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Synthesis of Cubic Mesoporous Silica MCM-48 by Mixed Micellar Templates

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Abstract: High-quality mesoporous silica MCM-48 were synthesized under basic conditions by using the mixture of cetyltrimethylammonium bromide (CTAB) and alkylamine (C_nNH_{2n+3}, n=8,10,12,14, respectively) as templates. The effects of the alkylamines with different chain lengths (n=8,10,12,14,16,18, respectively) on the silica structure were investigated.

Keywords: Mixed micellar template, cubic mesoporous silica, synthesis.

In 1992, Mobil researchers introduced a novel concept in the synthesis of mesoporous silicas (M41S)[1,2] by using a self-assembled molecular array of surfactant molecules as structure-directing template. Depending on the shape of their templates and the respective resulting pore structure, the M41S family was identified : MCM-41(hexagonal), MCM-48(cubic), and other species. MCM-41 with honeycomb arrays of nonintersecting channels was shown to be the easiest to synthesize[1]. MCM-48 containing a three-dimensional network has potential applications as versatile catalyst, molecular sieves, or as host structures for nanometer-sized guest compounds[3,4] because of its insensitivity to blockage, which is a great advantage in comparison with MCM-41. But it was difficult to prepare MCM-48 by using surfactant alone as template[2,5].

Recently, mixed surfactants have been used as mixed micellar templates for the synthesis of mesoporous silica with modified properties[5,6,7]. On the other hand, using mixed surfactants template is an easy way to change the surface charge distribution and the packing parameters of the surfactant aggregates, and hence provides a favorable route to synthesize mesoporous silicas with different pore-size and structure.

In this paper, we have focused our work especially on the synthesis of cubic MCM-48 by using the mixture of cetyltrimethylammonium bromide (CTAB) and alkyl amine ($C_nH_{2n+1}NH_2$, n=8,10,12,14,16,18, respectively) as templates. It was revealed that the long-range order of cubic structure increases with increasing alkylamine chain length from C_8 to C_{14} and the phase transition from cubic to lamellar will occur when the chain length of alkylamine increases to C_{16} or C_{18}.

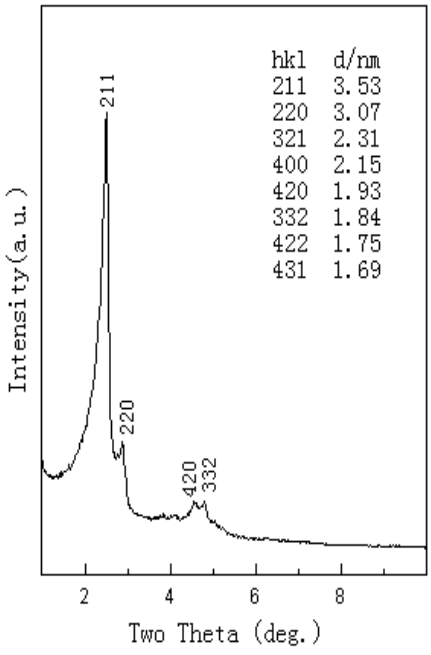
In a typical synthesis, CTAB, $C_nH_{2n+1}NH_2$, and NaOH were dissolved in water at 45^0C and then tetraethylorthosilicate (TEOS) was added to the solution. The molar

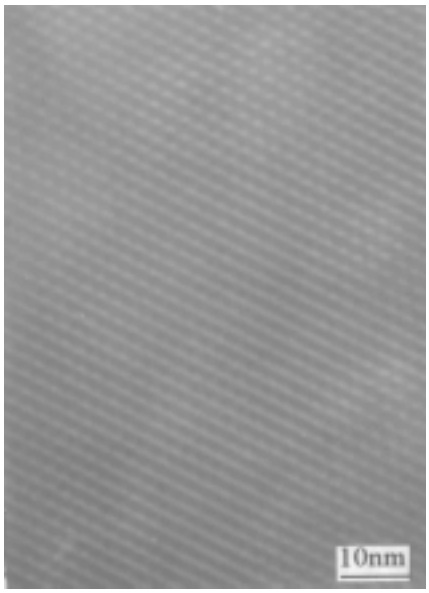
composition of the mixture was: 1.0 TEOS:0.24 CTAB:0.012 $C_nH_{2n+1}NH_2$: 0.45 NaOH:56 H_2O with n=8,10,12,14,16,18, respectively. In this mixed template system, the molar ratio (0.251:1) of the mixed surfactants to silica is low in comparison with the molar ratio (0.65:1) of the surfactant alone to silica presented by Monnier *et al*[8]. After stirring for 1h, the mixture was filled into a teflonlined steel autoclave and statically heated at 100^0C for 3 days. The resultant white product was filtered and washed several times with deionized water. After drying it was calcined at 550^0C in air for 4h.

The XRD pattern of a calcined MCM-48 is shown in **Figure 1**. The pattern exhibits a typical *hkl* reflections which can be indexed in the cubic space group Ia3d with lattice constant of 8.52 nm. The high order reflections at low angle range provided direct evidence for a good long-range order of pore structure, and this sample kept the cubic structure without collapse after calcination at 550^0C for 4h, demonstrating a good thermal stability.

Figure 1 XRD Pattern of the calcined MCM-48 templated by CTAB-$C_{12}NH_{27.}$ This pattern was obtained with a RigakuDmax-2000 diffractometer using Cu Kα radiation

Figure 2 HRTEM image of calcined MCM-48 showing the sample on the (110) cubic plane. This image was taken with Hitachi H-9000 HA microscope operated at 300kv.





A representative TEM micrograph of the calcined MCM-48 is given in **Figure 2**, which reveals the presence of a regular pore system with high order in long-range structure. The corresponding XRD pattern shown in **Figure 1** demonstrates sharp

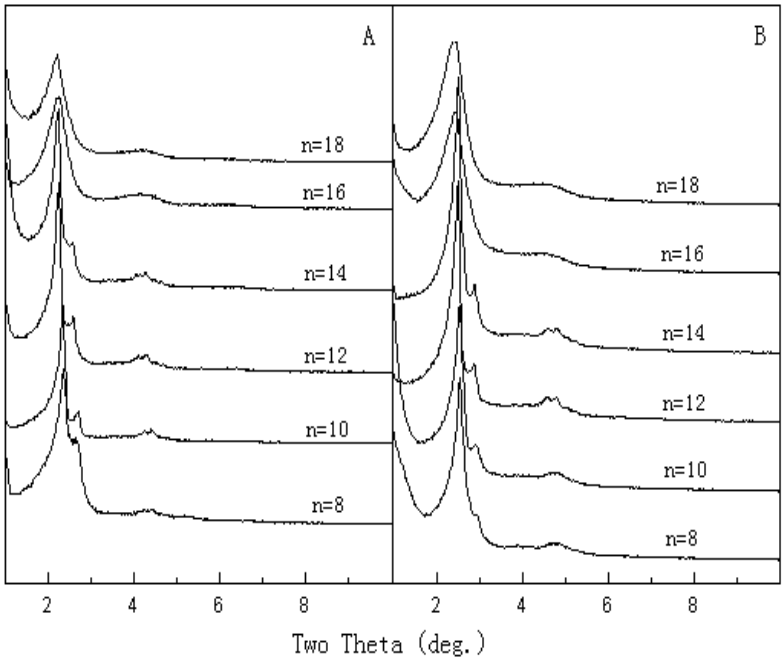
diffraction peaks at low angles. This TEM image is in good agreement with the results reported in the literature[9].

Nitrogen adsorption-desorption isotherm showed that the calcined MCM-48 exhibited sharp step of capillary condensation at a relative pressure P/Po of *ca.* 0.27, which is indicative of the filling of framework-confined mesopores[10]. The BET surface area is 1217 m^2/g, and the single-point total pore volume at a relative pressure of 0.994 is 1.064 cm^3/g, which gives an average pore diameter of 3.47 nm.

Figure 3 shows XRD patterns of the as-synthesized (A) and the calcined (B) MCM-48 obtained by using mixed CTAB-$C_nNH_{2n+1}NH_2$ surfactants as templates, and n is 8,10,12,14,16,18, respectively. It can be seen that when mixed CTAB-$C_nNH_{2n+1}NH_2$ (n=8,10,12,14, respectively) surfactants were used as templates, the patterns exhibited the typical hkl reflections corresponding to cubic Ia3d symmetry. The d-spacings as well as the long-range order of the cubic structure increases with increasing alkylamine chain length from C_8 to C_{14}. But if the number of carbon in alkylamine chains varies from C_{14} to C_{16}, the structure of the mesophase SiO_2 changes from cubic to lamellar. As the molar ratio of the alkylamine to silica increase from 0.012 to 0.12 in the mixed surfactants system, the phase transition from cubic to lamellar occurred too.

The phase transition from cubic to lamellar with increasing alkylamine chain length indicated that CTAB and C_nNH_{2n+3} formed a mixed surfactants micellar aggregates. As

Figure 3 XRD Patterns of the as-synthesized (A) and the calcined (B) MCM-48 templated by mixed CTAB-$C_nNH_{2n+1}NH_2$, n =8,10.12,14,16,18, respectively.



an approximation, we can use the local effective surfactant packing parameter, $g = V/a_0l$[11], to explain this phase transition, where V is the total volume of the surfactant chains plus

any cosolvent organic molecules between the chains, a_0 is the effective head group area at the micelle surface, and l is the kinetic surfactant tail length. In classical micelle chemistry, the expected mesophase sequence as a function of g is cubic (pm3n) with g =1/3, hexagonal(p6m) with 1/3<g<1/2, cubic(Ia3d) with 1/2<g<2/3, lamellar with g =1[5]. When CTAB alone is used as template, hexagonal MCM-41 can be easily synthsized because of the value of g with1/3~1/2. If a mixture of CTAB and $C_nH_{2n+1}NH_2$ with appropriate ratio was used as a mixed micellar template, alkylamine may enter the palisade layer of CTAB micelles to decrease the electrostatic repulsion between the head group of quaternary ammonium ion. The average value of a_0 will decrease, so that the value of g may increase to 1/2~2/3, and therefore the cubic MCM-48 is favored in the case of alkylamine with a carbon atom number of 8,10,12,14. As the chain length of the alkylamine increases further to C_{16} or C_{18}, a thick palisade layer may be formed. The value of V will increase and correspondingly the value of g will approach 1, consequently the structure becomes a lamellar one. It was found that the mesoporous silica structure can be controlled by varying the chain length and the amount of the alkylamine in these mixed templates.

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