM-41	PMA/PTA[a]	4	41.16 (100)	47.52	1271	0.49 (0.16)
MCM-48	none	36	38.08 (211)	93.28	1413	0.79 (0.18)
MCM-48	MA/WA	24	37.55 (211)	91.98	1520	nd
MCM-48	PMA/PTA	12	37.11 (211)	90.90	1701	0.47 (0.15)

[a] PMA ($PMo_{12}O_{40}^{3-}$), PTA ($PW_{12}O_{40}^{3-}$), MA (MoO_4^{2-}), WA (WO_4^{2-}). [b] $a_0 = 2d_{100}/\sqrt{3}$ (MCM-41); $a_0 = d_{211} \times \sqrt{6}$ (MCM-48). [c] As-synthesized samples, values in parentheses are for calcined samples. nd = not determined.

the effect of HPA in rapid nucleation, that with advancement of time produced a very high degree of silanol condensation. Similar results were also achieved in the case of MCM-41 syntheses.

We presume that oxoanions of HPAs play a crucial role by bringing down the surface energy[11] (free energy of the crystal/liquid interface) and dissipating the surrounding aqueous layer that hinders the formation of the critical nuclei, essential for the nucleation of the mesoporous materials. Based on the HSAB theory,[12] we infer that rapid nucleation of mesoporous materials has occurred due to the presence of '*hard–hard*' interaction arising out of the hydration sphere of water molecules and the oxoanions of HPAs used. Thus, the water molecules surrounding the nucleus are extracted out, leaving the silicates and CTABr to have a '*soft–soft*' interaction in between them for the formation of the mesoporous nuclei. Hence, water extraction from the vicinity of the silicate species probably plays a crucial role in bringing down the syntheses times of the mesoporous materials, unlike conventional synthesis procedures in the absence of promoters. HPAs are known to dissociate into their respective oxoanions in alkaline media.[13] To explore the effects of PO_4^{3-} and WO_4^{2-} in the hydrothermal synthesis of MCM-41 (for 4 h), these anions were added simultaneously at various ratios (keeping Si : PO_4^{3-} = 300 and WO_4^{2-} : PO_4^{3-} varied from 1 to 15) to the synthesis gel. From the XRD patterns (see Fig. S2 of supplementary information†) we observed that at lower WO_4^{2-} : PO_4^{3-} ratios (1 to 6) poor hexagonal mesophases of MCM-41 were obtained. At WO_4^{2-} : PO_4^{3-} = 12 which is exactly similar to that of $PW_{12}O_{40}^{3-}$, excellent and distinct hexagonal patterns were observed. Thus, the crucial role for the rapid nucleation of MCM-41 and MCM-48 is played by the oxoanions generated from the HPA dissociation in the syntheses media (pH ≈ 11).

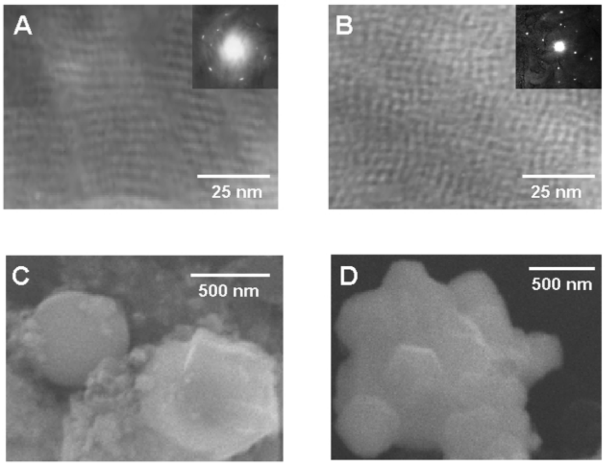

Fig. 2 TEM images† of calcined (A) MCM-41, 4 h and (B) MCM-48, 12 h (insets show respective electron diffraction patterns). SEM images of calcined (C) MCM-41, 4 h and (D) MCM-48, 12 h; synthesized using PTA.

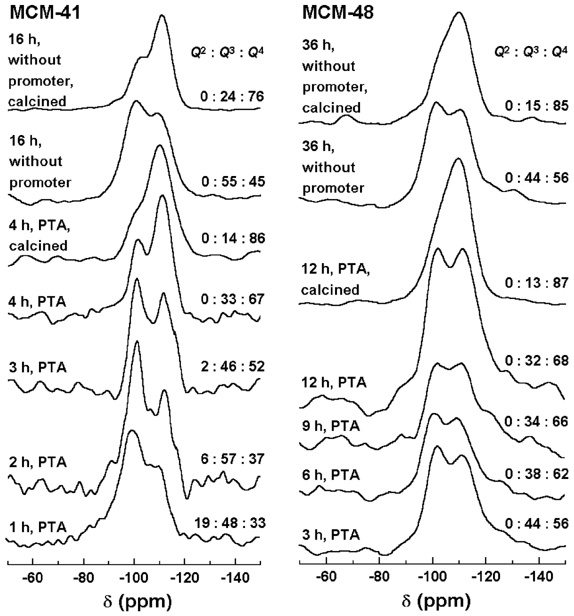

Fig. 3 ^{29}Si MAS NMR spectra† of as-synthesized MCM-41 and MCM-48 at different time intervals.

Interestingly, we have observed atleast a 3 to 4 fold decrease in the syntheses times of the mesoporous materials by catalytic addition of HPAs, compared to the conventional approaches. These promoters can further be exploited in rapid syntheses of other types of porous materials.

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