

# PREPARATION OF MESOPOROUS MCM-41/POLY(ACRYLIC ACID) COMPOSITES USING SUPERCRITICAL CO<sub>2</sub> AS A SOLVENT

Zhimin Liu, Zexuan Dong, Jianling Zhang, Zhenshan Hou, Yong Wang,  
Jiaqiu Wang, Ying Huang, Buxing Han\*

The Center for Molecular Science, Institute of Chemistry, The Chinese Academy of Sciences,  
Beijing 100080, P. R. China; Email: [Hanbx@infoc3.icas.ac.cn](mailto:Hanbx@infoc3.icas.ac.cn); Fax: 86-10-62559373

**Abstract** Synthesis of host-guest composites consisting of entrapped poly(acrylic acid) (PAA) and inorganic host MCM-41 was described. The monomer acrylic acid (AA) and initiator 2,2'-azoisobutyronitrile (AIBN) were introduced into the channels of MCM-41 using supercritical CO<sub>2</sub> as a solvent at 35.0°C, followed by free radical polymerization at a higher temperature, resulting in MCM-41/PAA composites. The composites were characterized using thermogravimetry (TG), Fourier transform infrared spectroscopy (FTIR), nitrogen adsorption and desorption, scanning electronic microscopy (SEM), X-ray diffraction (XRD). It has been confirmed that PAA was indeed entrapped into the pores of MCM-41, and the structure of MCM-41 was not destroyed. The composites with different compositions were obtained by controlling the processing parameters, such as the adsorbing time, concentration of AA in the fluid phase, and pressure of CO<sub>2</sub>.

## Introduction

In recent years, the need to create new materials with optimized, predetermined characteristics has spurred an increasing interest in hybrid materials, especially in organics and inorganics composites. MCM-41 mesoporous molecular sieves are hexagonal silicates or aluminosilicates with ordered pores. The dimensions of these pores can vary between 15 and 100 Å when a surfactant template was used, or between 70 and 300 Å when block copolymer templates were used(1,2). As inorganic component, MCM-41 has been used to prepare inorganics/organics hybrid materials. The MCM-41/polymer composites have been fabricated (3-10) by polymerization of monomers within MCM-41 pores. Moller and coworker(5) described a comparative study on the polymerization of methyl methacrylate (MMA) in the internal cavities and channels of microporous as well as mesoporous hosts. In their study, MMA was introduced via gas-phase adsorption into the pore system at high-vacuum condition. Polymerization was induced by benzoyl peroxide (BPO) during thermal treatment.

Recently, supercritical fluids (SCFs) have been utilized to fabricate composites, especially polymer-polymer composites(11,12). However, it has seldom been utilized in fabrication of inorganics/organics composites, especially MCM-41/polymer composites.

In this paper, we report a method to synthesize the molecular sieve/polymer composites with the aid of supercritical CO<sub>2</sub>. The synthesis of composites of mesoporous MCM-41 hosts with encapsulated PAA is investigated.

## Experimental section

**Materials.** MCM-41 was synthesized by the method reported by Anderson et al.(2), which produced typical regular arrangement of the straight one-dimensional pores. CO<sub>2</sub> with a purity of 99.95% was supplied by Huanxin Gas Co., and was used as received. AA purchased from Beijing Chemical Reagent Plant was distilled under reduced pressure. Initiator AIBN from Beijing Jinlong Chemical Reagent Company was used after recrystallization from acetone twice.

**Synthesis of MCM-41/PAA composites.** A suitable amount of AA monomer containing 0.3 mol% initiator AIBN was charged into a high-pressure stainless steel vessel of 31.4 ml. A small glass tube containing about 200 mg MCM-41 material was then placed in vessel. The liquid monomer did not contact with the MCM-41 in the high-pressure vessel because the MCM-41 was in the tube. The vessel was placed into a water bath whose temperature was controlled at 35.0°C by a HAAKE D3 temperature controller with accuracy of  $\pm 0.1^\circ\text{C}$ . After the air in the vessel was replaced by CO<sub>2</sub>, CO<sub>2</sub> was charged into the vessel by a high-pressure syringe pump (Beijing Xiantong Scientific Co.) until the pressure reached the desired value. The monomer and the initiator were dissolved in SC CO<sub>2</sub>, and MCM-41 absorbed the monomer and the initiator from the fluid phase. After a desired adsorbing period, CO<sub>2</sub> was released. The tube containing MCM-41 powder was taken out from the vessel, and was put into another vessel, heated to 80°C to initiate the polymerization of AA within the MCM-41 channels under the protection of nitrogen. The reaction time was 5 hrs. Then nitrogen was vented, and the vessel was evacuated to remove the unreacted AA monomer until the weight was constant.

**Sample characterization.** FTIR (Perkin-Elmer 180) was used to characterize the MCM-41 and MCM-41/PAA composite. Gravimetric determination of the entrapped amount of PAA was performed using a thermogravimetry analyzer (TGA). About 10 mg of sample was heated to 700°C at 5°C/min in a stream of air. The morphology of various samples was observed with Hitachi S-530 SEM in the normal secondary electron imaging (SEI) mode. The surface was coated with gold to avoid charging under an electron beam.

Surface areas and pore volumes of the materials were determined by nitrogen adsorption/desorption isotherms collected at 77K with a Coulter Omnisorp 100 instrument using static sampling. The samples were degassed at 80°C for 24 hrs on a high-vacuum line prior to adsorption. Micropore volume was determined from T-plots, while the pore volume of the mesoporous materials was calculated from the adsorbed nitrogen after complete pore condensation using the ratio of the densities of liquid and gaseous nitrogen.

X-ray diffraction study of MCM-41 and MCM-41/PAA composites was performed by means of D/MAX.RB diffractometer (made in Japan) with CuK $\alpha$  radiation ( $\lambda = 0.154 \text{ nm}$ ) at a generator voltage of 40 KV and a generator current of 100 mA. The scanning speed and the step were 2°/min and 0.02°, respectively. The beginning  $2\theta$  value was 1°.

## Results and Discussion

In order to detect whether PAA was entrapped into the channels of MCM-41, the MCM-41/PAA composite prepared at 12.0 MPa with a monomer concentration of 0.568 mol/L in the fluid phase was first characterized using different methods.

**IR study** The MCM-41 molecular sieves and MCM-41/PAA composites were first examined by FTIR, and their spectra are shown in Figure 1. It can be seen that the spectrum of MCM-41/PAA shows new peaks at  $1460\text{ cm}^{-1}$ ,  $1729\text{ cm}^{-1}$ ,  $2500\text{--}3700\text{ cm}^{-1}$ , compared to that of MCM-41, which correspond to bend vibration of  $\text{CH}_2$ , stretch vibration of  $\text{C}=\text{O}$  and  $\text{OH}$ , respectively. These indicate that PAA indeed exists in the composite. In order to know whether PAA was entrapped into the channels of MCM-41, other characterization methods were performed.

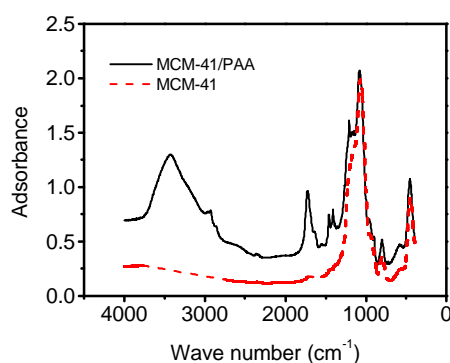


Figure 2. The FTIR spectra of MCM-41 and MCM-41/PAA composite with PAA content of 34 wt%.

**Nitrogen adsorption study** Nitrogen adsorption/desorption study is an effective method to investigate the changes of surface area and pore volume of porous materials. The MCM-41 molecular sieves and MCM-41/PAA composite were investigated using this method, and their adsorption isotherms were shown in Figure 2. Clearly, both materials exhibit type IV isotherms. However, their isotherms are different greatly. The BET area of MCM-41 is  $1232\text{ m}^2/\text{g}$ , which is similar to the reported value(2), while the residual BET area of MCM-41/PAA composite is  $137\text{ m}^2/\text{g}$ . We can also observe a large loss of pore volume from  $0.99\text{ ml/g}$  for

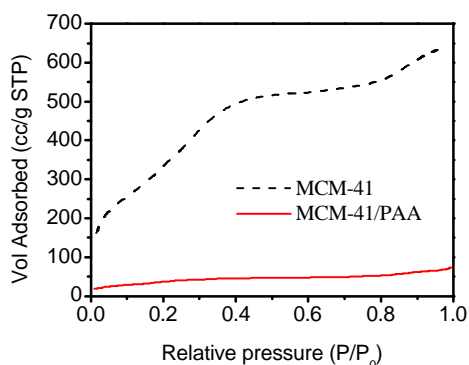


Figure 2. The adsorption isotherms of MCM-41 and MCM-41/PAA composite with PAA content of 34 wt%.

MCM-41 to  $0.11\text{ ml/g}$  for MCM-41/PAA composite. Table 1 shows the effect of PAA content

of the composites on the BET area and pore volume, which indicates that both BET area and pore volume decrease with PAA content. All these illustrate that PAA indeed exists in the channels of MCM-41. Moreover, PAA occupies most of the spaces of the channels of MCM-41 molecular sieves, which results in the large loss of BET area and pore volume of the molecular sieves.

**TG study** The loading level of PAA in the mesoporous supports was examined using TG in air atmosphere. The weight loss vs temperature curves of MCM-41 and MCM-41/PAA composite are plotted in Figure 3. An initial weight loss is observed on each curve, which corresponds to desorption of water. All the adsorbed water on the MCM-41 sample is removed at about 100°C. Additionally, there are two weight losses on the MCM-41/PAA curve, which stand for the desorption of the extra water adsorbed by PAA and the decomposition of PAA, respectively. The extra water adsorbed by PAA in the MCM-41/PAA composite was removed completely at temperature much higher than 100°C. PAA starts to decompose when temperature reaches about 350°C. From Figure 3, it can be estimated that the total amount of PAA in the composite is about 34 wt%, and that of the absorbed water is about 10 wt%.

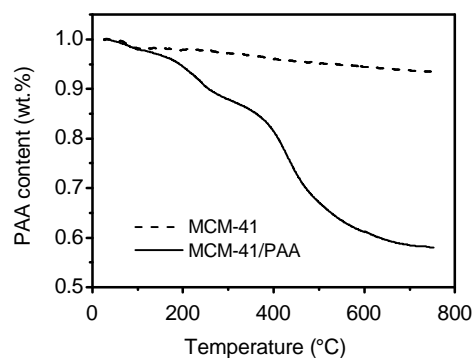


Figure 3 The weight loss vs temperature curves of MCM-41 and MCM-41/PAA.

**XRD study.** To investigate the effect of the entrapped PAA on the structure of MCM-41, X-ray diffraction was performed. Figure 4 compares the X-ray powder patterns of the parent

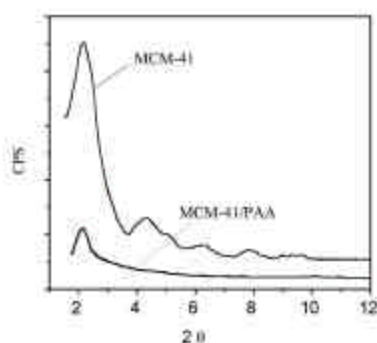


Figure 4. The X-ray powder patterns for the parent MCM-41 and MCM-41/PAA composite with PAA content of 34 wt%.

MCM-41 and the composite. Only one reflection with lower intensity remains in the small

angle  $2\theta$  region for the composite. This can be attributed to pore filling, which reduces the scattering contrast between the pores and the wall of the molecular sieves, e. g., the material is incorporated into the pores, which agrees with the conclusion obtained by the nitrogen adsorption/desorption study, as discussed above.

***Effect of operating parameters on composition of the composites.*** One aim of this work is to synthesize MCM-41/PAA composites with controlled composition. This can be done by changing the parameters of the process to introduce monomer molecules into the pores of MCM-41. As known, SCFs have high diffusing ability, which makes them enter any spaces rapidly; moreover, SC  $\text{CO}_2$  can dissolve small organic molecules, and its solvent strength increases with pressure. Thus, we can adjust the amount of AA entrapped into the pores of MCM-41 by altering the absorbing time, concentration of AA in SC  $\text{CO}_2$  and pressure. The effects of these parameters on the composition of MCM-41/PAA composites were studied. The TG technique was used to determine the mass percentage of the polymer in the composites, which has been discussed above.

Figure 5 illustrates the effect of adsorbing time on the PAA content in the composites. As expected, the PAA content increases with time initially, and reaches a constant value. During the absorbing process, AA and AIBN dissolved in SC  $\text{CO}_2$  distribute between the fluid phase and MCM-41 solid phase. Because the SCF phase has low viscosity, the monomer and the initiator can easily diffuse into the channels of MCM-41, and adsorbed onto its inner surfaces. There are some Si-OH groups on the inner surfaces, which can form hydrogen bond with AA. Thus AA is more easily adsorbed than  $\text{CO}_2$ . The AA molecules in the channels exist in two styles: some are adsorbed on the inner surfaces, and the others are in SC  $\text{CO}_2$  phase. Absorption equilibrium can be reached after enough equilibration time. The Figure shows that equilibrium can be reached in 2 hrs.

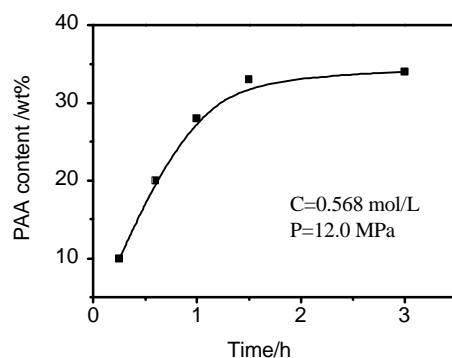


Figure 5 The effect of adsorbing time on the PAA content in the composites.

Figure 6 shows that the content of PAA in the composites increases with the concentration of the monomer in the fluid phase. This is easy to understand because larger concentration of AA in the fluid phase is favorable to its absorption. As a result, the there is more PAA in the composite.

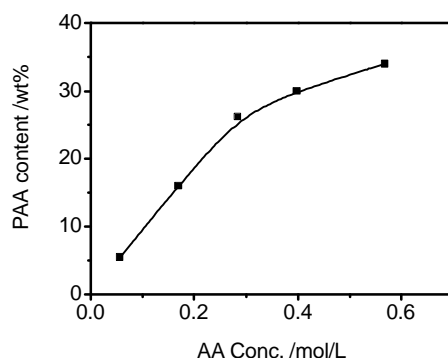


Figure 6. The dependence of PAA content in the composites on the concentration of monomer in the fluid phase with the adsorbing time of 2 hrs and pressure of 12.0MPa.

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