546c Synthesis of Metal Oxide Nanoaerogels Via a Sol-Gel Route in Supercritical CO2

Ruohong Sui, Amin S. Rizkalla, and Paul A. Charpentier

Our research has focused on the synthesis of metal oxides through a modified sol-gel route by using metal alkoxides as precursors and supercritical carbon dioxide ($scCO_2$) as the reaction media. Our results show the promise of $scCO_2$ on synthesizing metal oxide nanomaterials with well-defined nanostructures of TiO_2, ZrO_2, and SiO_2 by this method. The utilization of the green solvent, $scCO_2$, as a substitute for conventional organic solvents for the processing of nanomaterials has been widely reported.[1] The reasons are due to $scCO_2$ being of low viscosity, high diffusivity, and negligible surface tension, which are considered highly effective for producing superior products of fine and uniform particles. In addition, removal of $scCO_2$ can be easy achieved by venting, hence no evaporation or drying processes are required. For aerogels, supercritical drying extinguishes the liquid surface tension that causes the shrinkage of the solid, hence maintaining the microstructure of the aerogel.[2] Metal Oxide aerogels are of significant interest for emerging areas of alternative energy and developing advanced materials. TiO_2 aerogels can be used in various applications such as a structural ceramic, filler for bone cements, nanofiltration membranes, glass coating material for antifogging and self-cleaning, catalyst support for oxides and group VIII metals, photocatalysts, dye-sensor in solar cells, electrolyte in fuel cells and semiconductors for the electronic industry. Zirconia aerogel also has properties desired for catalytic applications. Its surface has both acidic and basic properties, as well as both oxidizing and reducing properties. Additional applications of zirconia aerogel are in refractory materials, ceramic hardener, and ceramic filler in composite biomaterials for joint prostheses. Designing new and improved silica aerogel particles also has many potential applications, including catalyst matrices, chromatography resins, and precursors for ceramic powders for biomaterials. One of the attractive features associated with our new method[3-4] is that the oxide nanomaterials can be readily and reproducibly prepared in a large scale in an autoclave reactor, and nanocrystallites can be obtained after calcination at different temperatures. Furthermore, the morphology and dimensions of the nanomaterials can be tuned by varying the concentration of the precursors and acetic acid. Nanospheres of SiO_2 with a diameter from 50 to 100 nm were prepared using a Rapid Expansion of Supercritical Solutions (RESS) process which allows tuning the particle size distribution.[3] Nanofibers and nanospheres of TiO_2 were obtained with diameters ranging from 10 to 100 nm.[4] Mesoporous monoliths and nanospheres of ZrO_2 were also formed (see Figure 1). The condensation reactions were performed in small 20 ml batch view cell reactors to monitor the condensation reactions and self-assembly process. Controlled venting through a control-valve was utilized to maintain aerogel structure. After calcination in the air at a temperature ranged from 380 to 600 °C, amorphous titania crystallized into anatase and/or rutile phases, while amorphous zirconia changed into tetragonal and/or monoclinic phases, according to the powder XRD and TEM results. The resulting materials exhibited mesoporous structures and high surface areas by using N_2 physisorption analysis. The surface areas of TiO_2 as high as 642 (before calcination) and 281 m2/g (calcined at 380 °C), while those of ZrO_2 as high as 399 (before calcination) and 71 m^2/g (calcined at 500 °C), were obtained. The mechanisms of condensation and self-assembly were monitored using *in-situ* ATR-FTIR in order to control morphology and surface functionality. This technique showed the metal-acetate complexes, i.e. bridging bidentate, chelating bidentate and monodentates, were formed during the polymerization of the metal alkoxides. The coordinate Ti-acetate bridging complex leads to one-dimensional step-growth of the polymer molecule, which results in the formation of nanofibers in $scCO_2$. The hydrogen bonding between CO_2 and acetic acid remarkably slows down the condensation process and facilitates the formation of nanostructures. During washing of the gel with $scCO_2$, the ester and alcohol condensate products are removed, along with any unreacted acetic acid. Due to the low surface tension of CO_2, careful venting maintains the pore structure of the solid network, allowing the mesoporous fibers or spheres to be obtained. Figure 1. (a) TEM: TiO_2 nanofibers with anatase crystallites. (b) TEM: ZrO_2 nanoparticles with monoclinic crystallites. (c) SEM: TiO_2 nanofibers. (d) TEM: mesoporous ZrO_2. References (1) Johnston, K. P.; Shah, P. S. Science 2004, 303, 482. (2) Pierre,

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