

# Fine-tuning of pore size of MCM-41 by adjusting the initial pH of the synthesis mixture

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The pore size of MCM-41 can be finely tuned from 38.3 to 52.7 Å with a narrow distribution by carefully adjusting the initial pH of the synthesis mixture from 11.5 to 10.0.

MCM-41, with well-defined mesopores and extremely high surface area, has been the focus of much research interest since its discovery by the researchers at the Mobil Research and Development Corporation in 1992.<sup>1</sup> The precise tuning of its pore size is among the many favorable properties of MCM-41. Recently, many synthesis techniques, aiming at enlarging the pore size with narrow distribution, have been developed.<sup>2</sup> Some approaches use surfactants with different chain lengths or binary templating agents to expand the pore size.<sup>1–3</sup> Other routes use high temperatures in synthesis or postsynthesis treatment.<sup>4–6</sup>

It is well known that MCM-41 is typically characterized by an X-ray reflection in the vicinity of  $2\theta = 2^\circ$ . However, the mesoporous materials synthesized by different researchers were not exactly the same under similar synthesis conditions (temperature, mixture composition, etc.),<sup>1,7</sup> unlike the case of microporous zeolite synthesis in which the characteristic X-ray reflections are well known. In our recent study, it was shown that the difference in the  $d_{100}$  spacing stems from the initial pH of the synthesis mixture, and we found that the pore sizes of the synthesized materials can be adjusted in a relatively wide range ( $> 14$  Å) with a narrow pore distribution by varying the initial pH of the synthesis mixture.

The general procedure for synthesizing MCM-41 is as follows: 5.2 g of sodium silicate hydrate from Kigida Chemical Co. Ltd. (Japan) was dissolved in 25 ml of deionized water. The pH of the solution was adjusted to the desired value by adding 4 M  $\text{H}_2\text{SO}_4$  to obtain a silica gel. A precision pH paper (Macherey-Nagel, Germany) was used to determine the pH of the gel. After vigorously stirring for 30 min at ambient temperature, an aqueous solution of CTAB (cetyltrimethylammonium bromide) was added into the gel to produce the synthesis mixture (typical composition:  $\text{SiO}_2 \cdot 0.5\text{Na}_2\text{O} \cdot 0.24\text{CTAB} \cdot 60\text{H}_2\text{O}$ ). The mixture was allowed to stir at ambient temperature for 1 h, then placed in a static stainless steel autoclave kept at different temperatures for various time periods. After cooling to ambient temperature, the resulting solid material was recovered by filtration, washed with water and dried at 353 K for 4 h. The as-synthesized materials were calcined at 823 K for 6 h.

The X-ray diffraction patterns were recorded on a Rigaku RAD-2X diffractometer using nickel-filtered  $\text{Cu-K}\alpha$  radiation at 35 kV and 20 mA. Nitrogen adsorption measurements were performed using a Coulter SA 3100 adsorption analyzer which reports adsorption isotherm and BET specific surface area and pore volume automatically. Before the adsorption analysis the samples were outgassed for 4 h at 573 K. The primary mesopore size  $w_d$  is determined by using eqn. (1), the distance between pore centers  $a_0$  is calculated using eqn. (2), and the pore wall thickness  $b_d$  is given by eqn. (3).<sup>8</sup>

$$w_d = 1.213d_{100} \sqrt{\frac{2.2V_p}{1 + 2.2V_p}} \quad (1)$$

$$a_0 = 2d_{100}/\sqrt{3} \quad (2)$$

$$b_d = a_0 - w_d \quad (3)$$

The X-ray diffraction patterns of samples synthesized at different pH are shown in Fig. 1. It can be seen that all the samples prepared at pH 10.0–12.0 show strong reflections at *ca.*  $2\theta = 2^\circ$ , indicating that the mesostructures are well developed. Moreover, the interplanar spacing  $d_{100}$  changes between 38.4 and 53.8 Å when the initial pH of the synthesis mixture varies from 11.5 to 10.0. The material prepared at pH 12.0 seems to be a lamellar mesophase, showing no distinct X-ray diffraction peaks after calcination. And no X-ray reflections were determined for the samples prepared at  $\text{pH} < 10.0$  and  $\text{pH} > 12.0$ .

The synthesis conditions and characteristic parameters of the obtained mesoporous materials are summarized in Table 1. It is indicated that the mesostructures prepared at pH 10.0–11.5 are well developed with high surface area and large pore volume. When the initial pH of the synthesis mixture changes from 11.5 to 10.0, the pore size of the product varies from 38.3 to 52.7 Å and the pore wall thickness increases from 6.0 to 9.4 Å. The mesophase obtained at pH 12.0 has relatively low surface area and small pore volume, indicating that the structure may collapse after calcination.

The effects of CTAB/silica ratio and synthesis temperature on the pore size were also investigated. As shown in Table 2, the

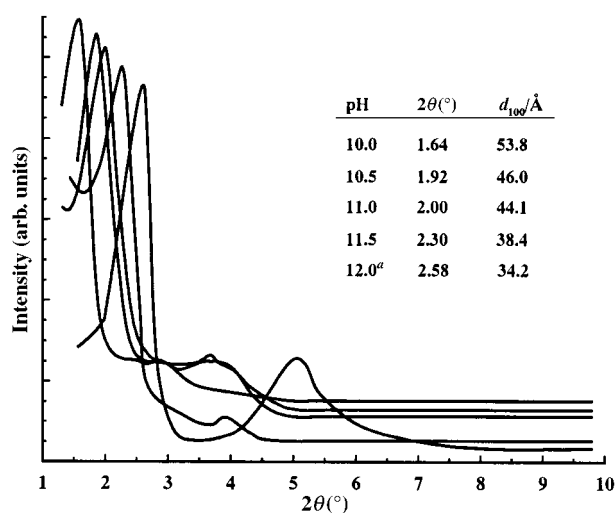


Fig. 1 X-Ray diffraction patterns of the mesoporous materials synthesized at pH 10.0–12.0. <sup>a</sup> As-synthesized material which showed no reflections after calcination at 823 K for 6 h.

**Table 1** Synthesis conditions and structural parameters of MCM-41 prepared at different pH using the same mixture composition

T/K	t/h	pH	$d_{100}$ spacing/Å	$S_{\text{BET}}$ / $\text{m}^2 \text{g}^{-1}$	$V_p$ / $\text{cm}^3 \text{g}^{-1}$	$w_d$ /Å	$a_0$ /Å	$b_0$ /Å
403	36	10.0	53.8	833	0.85	52.7	62.1	9.4
403	12	10.5	46.0	1046	1.00	46.3	53.1	6.8
403	12	11.0	44.1	1022	1.05	44.7	50.9	6.2
403	11	11.5	38.4	1261	0.95	38.3	44.3	6.0
403	36	12.0	34.2 <sup>a</sup>	421	0.49	—	—	—

<sup>a</sup> The as-synthesized sample, which showed no X-ray diffraction reflection after calcination at 823 K for 6 h.

**Table 2** Preparation of MCM-41 at different CTAB/SiO<sub>2</sub> molar ratios and temperatures

T/ K	t/h	pH	CTAB/SiO <sub>2</sub> ratio	$d_{100}$ spacing/Å
403	12	11.0	0.24	44.1
403	12	11.0	0.18	43.7
403	12	11.0	0.12	43.3
373	72	11.0	0.24	42.0

mesostructure characterized by the  $d_{100}$  spacing undergoes little change when varying the CTAB/silica ratio from 0.12 to 0.24 at pH 11.0. The synthesis temperature greatly affects the polymerization rate of the silica wall, but has little influence on the pore size of MCM-41, when elevated from 373 to 403 K.

Since the variation of pH only changes the OH<sup>-</sup> concentration in the mixture, we propose that the pH of the synthesis mixture may affect the mesopore size by altering the charge matching pattern in the mixture. According to the model proposed by Huo and co-workers,<sup>9</sup> there are two basic pathways, one *via* direct self-assembly of a cationic inorganic species (I<sup>+</sup>) and an anionic surfactant (S<sup>-</sup>), and the other mediated by counterions of opposite charge. Our results seem to suggest that the synthesis of MCM-41 by our approach may take the mediated pathway, with OH<sup>-</sup> working as the counterion. Because the mesopores are hexagon-shaped due to the Si–O bond conformation, while the micelles of the surfactant are theoretically spherical to minimize surface tension, the pores and the micelles do not match geometrically. We propose that

the I<sup>-</sup> anions and S<sup>+</sup> cations may be mediated by a layer of aqueous solution of inorganic ions (*i.e.* OH<sup>-</sup>) which balance the charges. At lower pH, the thickness of the counterion layer may increase to keep the total OH<sup>-</sup> constant in order to balance the charge, resulting in the enlargement of the pore size of the product. pH variation may also change the electrostatic charge distribution in the mixture, affecting the interactions of head groups in the micelle and resulting in the expansion of the micelle.<sup>10</sup>

The results reported here provide a convenient way of finely tuning the pore size of mesoporous MCM-41, which is promising in pore engineering and ‘molecular sieving’ with adjustable pore size, and may find wide application in shape-selective catalysis in fine chemicals, bio-separation and adsorption.

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