

REMOVAL OF ORGANIC TEMPLATE FROM MESOPOROUS MCM-41

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Abstract. The removal of cetyltrimethylammonium bromide from as-synthesized MCM-41 in different methods has been investigated. The removal of template from MCM-41 precursors was conducted by reflux, Soxhlet extraction and magnetic stirring extraction at ambient room temperature in ethanol and ethanol-containing hydrochloride solvents. The obtained materials were characterized by TG-DSC, XRD, SEM, TEM and isotherm of adsorption/desorption of nitrogen. The results show that the treatment of MCM-41 precursor in the C₂H₅OH-HCl-H₂O system allows a complete removal of organic template in range of 5-60 minutes at room temperature. The obtained MCM-41 materials possess highly ordered mesoporous structure.

1 Introduction

Mesoporous silica materials of MCM-41 type are synthesized from the surfactant micellar template addition of an inorganic silica source [1]. Cetyltrimethylammonium bromide (CTA⁺ Br⁻) is most commonly used as template. It is necessary to remove the occluded organic molecules to make the sieves porous for adsorption and catalysis. In general, the template molecules are burned off by calcination at 500-600°C in air or oxygen. Although calcination is largely satisfactory, it occasionally leaves carbonaceous residue in the molecular sieves. Sometimes the situation may be ameliorated by slow and/or step heating. However, there are at least three inherent problems associated with the calcination process that is frequently used to remove template molecules from molecular sieves. (1) The sample in question may not be stable at the temperature at which the organic molecules are removed, eg. Organo functionalized MCM-41; (2) the sample may be stable at a high temperature at which the organic molecules are removed, but the removal of organic molecules makes the structure susceptible to attack by water vapor (humidity); (3) the transformation of crystalline phase to another may occur, resulting in damage of mesoporous structure. These problems demand a search for other ways to remove organic molecules from molecular sieves. Recently, a new method was suggested to burn the template off [2], [3]. In this procedure ozone-containing air generated by UV lamp irradiation was used at low temperature; An alternative method for template removal is extraction with conventional solvent [4-8] or

supercritical fluid [8], [9] which allows the templates to be removed without decomposition, permitting its recovery and reuse. In this paper, authors present a method of pore emptying is extraction by use various solvents. The ethanol acidified by HCl acid provided efficient solvent to remove CTA⁺ from as-synthesized MCM-41. The textural properties of MCM-41 removed by different methods also were evaluated.

2 Experimental

Mesoporous silica MCM-41 was synthesized using cetyltrimethylammonium bromide (CTAB, 98%, Merck) as surfactant. Tetraethoxysilane (TEOS, 98%, Aldrich) was used as a silica source. The preparation procedure followed the method described in literature [7]. In briefly, 0.5 g of CTAB, 480 mL of distilled water and 7 mL NaOH 2M were mixed at 80°C for 30 minutes. Then, resulting mixture was added by 9.8 g of TEOS under strong stirring for 2 h. The solid was collected by filtering, washing by distilled water. The obtained solid (as-synthesized powder) dried 60°C at without further thermal treatment was denoted as parent MCM-41P in which micellar filling was entirely preserved.

Prior to the experiments a part of as-synthesized MCM-41 was calcinated at 500°C for 6 h (denoted as calcined MCM-41C). Next samples were prepared using extraction method. The part of as-synthesized MCM-41 sample was placed into Soxhlet apparatus and extracted with ethanol for 36 h. This sample is denoted as MCM-41S(36h). The extraction of the template was carried out using the mixture of 1g of as-synthesized MCM-41 and 200 ml of ethanol under reflux for 6h (denoted as MCM-41R(6h)). Next sample was prepared by the reflux of 1g of as-synthesized MCM-41 in 200 ml of acidified ethanol (1 ml of concentrated HCl : 100 ml of ethanol). This sample is denoted as MCM-41RHCl. The extraction of the template was carried out using the mixture of 1g of as-synthesized MCM-41 and 200 ml of acidified ethanol (1ml of concentrated HCl : 100 ml of ethanol) under magnetic stirring at ambient room temperature (denoted as MCM-41SRHCl).

Nitrogen adsorption and desorption isotherms at 77K were measured using a Micromeritics Tristar 3000 equipment. The specific surface areas, S_{BET} , were calculated using the BET method. Pore size and pore size distribution were determined using the BJH procedure. X-ray powder diffraction (XRD) patterns were recorded using Cu K α radiation source on a 8D Advance powder diffractometer. Thermal analyses of the samples were made with thermal analyzer (SETARAM). Scanning electron micrographs (SEM) were obtained with an IMS-NKL, magnifications varied between X 30 k and X 100 k. Transmission electron micrographs (TEM) were obtained using an EMLab-NIHE at an acceleration voltage of 80.0 kV.

3 Results and discussions

Fig. 1 shows the TG and DSC diagrams of as-synthesized MCM-41 and MCM-41 samples after removal of template and calcined MCM-41 for the sake of comparison. For as-synthesized MCM-41, the large amount of weight losses (16%) in several steps corresponding to exothermic peak in DSC from 200-500°C before leveling off at around 600°C was observed. Since its DSC consisted of exothermic peak only, the removal of template appears to be by oxidative decomposition rather than by evaporation (desorption). The TG curves of MCM-41S(36h) (weight loss ~19.4%) and MCM-41R(6h) (weight loss ~17.6%) possess the behaviors as same as that of as-synthesized MCM-41 indicate the removal of templates was not complete. For MCM-41RHCl and MCM-41SRHCl samples, the endothermic peak at ~100°C can be attributed to desorption of water from channels. The TG curves leveling off at 100°C and similar to that of calcined MCM-41 indicated that the templates were removed completely according to TG analysis. The broad exothermic peaks of DSC for MCM-41RHCl and MCM-41SRHCl around 350°C were attributed to crystallization of amorphous silica. From results mentioned above, it is clear that the acidified ethanol is effective in the removal of occluded CTA⁺. The role of HCl in the mixture of ethanol and HCl is supposed to provide the relevantly polar solvent to dilute the template of CTAB with inherent polarization. Goepper et al. [10] suggested a chemical method (methanolic HCl) and showed its effectiveness for the removal of organic template from AlPO₄. Kokotailo et al. [11] have suggested repeated washing with metal salts and calcination to remove the organic molecules.

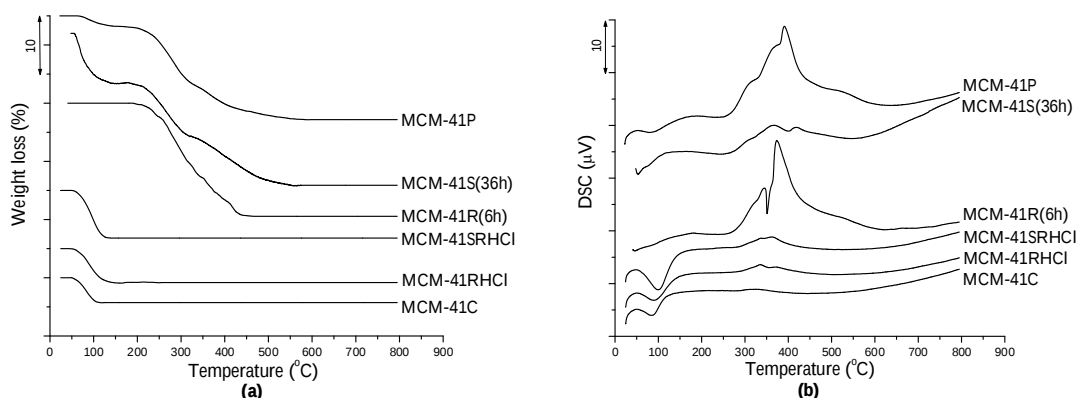


Fig. 1. (a) TG curves and (b) DSC curves of as-synthesized MCM-41; MCM-41S(36h); MCM-41R(6h); MCM-41SRHCl; MCM-41RHCl; and calcined MCM-41.

The TG-DSC curves for as-synthesized MCM-41 after treatment of acidified ethanol at different times in reflux and magnetic stirring conditions were presented in Fig. 2. As it can be seen in Fig. 2, after 5 minutes of treatment, the weight losses in three stages become only one stage of physical water desorption around 100°C indicating the

removal of CTA^+ is complete in the view of TG. In all of samples, the exothermic peaks in range 300-400°C without any weight losses were attributed to the crystallization of amorphous phase.

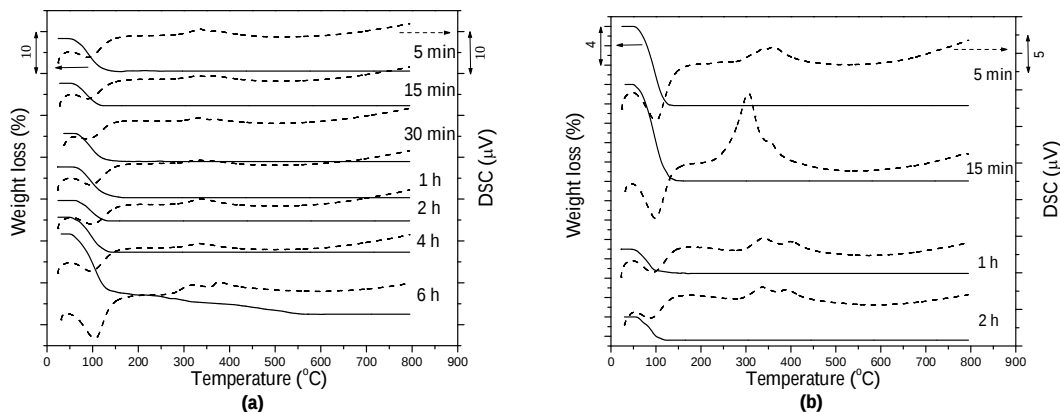


Fig. 2. Diagrams of TG-DSC for MCM-41RHCl samples (a) and template-removed MCM-41SRHCl samples (b) for different times.

XRD patterns of as-synthesized MCM-41, calcined MCM-41, MCM-41RHCl and MCM-41SRHCl were presented in Fig. 3. The characteristic peaks of (100), (110) and (200) for the hexagonal mesoporous structure of MCM-41 were observed clearly. The intensity of (100) peak does not seem to be changed in the range of 5-60 min. of reflux time and decreases relatively with prolonging the reflux times. The same results were also observed for magnetic stirring conditions. In both cases, the treatment of acidified ethanol around 5-60 min. is required to remove completely CTA^+ from as-synthesized MCM-41.

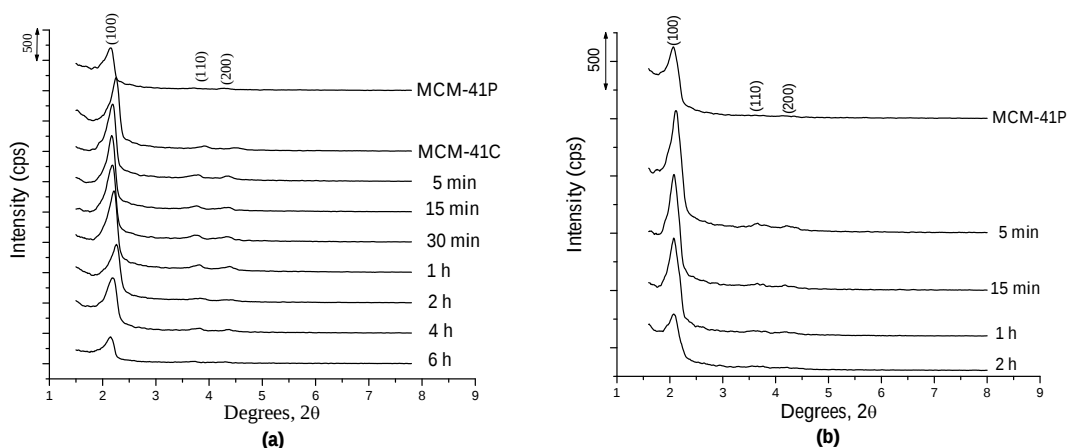


Fig. 3. XRD patterns of as-synthesized MCM-41, calcined MCM-41, MCM-41RHCl (a) and MCM-41SRHCl (b) removed CTA^+ at different times.

Fig. 4 and 5 show SEM and TEM observations of calcined MCM-41, as-synthesized MCM-41 after the treatment of acidified ethanol for 15 min. Although the removal of template was conducted by different methods, the morphologies of samples do not seem to be changed. As it can be seen in Fig. 4 and 5, morphologies of all

samples were similar and consisted of spherical particles with 100-200 nm in diameters.

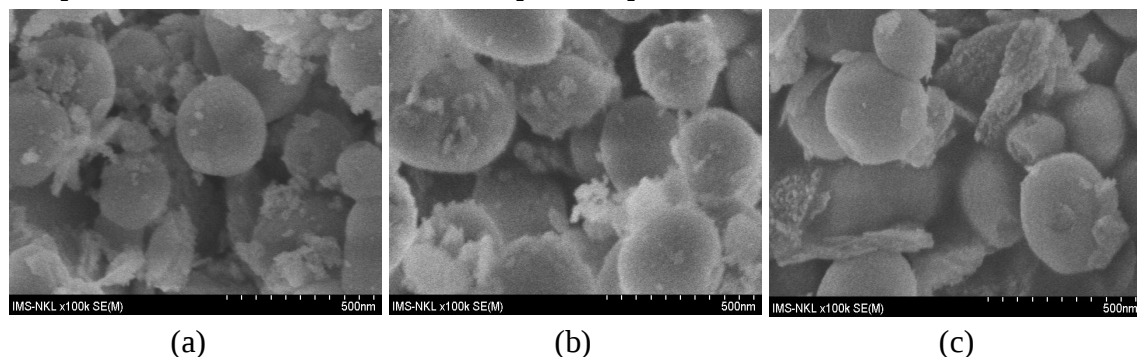


Fig. 4. SEM observation of calcined MCM-41 (a), MCM-41RHCl (b) and MCM-41SRHCl (c).

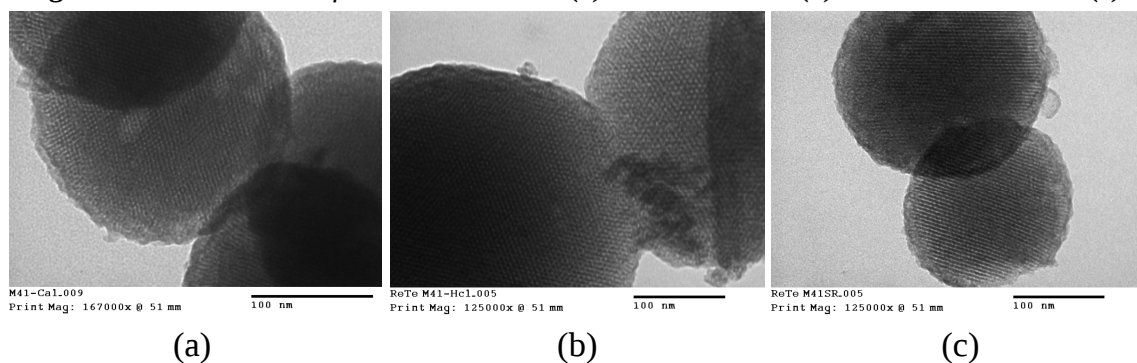


Fig. 5. TEM observation of calcined MCM-41 (a),
MCM-41RHCl (b) and MCM-41SRHCl (c).

The textural properties of MCM-41 samples were investigated by nitrogen adsorption as shown in Fig. 6. All the nitrogen adsorption isotherms corresponded to typical type IV [12]. This means that they exhibit uniform hexagonal mesoporous structure. Their condensation steps are sharp at P/P_0 of ~ 0.35 . The specific surface areas were similar and around $537\text{-}570\text{ m}^2\text{ g}^{-1}$. The pore size distribution curves in the inset of Fig. 6 demonstrated a variety of pore size distribution. The pore of calcined MCM-41 thermal-treated at 500°C and MCM-41RHCl treated at 78°C possessed three kinds of pore ~ 22 , 27 and $40\text{ \AA}$ while that of MCM-41SRHCl treated at ambient temperature shows main pore of $\sim 27\text{ \AA}$. However, main pore size of three samples concentrated on $26.9\text{-}27.9\text{ \AA}$ (Table 1). It seems that the lower the treatment temperature the narrower the pore-size distribution. The value of d_{100} decreases with the increase in treatment temperature as shown in table 1 indicated the cell parameter is shrinkaged at high temperature. From results mentioned above, stirring as-synthesized MCM-41 with acidified ethanol by HCl provides a convenient method of template removal in comparison with the conventional method of thermal evacuation of template.

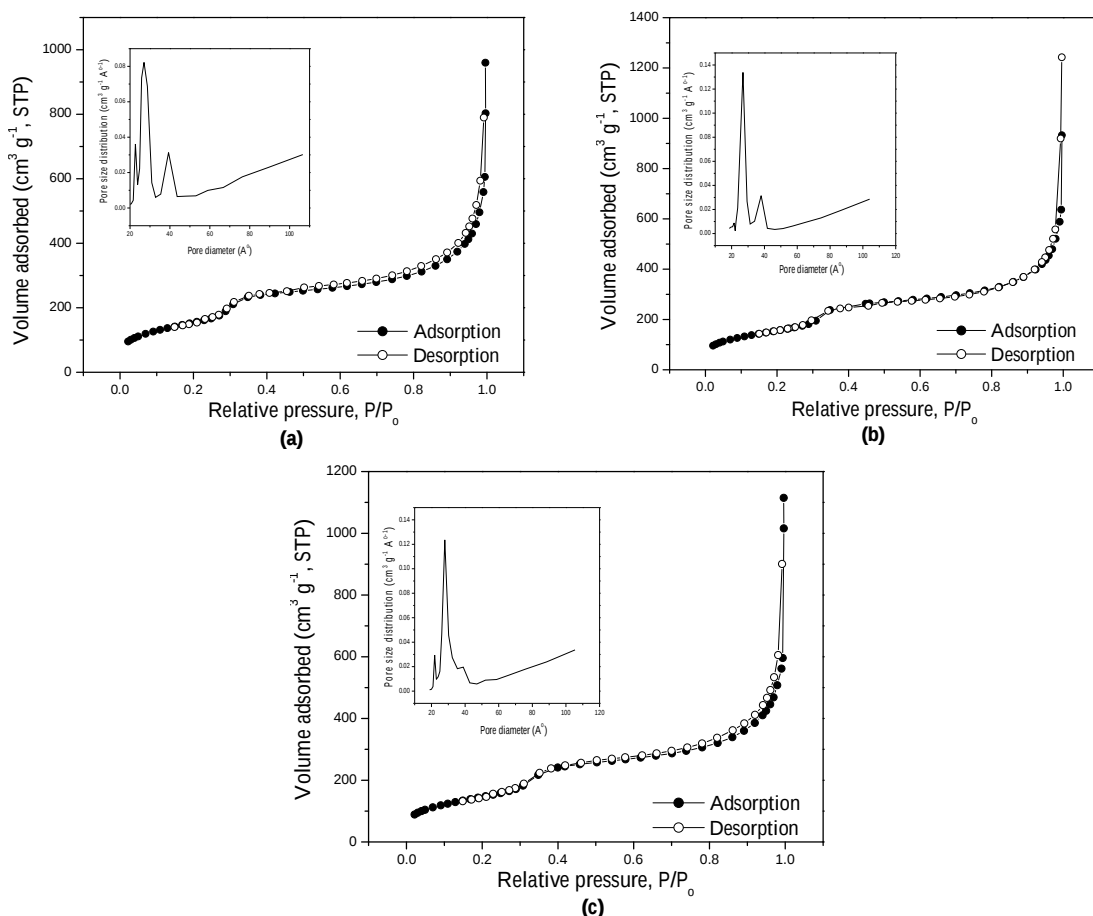


Fig. 6. Isotherms of adsorption/desorption of nitrogen and pore distribution of calcined MCM-41 (a), MCM-41RHCl (b) and MCM-41SRHCl (c).

Table 1. Textural properties of MCM-41C, MCM-41RHCl and MCM-41SRHCl

Sample	$d_{(100)}$ (Å)	a_o^* (Å)	d_{pore} (Å)	t_w^{**} (Å)	S_{BET} ($m^2 g^{-1}$)	V_{pore} ($cm^3 g^{-1}$)
MCM-41C	39.29	45.37	27.0	18.37	564.5	1.53
MCM-41RHCl	40.65	46.94	26.9	20.04	570.2	1.41
MCM-41SRHCl	42.52	49.10	27.9	21.20	537.6	1.76

$$*a_o = 2d_{(100)} / \sqrt{3}; **t_w = a_o - d_{pore}.$$

4 Conclusions

An ambient temperature chemical method involving acidified ethanol can effectively remove occluded organic template molecules from mesoporous molecular sieve MCM-41, providing the framework with highly ordered hexagonal mesoporous structure. This method is especially advantageous for molecular sieves synthesized using ionic

template, whose structure is not stable against water vapor upon removal of template molecules by the calcination. This method may also be extended to remove organic molecules from aluminosilicate and other molecular sieves.

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