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Characterization of the location and interfacial states of gallium in gallium/MCM-41 composites

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Abstract

A broad based approach, using nitrogen adsorption, X-ray diffraction, DSC, solid-state NMR and X-ray photoelectron spectroscopy, has been used to characterize a series of Ga/MCM-41 composite materials. Rather than filling the mesochannels of the MCM-41 it is found, through this combination of techniques, that most of the Ga is present in the spaces between the particles of MCM-41. High-angle XRD and ^{71}Ga NMR indicate that at room temperature most of the Ga is in the liquid metal state. ^{29}Si and ^{1}H MAS NMR, and XPS reveal that at the Ga/MCM-41 interface the Ga reacts with silanol groups to form new Ga^{+} states like Si—O—Ga, or bridging Si(OH)Ga hydroxyls.

Keywords: Gallium-MCM-41 nano-composites; Porosimetry; PXRD; Solid-state NMR; XPS

1. Introduction

Nanostructured materials have attracted a great deal of attention because of their unique optical, electrical and mechanical properties which are different from those in the corresponding bulk substances [1,2]. Various metal and semiconductor nanocrystals have been synthesized in microporous and mesoporous materials [3,4], and carbon nanotubes [5]. Mesoporous silica MCM-41 has a regular array of discrete cylindrical channels with controllable mesopore size distribution [6,7], which recent studies have suggested can provide a suitable framework to host semiconductor quantum dots and quantum wires [4e,8,9]. This paper presents studies on Ga/MCM-41 composite materials. Since the melting point of bulk gallium metal is 29.9 °C [10], liquid gallium might easily diffuse into the channels of MCM-41 under ambient conditions or slightly elevated temperatures to form nanowires, which would be expected to show quantum size effects. The general characterization of the materials posed quite a few challenges and surprises, and numerous different techniques, including porosimetry, low and high angle PXRD, DSC, and solid state NMR, were applied in order to reach a satisfactory conclusion on the whereabouts of the introduced Ga. Some of the experiments produced results which could have more than one interpretation, especially if taken in isolation. Also a number of methods sensitive to local chemistry and structure were used to try to shed new light on interactions between the MCM-41 framework and the gallium. These included ^{29}Si MAS NMR to determine the coordination around the silicon atoms [11], ^{1}H MAS NMR to quantitate the hydroxyl groups in the silica using an intensity reference material [12–14], and ^{71}Ga NMR and X-ray photoelectron spectroscopy to reveal the Ga oxidation states.

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2. Experimental section

2.1. Materials

MCM-41 was prepared as described previously [15,16] using cetyl-trimethyl-ammonium bromide (CTAB) as the structure-directing agent. 8.6 g of fumed silica (Aldrich) was mixed with 13.8 g of water and 14.7 g of 25% tetramethyl-ammonium hydroxide aqueous solution (Aldrich). Then, a solution comprising 8.5 g of CTAB (Aldrich), 15.7 g of water and 2.8 g of ammonium hydroxide (Fisher Scientific) was added under vigorous stirring. The mixture was hydrothermally crystallized at 70 °C for 3 days, then filtered and washed with deionized water. After drying in air at 120 °C for 4 h, the product was calcined at 550 °C for 8 h to remove the template and obtain MCM-41 in the proton form.

MCM-41 samples were degassed under vacuum, and then measured amounts of gallium (purity 99.99%, Strem Chemicals) were introduced under a high-purity nitrogen atmosphere. The mixture was stirred at 40 °C for ~2 h until a homogeneous sample was obtained. Finally, the sample was heated to 300 °C at 2 °C/min under vacuum ($<10^{-2}$ Pa) and held in these conditions for 8 h. The resultant Ga/MCM-41 composites were grey to black depending on the gallium loadings.

2.2. Characterization

Nitrogen adsorption–desorption isotherms were measured at −196 °C using a Micromeritics ASAP 2010 porosimeter. The volume of adsorbed N_2 was normalized to standard temperature and pressure. Samples were outgassed at 200 °C overnight before measurement, to remove water.

DSC measurements were carried out on a TA Instruments DSC 2920 with a heating rate of 5 °C/min from −90 to +150 °C. TGA was performed from room temperature to 250 °C using a TA Instruments 2050 Thermogravimetric Analyzer, with a heating rate of 5°/min.

Low-angle X-ray powder diffraction patterns were obtained at room temperature on a Scintag X2 Diffractometer using CuK_α radiation ($\lambda = 1.5406$ Å). Diffraction data were collected between 2θ of 1° and 8° with a scanning speed of 0.5°/min. High-angle XRD patterns were recorded between 2θ of 25° and 60° at various temperatures on a Rigaku X-ray Diffractometer using CoK_α radiation ($\lambda = 1.7902$ Å).

^{29}Si MAS NMR spectra were obtained at 59.6 MHz (Bruker AMX-300 spectrometer) using a 7 mm probe (Doty Scientific Inc.) with a spinning rate of 5 kHz, a 180 s recycle delay and 1600 scans. ^{29}Si chemical shifts were referenced to tetramethylsilane (TMS). ^{1}H MAS NMR spectra were obtained at 400.1 MHz (Bruker DSX-400) using a Bruker 4 mm MAS probe, with a sample spinning rate of 8 kHz, a 12 s recycle delay and 96 scans. ^{1}H chemical shifts were referenced to adamantane, at 1.74 ppm relative to TMS. The samples for ^{1}H NMR were dehydrated at 200 °C and pressures below 10^{-2} Pa for 10 h before being loaded into zirconia rotors in a dry box. In an attempt to quantitate the amounts of different H species present, each sample was weighed and its ^{1}H NMR spectrum calibrated against that of a known amount of 1,1,1,3,3,3-hexafluoro-2-propanol (Aldrich) [13,14]. The sample with 65.1 wt% Ga would not spin in the magnetic field. Static room temperature ^{71}Ga NMR spectra were acquired at 182.9 MHz (Varian Inova-600) using a home-built probehead with a 5 mm coil with a recycle delay of 0.1 s and 1024 to ~80,000 scans depending on the gallium loadings. A 1 M aqueous solution of $Ga_2(SO_4)_3$ was used as the chemical shift reference. Also, quantitative ^{71}Ga NMR measurements of the Ga liquid line were obtained at 91.49 MHz (Bruker AMX 300). Weighed amounts of sample were measured under the same NMR acquisition conditions relative to a known quantity of 11.04 wt% $Ga(NO_3)_3$ aqueous solution.

X-ray photoelectron spectra were recorded on a Kratos Ultra XPS instrument using monochromatic AlK_α radiation. A survey spectrum was run between 1400 and 0 eV to determine the elements present on the surface. High-resolution spectra were then recorded on the elements of interest for peak shape and position.

3. Results and discussion

There are many difficulties associated with the characterization of nanostructured materials, and the problems are compounded when it comes to locating materials which have been introduced into a porous framework. Probably the most direct means of demonstrating the presence of Ga in the channels of MCM-41 would be transmission electron microscopy, however, attempts to obtain TEM pictures were unsuccessful due to movement of the sample under the conditions in the spectrometer. In fact metal/SBA-15 (MCM-41) composites do not show clear TEM images with high metal loadings [4d]. Consequently one must rely on a synoptic approach, piecing together complementary information from numerous and diverse techniques in a fully self-consistent fashion, in order to produce a coherent picture of these materials.

3.1. Porosimetry

Important information for the discussion of the location of the gallium in MCM-41 is provided by the low-temperature N_2 physisorption isotherms shown in Fig. 1. Empty MCM-41 shows a typical stepped Type IV isotherm with two regions of strong N_2 uptake [17]. It is unusual that there is hysteresis in both regions. The hys-