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Manipulation of mesoporous structure and crystallinity in spontaneously self-assembled hierarchical metal oxides

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ABSTRACT

Spontaneous self-assembly starting from liquid metal alkoxide precursors offers a convenient template-free route to hierarchical meso/macroporous metal oxide materials with unique macroporous structure. Tailoring of the macropore morphology in these materials has been the focus of recent studies. However, the freshly prepared solids contained amorphous walls and, in many cases, poor structure at the micro/meso scale. While being closely associated to one another, the formation of pores at different scales is governed by independent mechanisms. Examined is the extent of manipulation and control of the structure at meso scale by means of hydrothermal aging in alumina, titania and zirconia materials that possess macroporous structure. The influence of this aging on the textural properties and crystalline phase composition as well as on the previously formed macropore structure is demonstrated. The results indicate that hierarchical materials with well-defined mesopores and macropores with crystalline walls can be successfully synthesized for all three metal oxides by a selective combination of spontaneous self-assembly, hydrothermal aging and thermal treatment. Aging results in the formation of crystalline phases for aluminum hydroxides/oxyhydroxides and titania, while the aged zirconia materials were amorphous. Hydrothermal treatment of the titania and zirconia materials produced higher surface area and mesopores with larger apertures while preserving the macropore structure. However, for aluminum hydroxides/oxyhydroxides, there was a relatively small increase in surface area, which was also accompanied by deterioration of the macropore structure.

1. Introduction

Metal oxides with hierarchical nanoporous structures have attracted attention due to their capability to offer multiple benefits from having pores at different length scales. Mesopores provide high surface area to materials, while macropores allow enhanced transport of the reactant species to the mesopore network. Such materials hold potential in a variety of applications such as heterogeneous catalysis, separations and storage materials. Significant effort has gone into synthesizing materials that integrate pores at different length scales in the same particle [1], with dual templating commonly employed [2]. However, these methods require post-synthesis removal of the sacrificial templates by heating or extraction, leaving final oxides that are contaminated with residual organic matter. Efforts have also been directed towards template-free pathways for obtaining hierarchical materials. Examples of these include redox cycling producing mesopores in a regenerative manner [3], selective leaching of one phase from a two phase composite [4], and coupling of polymer induced phase separation with gelation [5].

Our group has reported hierarchically structured alumina materials via spontaneous self-assembly in solution [6]. In this technique, starting from very reactive liquid alkoxides, solid metal oxides/oxyhydroxides are instantaneously produced in excess water as a result of very rapid hydrolysis-condensation reactions. Unique structures containing a parallel array of macropores (0.5–2 μm) with mesoporous (4–5 nm) walls were obtained. In this work, a single surfactant was used [7]. The synthesis of analogous zirconia [8] and titania [9] materials using a similar technique have also been shown. The formation of patterns in the absence of any surfactant in the latter study suggested that there is no direct role of the surfactant in the formation of the macropores. Thus, this technique offers a very convenient approach for obtaining hierarchical materials such as alumina, titania and zirconia. To exploit these architectures in many potential applications, a better understanding and control of the structure at the individual pore lengths is desirable.

It has been demonstrated that independent mechanisms underlie the formation of macropores and mesopores in hierarchical nanoporous materials obtained by spontaneous self-assembly [6].

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The formation of pores at these two scales can therefore be decoupled and studied separately. While the formation of macropores still remains a topic of active study, the formation of mesopores in these materials appears to be via a nanoparticle assembly mechanism [10]. In this mechanism, mesoporosity is created as interstitial spaces between the aggregating nanoparticles that are formed when the precursor species undergo rapid hydrolysis and condensation. Hicks and Pinnavaia [10] found in the formation of boehmite from aluminum alkoxide that the mesopores were created as a consequence of scaffold-like aggregation and intergrowth of boehmite nanoparticles. In separate work, Yao et al. also observed that the mesopores were formed due to voids between spherical alumina [11] and aluminosilicate [12] nanoparticles.

Although it appears that separate mechanisms govern the formation of pores at each length scale, their formation is associated with one another and controlling them independently without affecting the other presents a challenge. Previously, we investigated the formation of macropores and demonstrated that the pore size and extent of macroporosity can be tuned by means of various sol–gel parameters [13]. As a complement to identifying the synthesis conditions favoring maximum macroporosity, the focus of the current work was to understand and enhance the micro/mesopore structure and the phase transformations of the metal oxide framework formed under those conditions. The current work also investigated the influence of manipulation of the micro- and mesopore scale structures on the macropore structure.

The physical properties of surface area, pore size, pore volume, and phase composition, significantly impact the usefulness of materials in applications such as catalysis and adsorption. Higher surface area provides greater opportunity for fluid–solid contact and is crucial for higher activity. Catalyst materials with larger pores are desirable in liquid phase reactions involving bulky molecules [14]. Additionally, crystalline frameworks are commonly preferred as the performance of amorphous materials can be limited due to issues such as mechanical strength, chemical stability, and thermal and hydrothermal stability. Crystallinity is a basic requirement in many applications, such as the use of titania in photocatalysis where photocatalytic activity is strongly dependent upon the titania phase structure, crystallite size, specific surface area and pore structure [15].

Hydrothermal treatment of metal oxides has been shown to modify textural properties in terms of higher surface area and larger pores as well as to promote the formation of crystalline phases. The applicability of this method has been illustrated for all the three metal oxides discussed in the current work. Hicks and Pinnavaia reported the structural evolution of boehmite with hydrothermal treatment [10]. Chuah et al. using aluminum nitrate as precursor, obtained hydroxide gels that had a very small surface area when freshly prepared but was significantly improved after aging in the mother liquor solution [16]. Bimodal mesoporous [17] and hierarchically structured trimodal macro/mesoporous titania [18] have been hydrothermally synthesized. Hydrothermal treatment has also been suggested for zirconia as a replacement of the commonly employed technique of introducing framework stabilizing atoms, with the hydrothermal treatment yielding thermally-stable high surface area materials [19].

Crystallization of an amorphous framework can be achieved by heating the materials to elevated temperatures, but this calcination step can lead to the collapse of the mesostructure. Hydrothermal treatment provides a lower temperature alternative where molecular rearrangement and growth occurs by a dissolution-reprecipitation process [20], which results in strengthening of the network. Such structural rearrangement typically creates larger pores and promotes phase formation. Because of their ability to provide rigidity to the structure, hydrothermal treatment has also been suggested prior to calcination for increased thermal stability. For example, Chuah and Xu found great improvements in the surface area and phase stability of γ-alumina when the precursor hydroxides were subjected to digestion [16].

Efforts have also been made to enhance the mesopore structure in hierarchically porous materials. These methods mostly include classical hydrothermal treatment or minor variation from it. Konishi et al. synthesized hierarchical meso/macroporous zirconia from a route that coupled phase separation with gelation phenomenon [21]. The authors employed a solvothermal process at a temperature of about 210 °C after exchanging the mother liquor solution with ethanol to form mesopores. While the treatment produced crystalline zirconia walls, the macropores were unaffected by the solvothermal process. Collins et al. found that by controlled heating of the precipitates, amorphous titania walls could be converted into a mixture of crystalline anatase and rutile phases [9]. However, the procedure led to a tremendous reduction in surface area after calcination apparently due to the disappearance of smaller pores. By employing hydrothermal treatment or microwave heating, Ren et al. synthesized hierarchical meso/macroporous boehmite and γ-alumina from aluminum alkoxide via spontaneous self-assembly in solution in presence of a non-ionic poly(alkylene oxide)-based surfactant [22]. In subsequent work from the same group, the authors suggested that the presence of a non-ionic surfactant controlled the homogeneity of mesopores created as interparticle voids in hierarchically structured aluminosilicates [23]. Hicks et al. also suggested that use of a neutral amine surfactant mediated the mesostructure formation by regulating the growth and aggregation of boehmite nanoparticles [10]. Yuan et al. hydrothermally synthesized hierarchically structured high surface area zirconia from zirconium propoxide in the presence of a single surfactant [8]. The group also reported the synthesis in absence of any templating agent [24]. The macro-structure was stable after calcination, but the mesopore structure collapsed due to particle sintering.

In the current work, freshly prepared metal oxide solids formed from a spontaneous self-assembly process were subjected to hydrothermal aging in their mother liquor solution and the mesopore structure evolution and phase transformation in the aged materials were studied. The impact of this treatment on the previously formed macropore structure was also examined to evaluate the applicability of the method in synthesizing hierarchical meso/macroporous structures with improved stability.

2. Experimental section

2.1. Synthesis

The three metal oxides studied were alumina, titania and zirconia. The starting materials were liquid alkoxides: aluminum tri *sec*-butoxide (97%, Aldrich, USA), titanium ethoxide (33 + %TiO_2, Acros), titanium *iso*-propoxide (98 + %, Aldrich), and zirconium propoxide (70% sol. in 1-propanol, Aldrich), which were all were used as purchased. Deionized (DI) water was used in all the syntheses and the pH was adjusted using hydrochloric acid (HCl), or a stock solution of aqueous ammonia (>35% NH_4OH), or sodium hydroxide (NaOH). In a typical synthesis, 3 ml of alkoxide was introduced into 30 ml of a pH-adjusted aqueous solution using a syringe at a rate of about 1 ml/min in the form of 2.5 mm diameter droplets. All syntheses were performed at ambient temperature (25 °C) and in the absence of stirring. The mixture was allowed to react for 1 h and was then transferred to a round bottom flask where the solids were aged in their mother liquor for 24 h. The aging temperature was maintained by using a stirred oil bath and a condenser was used to retain the reaction solution. The aging temperatures were 60 °C, 100 °C, or 120 °C. After aging, the solid was retrieved by