A Simple Method to Prepare Template-removed Zeolite MFI Nanomaterials

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ABSTRACT

A nominally room temperature photochemical method, simply employing ultraviolet light (λ = 184-257 nm) generated ozone environment, is shown to provide an efficient alternative for the removal of organic surfactant for zeolite MFI nanoparticles and thin film. The MFI nanoparticles and thin films were exposed in the UV lamp for a certain time. Thermal calcination of the as-synthesized materials was also carried out to enable direct comparison of the template removal processes. XRD, FTIR and BET results show that UV/ozone treatment and conventionally thermal calcination play the same role on the removal of template. Therefore, this method yielded high-quality MFI nanomaterials as produced by conventional thermal calcinations, which is time-consuming and energy costly.

Keywords: MFI nanoparticles, MFI thin film, UV/ozone treatment, thermal calcination

1. INTRODUCTION

For synthesis of microporous and mesoporous materials, where organic template or organic surfactant are used as structure directing agents, the removal of these compounds is not completely free of difficulties. For traditional microporous and mesoporous materials, thermal method is commonly used to prepare template-removed materials [1]. However, the high temperature calcination process is not desirable for the quite fragile materials with unusual compositions and frameworks and unsuitable for synthesizing thin films on temperature-sensitive substrates due to large thermal stresses at the film-substrate interface. Several other methods, such as solvent, supercritical fluid extraction, template-ion-exchange, have been applied to remove the organic surfactants from the as-synthesized mesostructure materials [2-4]. However, these techniques are either difficult to completely extract the large template molecules or the technical requirements are not generally available. Recently, a nominally room temperature photochemical method, simply employing ultraviolet light (λ = 184-257 nm) generated ozone environment, is shown to provide an efficient alternative for the removal of organic surfactant for MCM-type mesoporous materials [5,6]. It is also found that ozone-treated MCM-type materials via ozone generator have larger pores than traditionally calcined samples [7,8].

In this paper, we show further applications of short-wavelength ultraviolet (UV) radiation to completely remove organic molecules for zeolite MFI nanoparticles and thin film. Ozone is produced by UV-light illumination in the air. This process coverts the organic to carbon dioxide, water, and nitrogen which escape the material surface and leave behind well-defined crystalline microporous materials displaying high surface area.

2. EXPERIMENTAL SECTION

Pure silica MFI nanoparticles and thin films (TPA-silicalite-1) were synthesized by the method described previously [9,10]. The final product is nanoparticles with the size of 80 nm. The thickness of the film is about 440 nm [11].

The template removal procedure using UV/ozone was as follows. For the MFI nanoparticles, around 10 mg sample was spread evenly on silicon wafer which was inside the custom-made UV-chamber. UV radiation was produced via an ozone generating short-wavelength UV lamp (λ = 184-257 nm, UV power 4.0 W) in a quartz envelope. The samples was placed 3 mm below the lamp surface and the exposure time was varied between 30 h and 60 h. For the MFI thin films, the exposure period was varied between 3 h and 6 h. Thermal calcination of the as-synthesized materials was also carried out to

enable direct comparison of the template removal processes. For MFI nanoparticles, the sample was calcined at a heating rate of 1 ºC/min, up to a 550 ºC plateau for 6 h. For the thin film, the sample was calcined at 550 ºC for 6 h using a heating rate of 0.2 ºC/min and a cooling rate of 0.3 ºC/min.

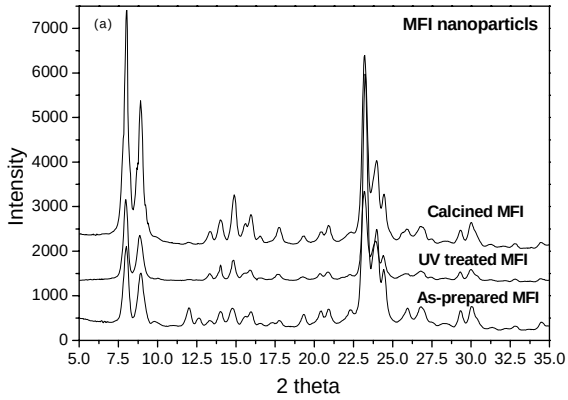
All materials were characterized using a combination of powder X-ray diffraction (Simens D5000), Scanning electron microscopy (SEM Philip XL 30) and Fourier-tranform infrared spectroscopy (FTIR Bruker). Pore properties of calcined and UV/ozone treated MFI nanoparticles were characterized using gas adsorption porosimetry (Micromeritics ASAP 2020).

3. RESULTS AND DISCUSSION

UV/ozone treatment exposes the samples to a freshly-cleaned UV lamp with samples placed 3mm below the lamp surface. The required exposure time for the complete removal of organic template depends on the distance of the sample from the lamp, the cleanliness of the UV generating lamp, and the amount of the sample powders as well as the thickness of the zeolite film. FTIR measurements show that 30 h and 4 h exposure time are found ideal in our UV exposure configuration to fully remove organic template from as-synthesized nanoparticles and thin films, respectively. However, the exposure periods and exposure geometry were not optimized for both of samples in this work.

It is well known that when pure silica MFI nanoparticles are thermally calcined to decompose the organic template, they retain their crystallinity and thus exhibit highly accessible porosity. [9]. Very similar changes are observed for the UV treated samples.

Fig. 1 shows the XRD patterns obtained for the as-synthesized, the UV/ozone treated and the thermally calcined MFI materials in the forms of nanoparticles and thin film. Independent of the MFI forms, the patterns for the as-synthesized MFI materials can be readily assigned to the (hkl) reflections for the Pnma orthorhombic symmetry, in good agreement with previous reports [12]. Thus, the as-synthesized MFI nanoparticles and films are fully crystalline. After the thermal calcinations or UV/ozone treatment, the first two lines at about 7.9 and 8.8º 2θ are lowered whereas the lines at about 11.9 and



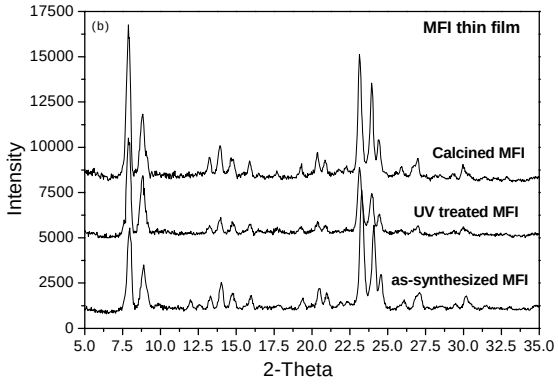


Figure 1. XRD patterns of the MFI for the as-synthesized, UV-treated and thermally calcined forms. (a) is for MFI nanoparticles; (b) is for MFI thin film.

12.5º 2θ decreased. These intensity changes result from the removal of extra framework organic template and inorganic species incorporated into the structural voids during synthesis [13].

The direct evidence for the removal of organic template was obtained from FT-IR spectroscopy measurements. Fig.2 shows FT-IR spectra of as-synthesized, UV/ozone treated and thermally calcined MFI samples in the forms of nanoparticles and thin films. For as-synthesized nanoparticles, the IR-spectra clearly show the characteristic signature resulting from methylene (-CH_2-) and methyl (-CH_3-) C-H stretching vibrations in the 2700-3100 cm^{-1} region [14] (The insert diagram in Fig. 2a magnifies the IR spectra of MFI nanoparticles at higher frequency (2400-3900 $cm^{-1)}$ region). These peaks straightforwardly indicate the

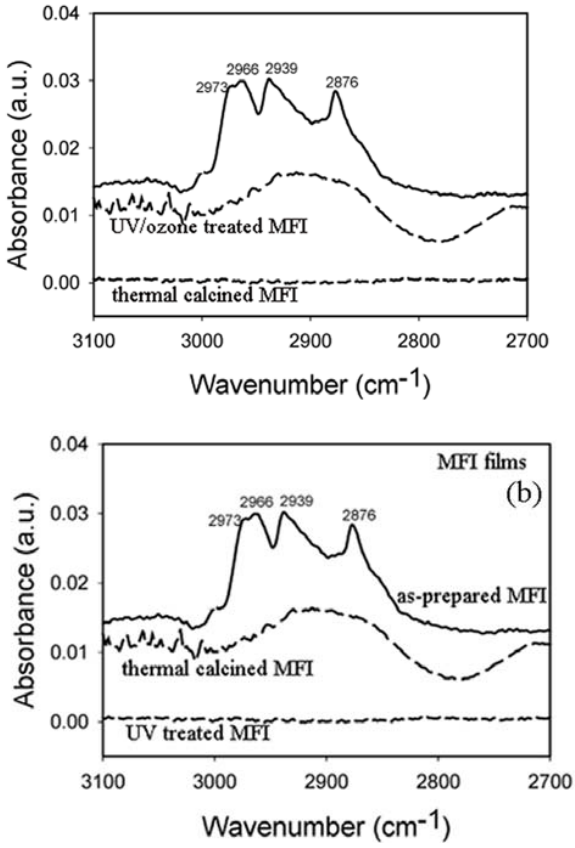


Figure 2. FT-IR spectra of the MFI for the as-synthesized, UV-treated and thermally calcined forms.(a) is for MFI nanoparticles, the insert diagram is the magnification of the high frequency IR regions; (b) is for MFI thin film in the high frequency mid-infrared for the MFI thin film.

presence of the organic template in the as-synthesized samples. The lower frequency (1300-1600 cm^{-1}) region of the spectra in Fig. 2a show methyl bending mode in the 1460-1470 cm^{-1} region. However, the lower frequency regions of the spectra for MFI film could not be easily resolved presumably because of low signal through-put obtained in the microscopy geometry for thin film. Thus, only high frequency (2700-3100 cm^{-1}) region is shown for MFI thin film in Fig. 2(b). After UV/ozone treatment or thermal calcination, the C-H peaks attributed to the methylene and methyl vibrations are absent (at least vanishing bellow the noise level in our spectra), confirming the essentially complete removal of the organic template. In addition, carbon analysis show that the C contents for as-synthesized, thermally calcined and UV/ozone treated MFI nanoparticles were 9.8%, 0.051% and 0.046%, respectively. These results provide additional evidence for the removal of organic template by UV/ozone treatment.

Nitrogen adsorption isotherm measurements were used to characterize nanoparticle porosities. BET surface areas are listed in Table 1. It is assumed that no internal surface area is vacated by simply drying the as-synthesized samples at room temperature since organic template tetrapropylammonium cations (TPA^+) are fully occluded in the channels. Thus, the data measured from the as-synthesized samples is considered as an estimate of the external surface area of MFI nanopartilces. As expected, the external surface area is about 47 m^2g^{-1}, larger than that of MFI microparticles [15]. BET surface area for the UV/ozone treated sample is 501 m^2g^{-1}. By comparison, thermally calcined sample has surface area of 498 m^2g^{-1}. The data obtained are considered to be the total surface area. The internal surface area, which demonstrates the characteristic porosity, is determined by the difference between the total surface area and the external surface area. The internal surface areas for both of samples are remarkably similar, 450-455 m^2g^{-1}. Due to the use of same samples in the different removal of template processes, it can be concluded that UV/ozone treatment and conventionally thermal calcination play the same role on the removal of template. For MFI thin films, the samples first polished on the backside and on the edges prior to gas adsorption measurements in order to remove all silicalite-1 except the film on top of the support. Kr adsorption data was recorded at liquid-nitrogen temperature. The surface areas of UV/ozone treated and thermally calcined films were very similar, 507 m^2/g and 502 m^2/g, indicating UV/ozone treatment has the same effect on the removal of template from zeolite films as the thermally calcined method.

MFI nanoparticles with size of 80 nm	BET surface area (m^2/g)	
	Total	Internal
As-synthesized	47	0
UV/ozone treated	501	454
Thermally calcined	498	451

Table 1. Surface area data from BET measurement

In addition, it should be pointed out here is that UV/ozone treatment dramatically shortened the time for the removal of template (from 3 days to 4 h). Thus, UV/ozone treatment may provide a more efficient way to prepare high-quality zeolite films.

4. CONCLUSIONS

UV/ozone treatment is a useful tool for the removal of the organic template from zeolite MFI materials. XRD, FT-IR and N_2 adsorption results indicate that the UV/ozone treatment allows complete removal of the organic template from MFI nanoparticles and thin films while remaining the inorganic framework, comparable to the thermal calcination. The main benefit of the method developed here is the nonthermal processing of the microporous materials. For this reason UV/ozone treatment could be well adapted to materials with a fragile structure where the nature of metal or other species occluded within the framework could be alerted on thermal treatment. Moreover, the use of low temperature can minimize the formation of cracks and defects of zeolite film caused by the different thermal expansion between substrate and zeolite during thermal calcinations process. Research is in progress to collect further experimental evidences for the application of this novel procedure in our group.

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