A New Method to Remove Neutral Template in the Synthesis of HMS

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Abstract: In the synthesis of HMS, Soxhlet extraction as a new method to remove neutral template was studied. HREM image, X-ray diffraction patterns and nitrogen adsorption-desorption results verified that this method can not only efficiently remove and recover the template, but also benefit the maintenance of the mesoporous framework structure.

Keywords: Soxhlet extraction, HMS, After-treatment.

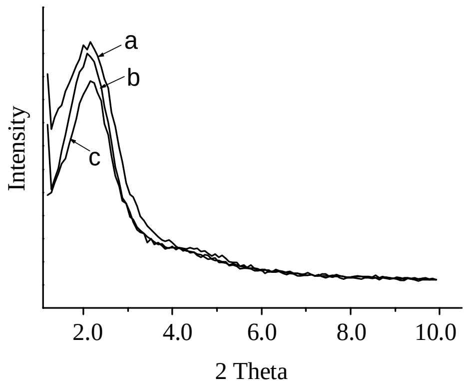
The synthesis of mesoporous molecular sieves is believed to be one of the most exciting discoveries in the field of material science[1]. The formation of mesoporous structure relies on the template effect of the surfactant micelles[2-4]. Generally three kinds of interactions are involved in this process, *i.e.* electrostatic charge matching, hydrogen bonding and coordinative interaction[5]. After template-directed synthesis procedure, the after-treatment process is needed to remove the surfactant template. Two methods normally used to remove surfactant templates are calcination and solvent extraction. Mesoporous materials generated through the charge-matching pathway mainly depend on calcination method to remove the templates, while materials through the hydrogen bonding pathways can depend on both methods. Calcination is widely adopted for its simplicity and efficiency. But noncorrosive solvent extraction possesses the outstanding advantages of surfactant recovery and environmental friendliness[6]. Compared with solvent extraction, another obvious disadvantage of calcination is that high temperature may cause framework collapse in molecule sieves[7].

HMS (Hexagonal Mesoporous Silica) is a kind of mesoporous molecular sieves generated through hydrogen bonding pathway first reported by Tanev *et al*.[8]. It is of great interest in the area of catalysis because of its thicker framework wall, which improves its thermal stability[6], and the wormhole framework structure[5]. We discussed the after-treatment methods for HMS synthesis in this paper.

Normal solvent extraction process includes duplication of refluxing mixture of the as-product and ethanol, followed by filtration[6]. It consumes large amount of solvent but still cannot remove the template efficiently. We used a new method - Soxhlet extraction in this paper to remove neutral primary amine template. Solxhlet extraction is very effective and economical.

Dodecylamine (DDA) was used as the template. Mixture of water and ethanol was used as solvent to improve template solubility. In a typical preparation, tetraethyl orthosilicate (TEOS) (2.0 g) was added under vigorous stirring to a solution of dodecylamine (1.0 g) in ethanol (8.0 g) and water (10.0 g). The reaction mixture was aged at room temperature for 0.5 hour. Then the template was removed by refluxing the resulted mesoporous silica in ethanol with Soxhlet extractor for 6 hours (denoted as HMS-S).

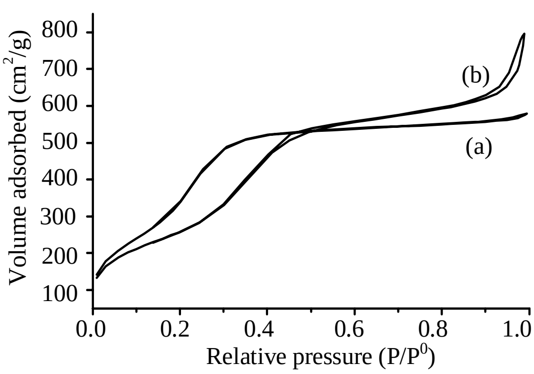
Figure 1 Powder XRD patterns of samples.



(a) HMS-C; (b) HMS-SC; (c) HMS-S

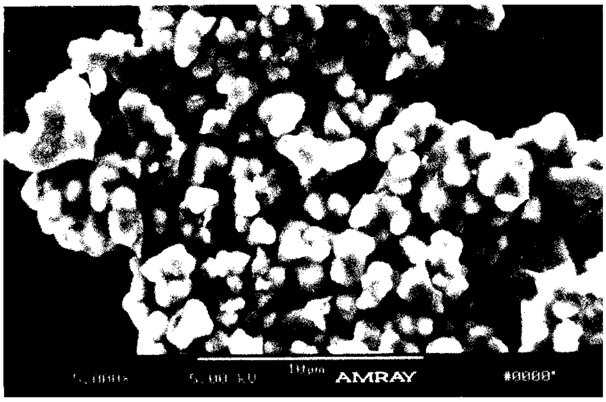
The XRD pattern of the sample is shown in **Figure 1**. Included for comparison are the patterns of a sample calcined in air at 773 K for 2 hours (denoted as HMS-C) and a sample calcined for 2 hours after Soxhlet extraction (denoted as HMS-SC). These samples are originated from the same gel. The three patterns in **Figure 1** are very similar and all exhibit a single diffraction peak corresponding to *d*-spacing of 4.4, 4.1 and 4.0 nm, respectively. There is only very small intensity difference among them.

Figure 2 Nitrogen adsorption and desorption isotherms for (a) HMS-S; (b) HMS-SC



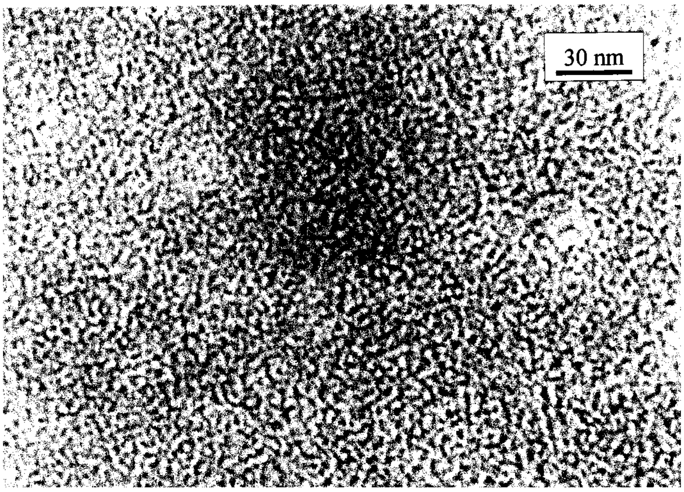
The results of N_2 adsorption-desorption were shown in **Figure 2**. The average pore diameters are all about 2.6 nm, the specific surface area is 948 and 1203 m^2/g for HMS-SC and HMS-S. The latter is larger than that of the sample treated with ordinary solvent extraction reported in ref. 6 as 1150 m^2/g. Compared with HMS-S, the smaller surface area of HMS-SC could be attributed to the pore collapse of the mesoporous framework on calcination.

Figure 3 SEM image of HMS



SEM image showing the particle texture of HMS materials silica is displayed in **Figure 3**. The materials exhibit a structure with large aggregates of smaller particles with average diameter of about 1 μm. High Resolution Electron Micrograph (HREM) image is presented in **Figure 4**. The image shows that the product contains a large number of channels. The channels lack long-range packing order, but they are regular in diameter.

Figure 4 HREM image of HMS



These results imply that the template DDA is efficiently removed by Soxhlet extraction from the pore network of the molecular sieves. Because the solution is kept pure and hot all the time, it can make the solvent extraction more efficient.

In conclusion, Soxhlet extraction is an efficient method to remove neutral template in the synthesis of HMS. This method not only makes template recovery practical and efficient but also avoids the destruction to the framework structure. It can be widely used in the after-treatment procedure of most mesoporous materials synthesized through hydrogen bonding or other weak interactions.

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