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Mechanism for the formation of tin oxide nanoparticles and nanowires inside the mesopores of SBA-15

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ABSTRACT

The formation of polycrystalline tin oxide nanoparticles (NP) and nanowires was investigated using nanocasting approach included solid–liquid strategy for insertion of $SnCl_2$ precursor and SBA-15 silica as a hard template. HR-TEM and XRD revealed that during the thermal treatment in air 5 nm tin oxide NP with well defined Cassiterite structure were formed inside the SBA-15 matrix mesopores at 250 °C. After air calcination at 700 °C the NP assembled inside the SBA-15 mesopores as polycrystalline nanorods with different orientation of atomic layers in jointed nanocrystals. It was found that the structure silanols of silica matrix play a vital role in creating the tin oxide NP at low temperature. The pure tin chloride heated in air at 250 °C did not react with oxygen to yield tin oxide. Tin oxide NP were also formed during the thermal treatment of the tin chloride loaded SBA-15 in helium atmosphere at 250 °C. Hence, it is well evident that silanols present in the silica matrix not only increase the wetting of tin chloride over the surface of SBA-15 favoring its penetration to the matrix pores, but also react with hydrated tin chloride according to the proposed scheme to give tin oxide inside the mesopores. It was confirmed by XRD, N_2-adsorption, TGA-DSC and FTIR spectra. This phenomenon was further corroborated by detecting the inhibition of SnO_2 NP formation at 250 °C after inserting the tin precursor to SBA-15 with reduced silanols concentration partially grafted with tin chloride.

1. Introduction

A series of mesoporous metal oxides have been successfully synthesized through nanocasting strategy, after Ryoo's group reported the synthesis of ordered mesoporous carbon using mesostructured silica as hard template [1]. Zhao et al. [2], first reported the synthesis of ordered mesoporous metal oxides including In_2O_3, Co_3O_4, Cr_2O_3, Fe_2O_3 by utilization of various mesoporous silica with cubic (*Ia*3*d*, *Im*3*m*) or 2-dimensional hexagonal (SBA-15, *p*6*mm*) phases as structure matrices. Usually, in nanocasting strategy the metal nitrates precursors are inserted into the mesopores of silica in dissolved state (e.g. in ethanol) followed by evaporation of solvent [3,4]. The [metal oxide–mesostructured matrix] composite can be prepared also by simple physical mixing of the precursor with mesoporous silica (solid–liquid route) [5–8]. During the heating of the precursor to its melting temperature it penetrates into the mesopores of silica through capillary action followed by decomposition at high temperature to form the metal oxide. Yue and Zhou [8] clearly demonstrated that in order to synthesize mesoporous metal oxide through solid–liquid method the metal nitrate precursor must have a melting point lower than its decomposition temperature. The solid–liquid method is preferable yielding higher integrity of target oxide nanocasts since it excludes the filling of pores with the solvent and does not require multiple impregnations to reach critical metal loading necessary for integrity of nanocasts. Unlike impregnation, solid–liquid method yields monocrystalline metal oxide nanowires with good integrity due to the dense packing of the melted precursor inside the mesopores before it decomposes [9]. In the synthesis of mesoporous metal oxide by hard template technique a shift in the oxide formation towards the lower temperature was observed [3,4]. It was explained as a result of high dispersion of metal precursor over the silica scaffold which accelerates the kinetics of the decomposition of smaller crystals inside the matrix compared with the bulk precursor.

Due to the fact that tin oxide is an n-type semiconductor with wide band gap ($E_g = 3.6\,eV$) it has been widely investigated in the areas of gas sensors, solar cells, and catalysts [10–13]. Few literatures are available for the synthesis of mesoporous tin oxide by nanocasting technique using mesoporous silica as hard template. Smatt et al. [14,15] recently synthesized tin oxide monoliths and spheres with hierarchical pore structure using hierarchically porous silica monoliths and spheres as hard templates. Synthesis of mesostructured tin oxide by nanocasting pathway using SBA-15, KIT-6, SBA-16 and spherical mesoporous silica as hard templates was also reported [16,17]. In the synthesis

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of mesostructured tin oxide by nanocasting pathway the common precursors are tin chlorides since tin nitrate is not available. In contrast to the other mesoporous metal oxides prepared using nitrate precursors, only polycrystalline tin oxide nanowires were obtained at high temperature [14,16,17]. Furthermore, in the case of metal nitrates the oxygen for the metal oxide formation is available from the precursor itself. For metal chloride precursors it is unclear whether silanols, reaction medium or coordinated water molecules act as an oxygen source. Understanding of SnO_2 formation mechanism is important for selecting the right strategy controlling its assembling mode and integrity of oxide assembles in corresponding nanocasts.

In the present work, polycrystalline tin oxide NP and nanowires were synthesized using SBA-15 as a hard template through solid–liquid method by nanocasting pathway. The experiments were carried out in air and inert atmosphere at 250–700 °C for tin chloride deposited over pure SBA-15 and Sn-grafted SBA-15 in order to understand the solid state reactions occurred between the hydrated tin chloride and silica scaffold. The materials obtained were characterized by XRD, HR-TEM, N_2-adsorption, TGA-DSC and FT-IR techniques. The experimental results revealed that interaction of tin chloride with the SBA-15 matrix is not the same as with metal nitrates, and the mesoporous oxide formation follows different mechanism. Based on the collected data a reaction scheme was proposed for the creation of nanocrystalline tin oxide at different assembling modes inside the mesopores of SBA-15 by solid–liquid route.

2. Experimental

2.1. Synthesis of tin oxide loaded SBA-15 and nanocast

All chemicals purchased from Aldrich were analytically pure. The SBA-15 was prepared according to the method described in literature [18]. To obtain a tin oxide-SBA-15 composite (Sn–SBA), first 0.5 g of SBA-15 was dispersed in hexane and the solution is stirred at 50 °C. Tin chloride corresponding to 65 wt% of SnO_2 loading was added slowly to the solution. Stirring continued till all the hexane gets evaporated. Finally the sample was dried in air overnight at 80 °C. Afterwards, the resulting material was heated in a ceramic crucible in muffle furnace at 250 and 700 °C for 4 h at the heating rate of 1 $^\circ C\,min^{-1}$. The thermal treatment of SBA-15 loaded with tin chloride was also carried out under helium flow in a tubular furnace at 250 and 700 °C for 4 h. Finally the silica matrix was removed by dissolution in 10% HF overnight at room temperature.

Tin chloride grafted SBA-15 (SBA–SnG) was obtained by following the procedure reported in literature [19]. Briefly, calcined SBA-15 was slurried in absolute ethanol solution containing the excess of anhydrous tin chloride for 1 h at 60 °C. The material was then washed with absolute ethanol and dried in air oven overnight at 80 °C. The so obtained SBA–SnG material was loaded with tin chloride at amount corresponding to 65 wt% of SnO_2 as in the case of as-synthesized SBA-15. This material denoted as Sn–SBA–SnG was heated in helium atmosphere at 250 °C for 4 h.

2.2. Materials characterization

The chemical composition of the materials was measured by energy dispersive X-ray spectroscopy (EDX) analysis with a JEOL JEM 5600 scanning electron microscope. Average of five data points at different locations of the solid was registered.

Wide-angle XRD patterns were obtained with a Philips 1050/70 powder diffractometer fitted with a graphite monochromator; software developed by Crystal Logic was used. Phase identification was performed by using BEDE ZDS computer search match program coupled with ICDD (International Center for Diffraction Data) Powder Diffraction File database (2006). The data were collected in a range of 2θ values from 10° to 80° with a step size of 0.05°. The (110) reflection for SnO_2 ($2\theta = 26.6^\circ$), (002) for $SnCl_2$ ($2\theta = 19.2^\circ$), (100) and (110) for $SnCl_2\cdot 2H_2O$ ($2\theta = 10.5^\circ$ and 16.1°), (200) for $Sn_4(OH)_6Cl_2$ ($2\theta = 17.4^\circ$), (11.15 and 12.11) for $Sn_{21}Cl_{16}(OH)_{14}O_8$ ($2\theta = 35.4^\circ$) phases were selected to determine their crystalline size. The crystal size was determined by using Scherrer equation $h = K\lambda/[(B^2-\beta^2)^{0.5}\cos(2\theta/2)]$, where $K = 1.000$ is the shape factor, $\lambda = 0.1541$ nm; β is the instrumental broadening; B is the experimental peak broadening corresponding to the selected reflections. Low angle XRD patterns were recorded using (1/12)°-divergence slit and 1/30 mm-receiving slit.

Surface area, pore volume and pore size distribution were obtained from N_2 adsorption–desorption isotherms, by using the conventional BET and BJH methods. The last two characteristics were calculated using desorption branch of the isotherm. The samples were outgassed under vacuum for 2 h at 250 °C. Isotherms were obtained at the temperature of liquid nitrogen with a NOVA-2000 (Quantachrome, Version 7.02) instrument.

The infrared spectra were recorded with a Nicolet Impact 460 FTIR spectrometer, with the use of KBr pellets (0.005 g sample and 0.095 g KBr), with 32 sample scans. The data were treated with OMNIC software. The thermal decomposition of the material was analyzed by thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) over a temperature range from room temperature to 600 °C with TG-50-Mettler-Toledo and Mettler-Toledo-DSC 823e instruments, respectively. The measurements were carried out in a flow of nitrogen at a heating rate of 5 $^\circ C\,min^{-1}$.

HRTEM (high resolution transmission electron microscopy) analysis was conducted on a FasTEM JEOL 2010 microscope operating at 200 kV. The samples for HRTEM were prepared by depositing a drop of ultrasonicated ethanol suspension of solid material on a carbon-coated copper grid.

3. Results and discussion

3.1. Synthesis of tin oxide NP and polycrystalline tin oxide nanowires

The low-angle XRD patterns of as-synthesized SBA-15 silica displayed a high intensity peak (100) with a d-spacing of 10.5 nm and two less intensive reflections with d-values consistent with hexagonal arrangement of the pores (Fig. 1). The as-synthesized SBA-15 silica had total BET surface area 817 $m^2\,g^{-1}$, pore volume 1.00 $cm^3\,g^{-1}$ and average pore diameter 5.5 nm in agreement with low angle XRD and HRTEM data. The surface area associated with micropores estimated by the t-plot method was 261 $m^2\,g^{-1}$.

The $Sn/Si = 0.92$ and $Cl/Sn = 1.94$ atomic ratios measured by EDX analysis in the Sn–SBA material dried at 80 °C were consistent with existence of tin in form of $SnCl_2$ which corresponds to 65 wt% SnO_2 in SnO_2/SiO_2 composite after calcination at 700 °C. Fig. 2 shows the wide angle XRD patterns of different phases in Sn–SBA material formed during the thermal treatment in air. The sample dried at 80 °C was characterized by reflections corresponding to tin chloride of particle size more than 50 nm (ICDD Card no. 72-137), which indicates the presence of tin chloride at the outer surface of SBA-15 micrograins. After heating at 250 °C, the X-ray diffractogram displayed patterns of tin oxide phase (Cassiterite) with 4 nm particle size (ICDD Card no. 5-467).