Synthesis, characterization and applications of metal oxides with hierarchical nanoporous structure

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Synthesis, characterization and applications of metal oxides with hierarchical nanoporous structure

by

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Hierarchical porous materials incorporate pores at two different length scales in the same body and thus offer multiple benefits from characteristic pore sizes. Smaller mesopores (3-10 nm) provide high surface area for fluid contact while larger macropores (0.5-5 µm) allow facile mass transport. Design of materials with structural hierarchy is of primary interest due to their potential applicability in a variety of fields such as catalysis, adsorbents, storage, and biomaterials. A better understanding of the synthesis factors can yield greater control over the porous properties, which, in turn, can lead to new applications for these materials.

In the current work, hierarchically structured porous alumina, zirconia and titania materials were synthesized via a spontaneous template-free self-assembly in solution. Starting materials are liquid alkoxides, which undergo rapid hydrolysis and condensation in aqueous solution to form a solid metal oxide network. The self-assembly taking place at two different length scales gives rise to bimodal porosity in the system. This study focused separately on the formation of macropores and mesopores. Firstly, the information available in literature regarding the formation of macropores in these materials was unified in a consistent fashion. A systematic comparison of these materials was provided, which were split based on the differences between their characteristic chemistries. The synthesis conditions and parameters producing a maximum extent of macroporosity were identified. The resultant materials were amorphous in nature and in some cases, the conditions leading to maximum macroporosity produced poor meso-structure. Thus, secondly, the as-synthesized materials were subjected to hydrothermal treatment and the influence on textural
properties, phase composition and, in turn, on previously formed macropore structure was
investigated under the conditions identified earlier for maximum macroporosity. The results
indicated that by a selective combination of self-assembly, hydrothermal treatment and
thermal treatment, hierarchical structures with crystalline walls can be obtained for all the
three materials: alumina, titania and zirconia.

Next, the knowledge from the study of porous structure at the individual length scale
was utilized to synthesize a hierarchically porous aluminosilicate material that is also
catalytically active. In this mixed metal oxide, alumina was the structure forming component
while mixing it with silica created surface acid sites. A hierarchical porous structure with the
presence of both Brönsted and Lewis acidity was confirmed by means of a variety of
characterization techniques. The activity of the acid catalyst was demonstrated with an
esterification reaction of palmitic acid with ethanol.
Chapter 1. General Introduction

Introduction

Porous materials play a key role in a variety of applications such as catalysis, separations, membrane reactors and biomaterials. The design and processing of novel porous structures have attracted considerable attention in the past decade due to the rapid growth of emerging applications such as energy conservation and storage, environmentally friendly catalysis, sensors, tissue engineering, DNA sequencing, drug delivery, photonics and many others. An important aspect in nanostructural design of materials is structural hierarchy. Hierarchical materials incorporate an interconnected network of pores of two different length scales, thus offering the benefits from each characteristic pore size. While the smaller pores provide the high surface area to contact the fluid, the larger pores enhance the accessibility of the smaller pores by reducing the diffusion resistance.

The inspiration for synthesizing these materials comes from nature, which has evolved such structures for performing tasks rapidly and with high efficiency. For example, lungs are hierarchical, fractal structures of increasingly fine branches designed to achieve rapid gas exchange. At maximum exertion, human lungs allow an exchange of up to one hundred liters of air over an effective surface area of 80 m$^2$. Another example is the hierarchical structure of trees from stem to leaves to allow rapid transport of water throughout the plant. The green leaves possess hierarchical structures to allow efficient diffusion of CO$_2$ in and diffusion of O$_2$ out and maximize the amount of energy capture during photosynthesis (Fig. 1).
According to the International Union of Pure and Applied Chemistry (IUPAC), pores are classified depending on their size as micropores (<2 nm), mesopores (2 nm - 50 nm) and macropores (>50 nm). Microporous and mesoporous materials possess high surface area, which is crucial for activity but their applications are limited due to diffusion restrictions. However, the presence of macropores in such materials can enhance their performance. This becomes particularly important for bulky molecules such as polymers and biomolecules as well as viscous systems, where diffusion rates are low. The beneficial role of hierarchical structures with remarkable increases in catalytic efficiency has been realized in many theoretical studies. A bimodal porous silica-alumina with both macropores and mesopores was found to be a more effective catalyst in dehydration of alcohol as compared to one that was purely mesoporous. A hierarchical hydrocracking catalyst was also found to have superior catalytic activity as compared to the one with particulate morphology. The advantage of hierarchical structure has also been demonstrated in the field of separations.
where a co-continuous porous silica column was found to provide better performance than conventional column that is packed with particles.\textsuperscript{9}

Thus, synthesis of materials with hierarchical porous structure is of primary interest. Key challenges include the creation of interconnected network of pores at different length scales in the same body and control over the individual pore size and structure. A multitude of synthesis techniques involving pre-formed templates, self-assembling systems and a variety of spontaneous processes have been realized.\textsuperscript{10}

**Synthesis routes to hierarchical materials**

A commonly employed pathway is dual templating, which includes a combination of individual techniques to incorporate mesopores and macropores in one system. For the creation of mesopores, self-assembled molecular aggregates or supramolecular assemblies are generally employed while for creation of macroporosity, large-sized substances such as colloidal crystals,\textsuperscript{11} polymer foams,\textsuperscript{12} starch-gel,\textsuperscript{13,14} emulsions,\textsuperscript{15} bubbles,\textsuperscript{16,17} vesicles,\textsuperscript{18} etc. are added in the synthesis. Desired pore sizes can be obtained by adjusting the synthesis parameters and by the choice of the templates that are used to induce pore formation.

The templating methods, which provide attractive routes to hierarchical materials with interconnected pores, tunable pore sizes and, in many cases, flexibility to introduce functional groups, they require post synthesis removal of the templates. This is usually accomplished by means of higher temperature treatment or solvent extraction. Thus, it adds an additional step and the final material can remain contaminated due to residual templating
material. Thus, many recent efforts have been directed towards template-free routes to hierarchical materials.\textsuperscript{19}

Selective leaching of one phase from a two-phase composite is one such template-free approach to producing porous materials. The pores at two levels were obtained by a combination of solid-state reactivity, and liquid and vapor phase leaching.\textsuperscript{2} Pores can also be generated in transition metal oxides through simple redox processes.\textsuperscript{20} Such redox cycling allows mesopores to be produced in a regenerative process in a material that is already macroporous. Nakanishi and coworkers demonstrated a method by which materials exhibiting both interconnected macropores and textural mesoporosity were obtained by polymerization induced phase separation process.\textsuperscript{21} Macropores were created as a result of concurrent gelation and phase separation, the kinetics of which was controlled by water-soluble polymers such as polyethylene oxide (PEO). Macropores size was controlled by varying the content of PEO while the mesostructure was tailored by solvent exchange and aging. Hierarchical structures for silica,\textsuperscript{22} alumina,\textsuperscript{23} titania,\textsuperscript{24} zirconia,\textsuperscript{25} alumina-silica\textsuperscript{26} and silica-zirconia\textsuperscript{27} have been demonstrated using this technique.

**Hierarchical materials via spontaneous self-assembly**

Another recent route to hierarchically porous inorganic materials is via spontaneous self-assembly in aqueous solution, which is also the focus of current work. In this technique, highly reactive liquid alkoxide precursors undergo rapid hydrolysis-condensation to produce a solid metal oxide network. The self-assembly occurring at the two length scales gives rise to the bimodal porosity in the system. The resultant materials have a unique morphology where macropores are present in the form of parallel channels and are interconnected by
means of mesopores in the macroporous walls (Fig. 2). Such architecture has not been reported by using any of the other methods mentioned above.

These structures were first spotted by Yoldas from experiments to understand the effect of hydrolysis conditions on the molecular and particulate morphology of titanium oxide particles. “Honeycomb” morphology of titania powders was observed starting from titanium ethoxide under alkaline conditions with ammonia, which contrasted particulate granular morphologies obtained under acidic or neutral conditions. Our research group reported an unprecedented one-pot synthesis of hierarchical meso-macroporous alumina. The original work was performed in the presence of a single surfactant. Subsequently, syntheses of meso-macroporous zirconia and titania in the presence and absence of surfactant were reported. The formation of this structure in the absence of any surfactant suggested no direct role of surfactant. Su and coworkers extended the applicability of the technique by obtaining a variety of binary metal oxides. The authors demonstrated that...
macropore size can be tailored and controlled by variation of molar ratios of the metal precursors. It was pointed out that the structural and textural properties of one metal oxide can be improved by the introduction of a secondary oxide to form binary metal oxide composite materials. The same research group also synthesized meso-macroporous structures for phosphated aluminum oxyhydroxides\textsuperscript{36}, titanium phosphate\textsuperscript{37} and zirconium phosphate\textsuperscript{38} materials, where phosphorus could be incorporated into the framework to create interesting acidic properties.

Although a variety of materials have been synthesized using this approach, the understanding of the process is rather limited. By means of a parametric synthesis study, Deng and Shanks illustrated that the formation of pores at each scale can be decoupled and studied independently.\textsuperscript{30} The mesopores are formed from the void spaces that originate in between the aggregating nanoparticles. Mesopores formation from interstitial spaces was suggested by Yao et al. in the preparation of mesoporous alumina\textsuperscript{39} and aluminosilicates\textsuperscript{40}. This mechanism was denoted as a \textit{nanoparticle assembly mechanism} by Hicks et al., who illustrated that the mesoporosity in boehmite (AlO(OH)) from aluminum alkoxide was created as a consequence of scaffold-like aggregation and intergrowth of boehmite nanoparticles.\textsuperscript{41}

While the formation of mesopores is well explained, the formation mechanism of macropores still remains a topic of active study. Some models have been postulated in the literature; the one that was able to explain most of the observations was proposed by Collins et al.\textsuperscript{34} According to the model, the immiscible alkoxide droplet when coming in contact with aqueous solution, undergoes a rapid hydrolysis and condensation, which results in the formation of a semipermeable metal oxide membrane separating the inner alkoxide from the
water outside. This compartmentalizes further reaction such that the reaction front proceeds inwards. Inside the shell-encased droplet, the hydrolysis and condensation were proposed to proceed in concert in such a way as to rapidly produce solid nanoparticles and liquid byproducts, which leads to the formation of micro-separated domains that gave rise to the macropore structure.

Two indispensible requirements have been realized for this process to happen. First, a liquid alkoxide with high reactivity is necessary. Unlike aluminum and transition metal alkoxides, silicon alkoxides are not very reactive with water; thus not satisfying the indispensable need of a rapid process producing solid nanoparticles and liquid by-products to yield macroporous materials. The synthesis attempts to obtain similar patterns using silicon alkoxides led to the formation of uniform spherical particles of 200 nm diameter and no macropores. Second, direct contact of the alkoxide in the form of droplets with aqueous solution is critical. Attempts to predisperse the alkoxide in alcohol solution did not result in the formation of macropores. The macropores also ceased to exist at very high stirring speeds (Reynolds No. R>100) due to the breakup of droplets. Not only the size of droplets, but the injection speed can also potentially influence the morphology in the final material. The size of droplets and rate of introduction thus can potentially influence the morphology. Collins et al. demonstrated that fibrous structures can be prepared by fast injection of the alkoxide.

It is important to note that there are differences between this technique and the sol-gel process. A typical sol-gel is a multistep process starting with a stable sol, followed by a gelation step and a drying step, all providing opportunities to influence structure evolution. However, in this technique, the self-assembly takes place on two length scales, resulting in
dual porosity in the system. First, the nanoparticles organize themselves in the form of the walls of the macropores. Secondly, the interstitial voids in between these nanoparticles give rise to mesoporosity. Such hierarchy is possible only when the self-assembly process occurs spontaneously and hence the name: *spontaneous self-assembly*. Inhibition of this spontaneous self-assembly would result in similar steps as those observed for the sol-gel process. However, the resulting materials from such a process will not contain a parallel array of macropores but instead will result in exclusively mesoporous materials as observed in literature.\textsuperscript{39-41}

Although the presence of surfactant is not required, synthesis in the presence of surfactant was observed to create homogeneity in mesopores.\textsuperscript{42} However, the surfactant only plays an indirect role by mediating the aggregation process.\textsuperscript{41} The evidence for a nanoparticle assembly process as opposed to a supramolecular assembly process can be obtained by nitrogen physisorption analysis. A type IV isotherm characteristic of mesoporous materials is displayed by materials with mesopores created by either processes (Fig. 3). H1 hysteresis is characteristic of regular cylindrical pores and is associated with templated materials, which also display a relationship between the average pore sizes and surfactant size. However, the hysteresis obtained for mesoporous materials from an aggregation process is type H2, which is representative of ink-bottle shaped pores between spherical aggregating particles with no relationship between the average pore size and the surfactant micelle size.
Thus, the spontaneous self-assembly process is a very convenient template-free route to create hierarchical structures in materials such as alumina, titania and zirconia with potential for key applications in a variety of industrial processes. The significance of the presence of parallel array of macropores is illustrated by the photocatalytic application of titania. Although the basic requirement for photoactive catalytic materials is high crystallinity and large surface area, the presence of macro-channels increased the activity by enhancing the light-harvesting capability of the material. Extinction of light is governed by the equation; $I=I_0 e^{-\alpha l}$; where $l$ is the penetration length and $\alpha$ is the reciprocal absorption length. The intensity is reduced to 10% of its original for a wavelength of 320 nm after penetrating a distance of only 8.5 µm on condensed titania. The presence of macrochannels makes it
possible to illuminate even the core titania particles. In preliminary studies, the activity of materials was reduced by 10-23% when the macropores were absent, while keeping all other parameters constant. Zirconia too, has shown promising results as a catalyst support with higher activity and selectivity than conventional supports for various reactions such as hydrodesulphurization, methanol synthesis, and Fischer-Tropsch reaction yielding higher hydrocarbons. However, its applications are often limited by its poor structural properties. The spontaneous self-assembly technique can potentially aid the development of more efficient zirconia catalyst materials.

Additionally, very pure oxide materials can be prepared starting from pure alkoxide precursors. Alkoxides as starting materials are better in general because they yield the oxides with maximum purity as compared to other precursors such as salts where counteranions remain in the product and deteriorate the purity of the product. Such chemical purity is especially beneficial in applications such as photocatalysis. With better understanding, a higher level of control over the porous properties can be obtained and these attractive architectures can be utilized in many potential applications.

**Dissertation organization**

This dissertation is organized into five chapters. Chapter 2 deals with the formation of macropores in alumina, titania and zirconia. It unifies the existing unorganized data in a very consistent fashion and by means of comparative analysis identifies synthesis conditions and parameters for obtaining maximum macroporosity with tunable pore sizes. Chapter 3 is a study of mesostructure and phase transformations in these materials under the conditions identified to create maximum macroporosity after subjecting the freshly prepared solids to
hydrothermal and thermal treatments. Chapter 4 demonstrates the synthesis of hierarchical porous structure for a catalytically active aluminosilicate material by utilizing the knowledge from previous chapters. Chapter 5 presents the general conclusions of the work and ends by providing direction for future work.

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A variety of macroporous metal oxides were synthesized via a spontaneous self-assembly process in aqueous solution starting from organic alkoxide precursors under a common set of conditions to present a consistent set of data for evaluation of macropore formation in these materials that are known to yield such structural patterns. Sol-gel type chemistry appears to be governing the structure formation in these materials, so the influence of sol-gel parameters such as the alkyl group in the alkoxide, the central metal atom and the pH of the reaction mixture were investigated in order to gain insight on the defining mechanism dictating the formation of these structures. The results revealed that depending upon the central metal atom or the alkyl group, the alkoxide precursors had characteristic hydrolysis and condensation rates, which when balanced appropriately resulted in structured macroporous pattern formation in the final materials. Powders obtained in the spontaneous self-assembly processes were found to have varying macropore sizes as well as extents of macroporosity by adjusting standard sol-gel synthesis parameters, which control the relative rates of the hydrolysis and condensation reactions.
Introduction

The nanostructural design of materials is attracting increasing attention in the development of improved catalysts. Of particular interest are materials with structural hierarchy. These unique structures incorporate interconnected pores of two different length scales. The mesopores provide high surface area and the macropores render the mesopores more accessible by reducing diffusion resistance, which can limit the application of mesoporous catalytic materials. Since macropores have the potential to enhance the catalytic activity of these materials, the design of catalytic materials with incorporated macropores is of interest. Introduction of secondary macropores in mesoporous framework has been demonstrated to increase the activity of solid catalysts significantly by enhancing the diffusion to and from the active sites.\(^1,2\) Incorporation of macroporous channels in mesoporous titania framework was also found to increase the photocatalytic activity of the catalyst by increasing the photoabsorption efficiency and efficient diffusion of gaseous molecules.\(^3\) Besides their applications in catalysis, hierarchically structured materials have also displayed remarkable properties in separations as a stationary phase of high performance liquid chromatography (HPLC) compared to conventional particle-packed systems.\(^4\)

A challenge is to synthesize materials with pores at two different length scales while being able to control independently the individual pore structures. A review of possible approaches has been recently provided by Yuan et al.\(^5\) For the creation of mesopores, self-assembled molecular aggregates or supramolecular assemblies are generally employed while for creation of macropores, appropriately sized sacrificial substances such as colloidal crystals, polymer foams, bio-celluloses, emulsions, and vesicles were added during the synthesis. Synthesis approaches have also been directed towards developing routes to
hierarchical materials and porous materials in general that do not involve any templating. Template free methods such as redox cycling to produce mesopores in a regenerative process in a macroporous material\textsuperscript{6} or selective leaching of one phase from a two phase composite\textsuperscript{7} have been reported. Nakanishi developed a route to obtain hierarchical materials by means of liquid-liquid phase separation induced by water soluble polymers such as PEO to control the phase separation/gelation kinetics.\textsuperscript{4} The phase separation driven by a repulsive interaction between the hydrophobic PEO-oligomeric complex and the hydrophilic solvent resulted in the macroporous morphology.

A simpler template-free technique, which is the focus of the current work, obtains hierarchically structured meso-macroporous or purely macroporous materials via a spontaneous self-assembly mechanism.\textsuperscript{8,9} In this technique, highly reactive liquid metal alkoxides are allowed to hydrolyze and condense to instantaneously form a porous metal oxide network. This technique produces powder particles with unique morphology in which parallel macropores (with micro/mesoporous walls in hierarchical materials) traverse through the particles. This architecture has not been reported using any of the other methods mentioned above. Very pure oxide materials can be prepared starting with just the alkoxide precursors in aqueous solutions as opposed to other synthesis strategies where the resultant oxides are often contaminated by residual species. Additionally, since the structures can be obtained in the presence or absence of surfactants (indicating no direct surfactant role in pattern formation other than potential improved mesostructure\textsuperscript{9,10}), either no post treatment is required or, if present, the surfactants can be easily removed. Crystalline phases were found to be present in the products obtained using this technique in contrast to completely amorphous products obtained via templating procedures.\textsuperscript{9,11} Some of these materials have
shown higher thermal stability relative to respective surfactant templated meso-macroporous materials.\textsuperscript{12}

A rapid precipitation of the metal oxide/hydroxide from solution is a key to the formation of macropores. Whether or not the final macroporous material will have a framework consisting of smaller pores (micropores or mesopores) depends upon the type of metal oxide material as well as on the synthesis conditions. A spontaneously formed macroporous structure was first reported by Yoldas\textsuperscript{13} from experiments examining the effect of hydrolysis conditions on the molecular and particulate morphology of titanium oxide particles. “Honeycomb” morphology of titania powders was reported when starting from titanium ethoxide under alkaline conditions, which contrasted with granular morphologies obtained under acidic or neutral conditions. Our group observed these macroporous structures in an one-pot synthesis of hierarchical meso-macroporous alumina starting from aluminum tri \textit{sec}-butoxide in the presence of a surfactant.\textsuperscript{8} Particles were found to contain parallel arrays of macropores with mesoporous walls. Also, the synthesis of meso-macroporous zirconia in presence of surfactant was reported by the Su group.\textsuperscript{14} A more detailed synthesis of macroporous titania powders by a self-assembly mechanism in the absence of any surfactant has been reported by the Mann group.\textsuperscript{15} Recently, the flexibility of the spontaneous self-assembly process has been demonstrated by extending the synthesis from hierarchically structured pure metal oxides to mixed metal oxides\textsuperscript{5,16,17} as well as metal oxides with phosphate groups incorporated into the oxide framework\textsuperscript{11,18,19} for potential applications as solid acid catalysts.

Depending upon the type of starting material, the spontaneous self-assembly process that gives rise to hierarchically structured materials can take place under a wide range of
synthesis conditions. For example, such an assembly is possible in an aqueous acidic solution using different inorganic acids or in an alkaline solution using aqueous ammonia or other bases; in the presence or absence of a surfactant or a co-solvent. Therefore, an array of individual studies have been reported that resulted in a range of purely macroporous or hierarchically structured meso-macroporous materials. While the range of synthesis approaches that have been reported provide an interesting background, the information is not easily compiled into a consolidated framework for the formation of these unique structures. Therefore, the motivation for the current work is to provide a more systematic basis for their synthesis thereby allowing comparison of different approaches.

Although hierarchically structured meso-macroporous metal oxides have been obtained by several researchers, the understanding of the pattern formation is very limited, which has led to a range of hypotheses. Su and co-workers has proposed a mechanism where the formation of supermicelles by the coalescence of multiple micelles and inter-aggregate interactions was interpreted to form macropores. In our recent paper, by means of a detailed parametric study, it was demonstrated that the pore structure at two length scales (mesopores and macropores) could be independently modified suggesting that individual mechanisms are associated with their formation. The formation of smaller mesopores appears to be governed by a nanoparticle aggregation mechanism, but the precise underlying mechanism of the formation of macropores in these materials remains elusive. Collins et al. developed a model to explain the formation of macropores in titania synthesized with titanium alkoxides using a self-assembly process. The model explains many characteristics of the formation process for all the materials in general but left several questions unanswered. In view of the current limited knowledge, there is need for further
work. A deeper understanding of the formation mechanism is required not only in order to understand the pattern formation, but can also help in the design of materials with adjustable and well defined macropores, which is important for the application of these materials in catalysis.

The rapidity of the formation process makes the direct visualization needed for a mechanistic study of macropore formation very difficult. However, exploring the chemistry behind the process serves as an indirect approach for identifying the defining forces for the pattern formation. Understanding the behavior of different materials producing macroporous powders, under a particular reaction environment offers useful insights. The current work performs a unified synthesis of a range of macroporous metal oxides following a consistent methodology under identical conditions. This work provides a systematic comparison of these materials which are split based on the differences between their characteristic chemistries. The majority of the results concern macropore formation, which is the focus in the current work, so only a generalized description of the meso-structure is provided.

**Experimental Section**

**Synthesis**

Micro/meso-macroporous materials were obtained for titanium oxide, zirconium oxide and aluminum oxy-hydroxide. The titania powders were prepared using five different alkoxide precursors: titanium ethoxide, titanium \( n \)-propoxide, titanium \( iso \)-propoxide, titanium \( n \)-butoxide and titanium \( tert \)-butoxide. For zirconium, two alkoxides with normal alkyl chains: zirconium propoxide and zirconium butoxide were used while only a single liquid alkoxide of aluminum was investigated. The liquid precursor metal alkoxides:
aluminum tri sec-butoxide-97% (TBOA, Aldrich), titanium ethoxide-33+%TiO₂ (Acros),
titanium n-propoxide-98% (Aldrich), titanium iso-propoxide-98+% (Aldrich), titanium n-
butoxide-99% (Acros), titanium tert-butoxide (Acros), zirconium propoxide-70% sol. in 1
propanol (Aldrich) and zirconium butoxide-80% sol. in 1-butanol (Aldrich) were used as
purchased. Deionized water was used in all syntheses and the pH was adjusted using
hydrochloric acid or a stock solution of aqueous ammonia (>35%).

In our earlier paper⁹ which dealt in detail with the hydrodynamic condi-
tions during the syntheses of hierarchical alumina materials, it was found that stationary medium
syntheses produced powders with a high extent of macroporosity. The stationary medium for
syntheses was also recommended by Collins et al. for the synthesis of macroporous titania.¹⁵
Thus, all syntheses here were performed in stationary medium in the absence of any stirring
for the sake of consistency.

In a typical synthesis, 3 ml of alkoxide was added to 30 ml of pH adjusted aqueous
solution using the method described previously.⁹ For each alkoxide, the synthesis was
performed at starting pH values ranging from 0.5 to 13.5. The alkoxide droplets were then
introduced directly into the solution at room temperature, as the direct contact of the droplet
is indispensable for obtaining the desired morphology.⁹ The alkoxide was introduced in the
reaction solution at a rate of about 1 ml/min by using a syringe in the form of 2.5 mm
diameter droplets. Immediate reaction was observed upon introduction of the alkoxides.
TBOA droplets became smaller as a result of the formed alumina particles detaching from
the droplet surface. This particle detachment was not observed for titania and zirconia, where
the final solid particles retained the general shape of the initial droplets. The high reactivity
of alkoxides in excess water resulted in instantaneous formation of solid oxide/ oxy-
hydroxide except for very acidic pH values such as 0.5 where the droplets hydrolyzed rapidly yielding clear solutions for all the three materials. The mixture was then allowed to react in the mother liquor solution at room temperature for one hour. The powder sample was retrieved by filtration and washed with DI water. It was then allowed to dry in air at ambient temperature for 12 hours and at 100°C for 5 hours.

Characterization

The macropores in the resulting metal oxides were analyzed using scanning electron microscopy (SEM). Images were taken using a JSM-840 scanning electron microscope (JEOL Inc.) with gold-coated sample preparation. Morphological information such as the fraction of particles containing macropores, the extent of macroporosity in the particles, and the pore size distribution as well as surface details regarding the aggregation of particles constituting the macropore walls was obtained by collecting images at various magnifications. The macropore diameters were measured using image processing software, Quartz PCI, for a statistically sufficient number of particles in each case to determine the median macropore diameter value.

Hg-porosimetry experiments were performed using a Quantachrome Corporation Poremaster 60 pore size analyzer. Low pressure Hg intrusion readings were obtained for a pressure range of 0 to 50 psi while the high pressure readings were obtained for the pressure range 20 to 10,000 psi. The preservation of the fragile oxide structures under the high pressure Hg-intrusion conditions was a crucial issue. Since Hg-porosimetry is a bulk technique, the results were obtained to compliment the results from SEM analysis, which was the primary technique for characterizing the macroporosity.
The micro/meso-structure in the sample was characterized using a Micromeritics ASAP-2020 analyzer. The specific surface area of the materials was obtained from the nitrogen adsorption-desorption isotherm at liquid nitrogen temperature by using the BET method. The pore size distribution and pore volume were calculated from the desorption branch of the isotherm using the BJH method. The contributions of the micropores were evaluated using t-plots.

X-ray diffraction patterns were obtained for information regarding the crystallinity of the resultant powders. The measurements were carried out on Siemens D-500 XRD using Cu Kα radiation.

**Results and Discussions**

In the spontaneous self-assembly phenomenon, the reaction conditions lead to an instantaneous precipitation reaction where a solid metal oxide phase is formed starting from the liquid precursor via a hydrolysis-condensation process. The self-assembly of the solid nanoparticles results in pores at two length scales. First, they organize themselves to form the macroporous structure. And secondly, the interstitial voids in between these nanoparticles give rise to mesoporosity. The hierarchical structure in the current study is possible only when the self-assembly process occurs spontaneously, which will be referred to as **spontaneous self-assembly**. This process is markedly distinct from the sol-gel process, which is a controlled multistep process with each step providing an opportunity to influence structure evolution. Slowing down of the current spontaneous self-assembly would result in similar steps; however, the resulting materials from these controlled processes would not contain a parallel array of macropores. The spontaneous self-assembly process can be viewed
as a limiting case of the sol-gel process; the major difference being the uncontrolled hydrolytic condensation chemistry occurring in the former. Collins et al. viewed the phenomenon as a coupling between sol-gel reactions and physical phenomena such as microphase separation.\cite{15} The synthesis of aluminosilicates under acidic conditions also led to the formation of gelatinous precipitates that contained macro pores.\cite{10} The important sol-gel parameters that influence the structure of the final gel network are the internal parameters such as the central metal atom of the precursor alkoxide and the alkyl group in the alkoxide and the external parameters of water/alkoxide ratio and pH of the solution.\cite{13,23,24} It is known that the chemistry occurring in the initial stages of the sol-gel process dictates the structure of the resulting gel.\cite{25,26} The hydrolytic condensation chemistry is the key factor determining the structure of final oxide product, consequently, investigating the ways in which it can be carefully controlled could also provide useful insight into understanding of the macroporous pattern formation. Therefore, the current work explores the influence of some of these parameters (except for the alkoxide/water ratio since the reaction takes place in excess water) on the macroporosity in the resultant powders from the spontaneous self-assembly process.

**Effect of central metal atom**

For very high reactivity towards hydrolysis and condensation, the central metal atom in the starting alkoxide must be highly electropositive. Such reactivity is present in alkoxides of metals like aluminum and transition metals such as titanium and zirconium. Materials synthesized from alkoxides with different central metal atoms displayed very distinct macroporous patterns that could easily be distinguished from one another. Differences in macropore sizes were also evident (Table 1). An appropriate material can be chosen for
specific applications where smaller pores were obtained with aluminum or zirconium oxides while bigger pores were found with titanium oxides. However, for a specific metal oxide material, with a careful choice of starting alkoxides and synthesis conditions, a tailored pore size can be obtained, as will be discussed under the effect of alkyl groups and pH.

Table 1. Range of median macropore diameters (MMPD in microns) for various materials obtained using different starting alkoxides and pH values.

<table>
<thead>
<tr>
<th>pH</th>
<th>Zirconium Oxide</th>
<th>Titanium Oxide</th>
<th>Alumina</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zr(OPr&lt;sub&gt;n&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Zr(OBu&lt;sub&gt;n&lt;/sub&gt;)&lt;sub&gt;4&lt;/sub&gt;</td>
<td>Ti(OEt)&lt;sub&gt;4&lt;/sub&gt;</td>
</tr>
<tr>
<td>3.0</td>
<td>-</td>
<td>3.5-4.5</td>
<td>-</td>
</tr>
<tr>
<td>7.0</td>
<td>2.0-4.0&lt;sup&gt;*&lt;/sup&gt;</td>
<td>2.2-4.0&lt;sup&gt;*&lt;/sup&gt;</td>
<td>-</td>
</tr>
<tr>
<td>11.5</td>
<td>4.5-5.0</td>
<td>4.5</td>
<td>6.0-8.0</td>
</tr>
<tr>
<td>13.5</td>
<td>1.2-2.0</td>
<td>2.5-5.5</td>
<td>-</td>
</tr>
</tbody>
</table>

* MMPD values remained approx. within this range for starting pH values in the range of 3.0-11.5

The difference in the central metal atom was also evident in the shape and size of the particles constituting the macroporous walls. SEM revealed that the macroporous walls were composed of individual or fused spherical particle aggregates for titanium and zirconium oxides. These aggregated particles were bigger for titanium oxide (600-800 nm) than zirconium oxide (400 nm). For alumina, the finer structure in the macroporous walls was not visible under SEM but has been reported elsewhere to be made up of fibrous nanoparticles of boehmite when observed under transmission electron microscopy (TEM).<sup>27</sup>

The macro-structure remained intact in all of the three materials after calcination at 550°C in flowing air. The macropores in titania and zirconia were stable after hydrothermal aging up to 100°C in their mother liquor solution. The extent of macroporosity in alumina appeared to decrease after aging and no macropores were observed after 100°C aging due to
increased solubility of alumina at higher temperatures; apparently dissolution re-precipitation led to the disappearance of the macropores. Since the focus of the current work is the formation of macropores, the influence of aging on the meso-structure of the metal oxides is not discussed here.

Fig. 1 (a) N$_2$ adsorption-desorption isotherm and corresponding BJH pore size distribution curve (inset), (b) XRD patterns for meso-macroporous alumina (TBOA, pH 7).

The micro/meso structure in the synthesized materials was analyzed using N$_2$ adsorption-desorption studies. A type IV isotherm with a H2 hysteresis (BDDT classification)\textsuperscript{28} was obtained for the alumina materials (Fig. 1(a)). The hysteresis suggested a network of ink-bottle shaped pores. The total surface area was 260 m$^2$/g and the BJH pore volume of 0.36 cc/g. The BJH pore size distribution determined by desorption branch indicated pore neck of size 4 nm or smaller.\textsuperscript{29} The meso-structure was thermally stable and there was no decrease in total surface area after calcination at 550$^\circ$C in flowing air for 5 hours.
For the titania and zirconia materials, the isotherm was a combination of type I and type IV indicating the presence of both micropores and mesopores (Fig. 2(a), 3(a)). Such bimodal porosity was due to intra- and inter-particle porosity.\textsuperscript{30} The intra-particle porosity resulted in smaller pores in the micro- to smaller meso-region while the inter-particle porosity resulted in larger slit-shaped pores (indicated by H3 hysteresis)\textsuperscript{28} in meso- to macro-pore region. The intra-particle pore size determined from adsorption and desorption branches were close to each other. However, the inter-particle pore size could not be accurately determined due to the presence of large meso/macro pores, which are outside the range of pore sizes that can be determined by nitrogen physisorption. A continuous intrusion was also observed during Hg-porosimetry analysis. Thus, the inter-particle pore size ranges from 50 nm to few hundred nanometers as suggested by nitrogen physisorption and SEM images. The total surface area was 320 m$^2$/g for titania with 120 m$^2$/g contributed by the micropores. Upon heat treatment, the sintering of particles led to a reduction in the total surface area and
the intra-particle pore size increased from the micro to meso range (2.6 nm). The total surface area was reduced to 103 m$^2$/g after calcination at 500$^\circ$C and to 2.5 m$^2$/g after calcination at 1000$^\circ$C. As-synthesized zirconia had a total surface area of 20-60 m$^2$/g, which increased to 450 m$^2$/g after aging in mother liquor solution for 24h at 100$^\circ$C. After calcination at 500$^\circ$C, the total surface area reduced to 136 m$^2$/g and to 8 m$^2$/g after 1000$^\circ$C.

**Fig. 3** (a) N$_2$ adsorption-desorption isotherm and corresponding BJH pore size distribution curve (inset), (b) XRD pattern for micro/meso-macroporous zirconia (Zr-butoxide, pH 7)

XRD patterns of the alumina particles indicated the presence of mixed boehmite and bayerite phases (Fig. 1(b)). The boehmite phase became more pronounced with increasing aging time and temperature. This observation was consistent with mesoporous materials resulting from the assembly of nanoparticles.$^{22}$ The as-synthesized titania materials were amorphous. Heat treatment transformed the channel walls into anatase after calcination at 500$^\circ$C and into a mixture of anatase and rutile after calcination at 1000$^\circ$C (Fig. 2(b)). As-synthesized as well as aged zirconia materials were amorphous, however, tetragonal phase appeared after calcination at 500$^\circ$C (Fig. 3(b)). The formation of crystalline phases did not influence the formation of macropores, but did change the meso-structures of the materials.
Effect of alkyl groups and pH

The effect of the alkyl group on morphology was best studied for titanium oxide materials because of the readily available variety of liquid titanium alkoxides allowing investigation of alkyl chain length as well as degree of branching, both of which are important sol-gel parameters. The morphology of the final materials from most alkoxide precursors considered here gave a strong dependence on the pH of the reaction mixture. Highly acidic conditions such as pH 0.5 resulted in a clear solution due to the inhibition of the polycondensation process. The structural properties in final aluminas were very similar for pH 2 and 3. However, pH values lower than 2 resulted in a gelatinous alumina precipitate. Therefore, a pH value of 3 was selected as the lower limit for the comparison study.

SEM analysis revealed different extents of macroporosity in the final powders obtained using various titanium alkoxide precursors. When the syntheses were performed under acidic conditions (pH 3), the highest extent of macroporosity was observed for iso-propoxide and tert-butoxide precursors, while ethoxide, n-propoxide and n-butoxide alkoxides produced powders with limited and localized macroporosity with irregularities and wide pore size distributions (Fig. 4). Under these conditions, although the powders obtained with titanium iso-propoxide had higher extents of macroporosity, the macropore structure appeared disordered. The macropores in the powders obtained using titanium tert-butoxide were smaller in size (~2.0-2.5 µm compared to 3.5-4.5 µm for powders obtained using iso-propoxide; Table 1), abundant, and appeared to have a higher structural order relative to macropores in powders obtained using other titanium alkoxides. The morphology and pore structure in the final metal oxide obtained using titanium n-butoxide, as seen from the figure,
is very different than powders obtained using other alkoxides. These particles have broad shallow pores with a wide size distribution and smooth walls between the pores.

**Fig. 4** SEM images (500X) of titanium oxide materials synthesized at pH 3 using (a) Ti(OEt)$_4$, (b) Ti(OPr)$^n$$_4$, (c) Ti(OPr)$^i$$_4$, (d) Ti(OBu)$^n$$_4$, (e) Ti(OBu)$^i$$_4$; scale bar = 50µm
When the pH was increased from 3 to 7, the effect on macroporosity was unsubstantial. However, on further increasing the pH to 11.5, a tremendous increase in order and macroporosity was observed for titanium ethoxide (~5 µm) and titanium n-propoxide (~7 µm). The extent and order also appeared to improve for titanium iso-propoxide (~4.5 µm). These results were in agreement with those obtained by Collins et al. where they observed
that lowering the concentration of ammonia retarded the rate of condensation, which reduced the extent of macroporosity. However, for titanium tert-butoxide, less abundant and localized macropores were observed. Powders obtained with titanium \textit{n}-butoxide also displayed some increased levels of porosity at this pH. This pH could be considered as an optimum pH for obtaining macroporosity in titanium oxides and also the pH where the difference between the powders obtained using different alkoxides was least significant (Fig.5).

![Fig. 6: SEM images (500X) of titanium oxide materials synthesized using Ti(OPr\textit{n})\textsubscript{4} at (a) pH 11.5, (b) pH 13.5; and using Ti(OBu\textit{n})\textsubscript{4} at (c) pH 11.5, (d) pH 13.5; scale bar = 50\textmu m](image)

When the pH was further increased to a more alkaline value of 13.5; the order and extent of macroporosity increased tremendously for titanium \textit{n}-butoxide (~2.5 \textmu m) but
decreased for all other alkoxides. A comparison with titanium \textit{n}-propoxide is presented in Fig. 6.

![SEM images](image)

**Fig. 7** SEM images (1000X) of zirconium oxide materials synthesized using Zr(OPr$^n$)$_4$ at (a) pH 3, (b) pH 13.5; and using Zr(OBu$^n$)$_4$ at (c) pH 3, (d) pH 13.5; scale bar = 20µm

For zirconia materials, the powders synthesized under acidic conditions (pH 3) were found to contain macropores that were confined to a small portion of the powder particles, while large portions in the particles did not exhibit macroporosity. These limited macropore regions were observed to be more ordered when the starting material was zirconium \textit{n}-propoxide rather than \textit{n}-butoxide. For the case of zirconium \textit{n}-butoxide, a greater number of particles were macroporous comparatively but had higher irregularities in structure. No significant influence on the macroporosity was observed when the pH was raised to 7 or to an alkaline value of 11.5. However, a further increase in pH to 13.5 significantly improved the
macroporosity in zirconia materials obtained using either of the two zirconium alkoxides (Fig. 7). As can be seen from the figure, zirconium \( n \)-butoxide produced powders with larger macropores (\( \sim 2.5-5.5 \) µm) than those obtained using zirconium propoxide (\( \sim 1.2-2.0 \) µm).

In contrast, a decrease in the quantity and order of macropores was observed with an increase in pH for the powders obtained using the less reactive aluminum tri \( sec \)-butoxide (Fig. 8). The results were in agreement with earlier work where boehmite powders synthesized at acidic pH were found to contain a higher population of macropores relative to those obtained under higher pH conditions. The effect of pH was observed not only in the terms of extent of porosity but also in terms of pore size (Table 1). Macropore size in boehmite powders appeared to be smaller (1.2-1.5 µm) for higher pH syntheses as compared to the syntheses performed at acidic or neutral pH (2.5 µm).

![Fig. 8 SEM images (2000X) of aluminum oxide materials synthesized at (a) pH 3, (b) pH 13.5; scale bar = 10µm](image)

Hg-porosimetry was performed to complement the results from SEM analysis. A representative Hg-intrusion curve for alumina (pH 3 synthesis) is shown in Fig. 9(a). The region from 300 to 200 µm corresponds to only powder compaction. The region from 200 to 20 µm represents linear intrusion into the interparticle void spaces. A plateau was reached in
the region from 20 to 4 µm, which was followed by a second linear increase in the region 4 to 0.4 µm due to intraparticle intrusion into the macropores. A plateau in the region from 0.4 to 0.02 µm indicated no more intrusion.

Fig. 9: (a) Hg intrusion curve and corresponding pore size distribution for alumina (pH 3), (b) Pore size distribution from mercury intrusion for titania.

The intrusion plots for the titania samples were more difficult to interpret due to the complex morphology as observed by SEM, which consisted of the macropores as well as distinct particles in the pore walls that gave inter-particle pores. As a result, a linear intrusion was observed for the entire plot and a discrete peak for macropores was not be obtained. The pore size distribution plot in Fig. 9(b) shows differences in the 2-4 µm pore diameter region between the titania materials obtained under alkaline conditions (macroporous) and neutral conditions (macropore free). The sample prepared under neutral conditions contained either no or a very small number of macropores; however, a large number of macropores were present in the powder synthesized under alkaline conditions (pH 11.5). A similar intrusion behavior was expected for the zirconia materials since they had inter-particle pores similar to the titania samples.
Discussion

The results clearly demonstrate that the pattern formation can be greatly influenced by carefully controlling the fundamental chemistry that takes place in the initial stages in the solution by means of adjusting the sol-gel parameters. As mentioned earlier, we have assumed sol-gel type chemistry to be applicable for the spontaneous self-assembly process, hence an appropriate starting point is to provide the basics of the sol-gel chemistry of the various materials considered in the current work for use in interpreting the observations in this study.

The starting metal alkoxides are very reactive in aqueous solutions and readily form hydrous oxides. The reaction can be written as:

\[
M(OR)_n + n\text{H}_2\text{O} \rightleftharpoons M(\text{OH})_n + n\text{ROH} \tag{1}
\]

Two chemical processes, hydrolysis and condensation, are involved in the formation of an oxide network from alkoxides via inorganic polymerization reactions. The first step is hydrolysis of the alkoxide, which occurs upon the addition of the alkoxide to an aqueous solution.

\[
\text{M—OR} + \text{H}_2\text{O} \rightleftharpoons \text{M—OH} + \text{R—OH} \tag{2}
\]

As a result of this reaction, a reactive hydroxo group (M-OH) is generated. As soon as the first alkoxy (-OR) group in the alkoxide M(OR)_n is substituted by -OH, condensation can occur. It is a very complex process and depending on the reaction conditions one or the other of the following is applicable. Olation leads to the formation of OH bridges. This occurs when the full coordination of the metal atom is not satisfied in the alkoxide (\(N-z \neq 0\); where \(N\)}
is the coordination number of the central metal atom and \( z \) is the oxidation state) and the reaction rate is usually very fast.

\[
\text{M—OH + M—XOH} \rightarrow \text{M—OH—M + XOH} \quad (X = \text{H or alkyl group}) \quad (3)
\]

Oxolation (elimination of water) and alcoxolation (elimination of alcohol) leads to the formation of oxygen bridges. These are relatively slower processes and follow a mechanism similar to that of hydrolysis.

\[
\text{M—OH + M—OX} \rightarrow \text{M—O—M + XOH} \quad (X = \text{H or alkyl group}) \quad (4)
\]

It has been demonstrated extensively in the literature that the chemistry taking place in the early stages of the process significantly determines the subsequent processes and the main properties of the synthesized gels.\(^{25,26}\) The relative contributions of these reactions determine the structure and morphology of the resulting oxides (Table 2).\(^{23}\) The contributions can be optimized by carefully adjusting the synthesis conditions relative to various parameters such as the central metal atom of the alkoxide, the alkyl group in the alkoxide, hydrolysis ratio, pH and temperature of the solution.\(^{13,23,24}\)

Macroporous powders were obtained under the conditions shown in the third row of Table 2, when both of the reactions were rapid. For sol-gel processes, it has been demonstrated that the chemistry controlling the resultant particle size and morphology often occurs within one second.\(^{26}\) The condensation process is relatively as fast as the rapid hydrolysis of the reactive alkoxides.\(^{25,26,32}\) The rate is comparable even in the presence of reaction inhibitors such as acids and complexation ligands.\(^{25}\) The reactions proceed even faster for spontaneous self-assembly of macroporous materials where the rates are not
inhibited as in sol-gel processes. Additionally, the syntheses were performed in excess water that led to almost instantaneous precipitation of the final metal oxide particles.

**Table 2.** Products obtained depending on the relative rates of hydrolysis and condensation.

<table>
<thead>
<tr>
<th>Hydrolysis Rate</th>
<th>Condensation Rate</th>
<th>Result</th>
</tr>
</thead>
<tbody>
<tr>
<td>Slow</td>
<td>Slow</td>
<td>Colloids/ Sols</td>
</tr>
<tr>
<td>Fast</td>
<td>Slow</td>
<td>Polymeric gels</td>
</tr>
<tr>
<td>Fast</td>
<td>Fast</td>
<td>Colloidal gel or gelatinous precipitate</td>
</tr>
<tr>
<td>Slow</td>
<td>Fast</td>
<td>Controlled precipitation</td>
</tr>
</tbody>
</table>

Amongst the sol-gel parameters mentioned, the ones that were found to affect the formation of macropores in the resultant precipitates were the central metal atom in the alkoxide, the alkyl group and the pH of the solution. Having a highly electropositive central metal atom was crucial as these patterns were not obtained when less reactive silicon alkoxides were used as starting materials. The transition metal alkoxides are most reactive because of their high electropositivity and the ability to readily expand their coordination number upon hydrolysis. Zirconium is the most electropositive of the metals considered in this work and it has the most rapid hydrolysis rate. Although, no clear comparison between the hydrolysis reactivities of aluminum and titanium are available in literature, the attempts to synthesize mixed alumina-titania materials required chemical modification of titanium alkoxide to match the reactivity with aluminum alkoxide. Thus, the reactivity order can be expected to be zirconium > titanium > aluminum. Unlike with our self-assembly process, structures from reactive transition metal alkoxides were somewhat difficult to obtain using either sol-gel or phase separation processes, because their high reactivity towards hydrolysis makes control of the structural development difficult until gelation.
Whether or not the macroporous structure will be obtained is determined by the reactivity of the alkoxide central metal atom, however, a finer adjustment of the macroporous pattern in a particular material can be achieved by an appropriate choice of the alkyl group comprising the alkoxide. The size and structure of the alkoxide group strongly influence the rate of hydrolysis. In general, the larger the alkyl group, the slower and less complete is the hydrolysis. The positive partial charge on the central metal atom decreases due to the inductive (electron releasing, +I) effect of the alkyl group, which increases with an increasing number of carbon atoms. The slower hydrolysis of titanium $n$-alkoxides with an increase in the size of the alkyl group has been confirmed. For isomeric alkoxides, the hydrolysis rate trend is tertiary (tert) > secondary (sec) > normal (n) in general as demonstrated for titanium butoxide in which the rate decreases as the branching decreases. Combining these observations, the hydrolysis rate for the various alkoxides, considered in current work, would be expected to follow the following trend:

\[
\text{Ti(OEt)}_4 > \text{Ti(OPr}^i)_4 > \text{Ti(OPr}^n)_4 > \text{Ti(OBu}^t)_4 > \text{Ti(OBu}^n)_4
\]

(5)

\[
\text{Zr(OPr}^n)_4 > \text{Zr(OBu}^n)_4
\]

(6)

Harris and coworkers observed that zirconium butoxide hydrolyzes rapidly and more extensively than titanium ethoxide. This result helps to define the relative positions for these two alkoxides in the above ordering. Additionally, with aluminum being the least electropositive metal atom, the overall hydrolysis rate order for the alkoxides use in this study is expected to be:

\[
\text{Zr(Pr)}_4 > \text{Zr(Bu)}_4 > \text{Ti(ET)}_4 > \text{Ti(OPr}^t)_4 > \text{Ti(OPr}^n)_4 > \text{Ti(OBu}^t)_4 > \text{Ti(OBu}^n)_4 > \text{Al(OBu}^n)_3
\]

(7)
While the hydrolysis process is well studied, relatively little exploration has been made towards the condensation phenomenon, which is very complex and might occur in a number of possible paths as mentioned earlier. One of the few known properties is that similar to hydrolysis, the low coordination number of the metal atom in non-hydrolyzed transition metal alkoxides is also correlated with their high rates of condensation. Moreover, it has been demonstrated that the condensation process also depends on the size of the alkyl group in the alkoxide (-OR). For example, slower condensation rates were found to be associated with larger alkyl groups in titanium alkoxides. It was observed that the precipitates were formed very quickly in the case of ethoxide (-OEt) and iso-propoxide (-OPr\textsuperscript{i}), while it took significantly longer for \textit{n}-butoxide (-OBu\textsuperscript{n}). However, a definitive trend for condensation rates is not available in the literature as it is for hydrolysis rates.

The importance of the alkyl group in the determination of the final morphology of the materials obtained by a spontaneous self-assembly route has been demonstrated by a number of researchers. Yoldas observed that the type of alkyl group strongly affected the particle size and morphology of their synthesized zirconium oxides. The macroporosity in the titania powders obtained by Collins et al. was observed to be a function of the starting alkoxides. In a study performed by Ren and coworkers, a bimodal morphology could be obtained only by using titanium \textit{tert}-butoxide as the alkoxide precursor and could not be obtained with any other titanium alkoxide precursor.

In sol-gel chemistry, it was found that particle morphology strongly depends upon the molecular structure of the alkoxy groups as well. The difference in molecular structure of these groups leads to different behavior towards hydrolysis and condensation. In general,
alkoxides with primary alkoxy groups associate to form trimers while those with secondary and tertiary alkoxy groups remain monomeric. In contrast to oligomeric titanium ethoxide and n-butoxide in their pure liquid state, iso-propoxide and tert-butoxide are monomeric and more reactive because titanium has only a coordination number of four and is attracted to nucleophilic species to expand its coordination sphere. In the hydrolysis experiments performed in the respective parent alcohols, it was observed that for titanium iso-propoxide condensation occurred as soon as the hydrolyzed species began forming. The simultaneous occurrence of comparably fast hydrolysis and condensation led to polydispersed species formation.\textsuperscript{25} Slower hydrolysis of oligomeric titanium ethoxide relative to condensation, however, led to monodispersed species formation under similar conditions.\textsuperscript{31} Thus, oligomerization provides a very convenient way to slow down hydrolysis thereby adjusting the contribution of hydrolysis and condensation.\textsuperscript{31}

Apart from the internal parameters discussed above, an important external parameter for regulating the relative contributions of hydrolysis and condensation reactions is the pH of the solution. In an acidic medium, rapid protonation of the negatively charged –OR groups leads to fast hydrolysis.\textsuperscript{25}

\[
\text{M–OR} + \text{H}_3\text{O}^+ \rightarrow \text{M} \leftrightarrow \begin{array}{c}
\text{O} \\
\text{R}
\end{array} + \text{H}_2\text{O}
\]

This result has been established as a general conclusion for all alkoxides.\textsuperscript{23} In the presence of an acid, the hydroxo groups are preferentially generated at the end of the chains giving rise to linear polymers and hence open structures.\textsuperscript{23} However, addition of acid slows down the condensation process considerably.\textsuperscript{13}
In contrast, a strong base can behave as an inhibitor to the hydrolysis of the metal alkoxide.\textsuperscript{26} The presence of a strong base can lead to nucleophilic addition of –OH decreasing the positive charge of the metal atom. In a basic medium, the condensation process is activated.\textsuperscript{25} A highly nucleophilic species M-O\textsuperscript{-} is formed in the presence of a base such as sodium hydroxide (NaOH) or ammonia (NH\textsubscript{3}) that rapidly attacks the positively charged metal, resulting in the formation of strongly cross-linked polymers.

\[
M{-}\text{OH} + :B \rightleftharpoons M{-}\text{O}^- + BH^+ \quad (B = \text{OH}^-, \text{NH}_3) \quad (9)
\]

As a result of these apposing effects, acid and base catalysts can be used to promote decoupling between the hydrolysis and condensation reactions. In a very acidic medium, hydrolysis is completed before significant condensation can begin. In a neutral or basic medium both reactions take place simultaneously.\textsuperscript{31} Therefore, to increase the contribution of hydrolysis, the synthesis is performed in an acidic medium, while a basic medium is used for condensation to proceed faster.

Consideration of a variety of precursor materials collectively in the current study enables association of the complex chemistry with the presence of macropores in the final materials while drawing conclusions that were difficult to ascertain from previous studies that explored only a portion of the synthesis space that result in macroporous materials. The observations made in the previous section can be organized as follows.

The powders obtained from the titanium alkoxides at either pH 3 or 7 had limited regions of macroporosity in general. However, the macroporosity increased significantly in the powders obtained from almost all of the titanium alkoxides when the starting solution pH
was increased to an alkaline value of 11.5. A further increase in pH to a value of 13.5 led to a decrease in macroporosity in powders from all but titanium \( n \)-butoxide.

When the more reactive zirconium alkoxides underwent hydrolysis/condensation at a pH value of 3, powders with limited regions of macroporosity were obtained. No significant change relative to the macroporosity was observed when the pH was increased to either a neutral or an alkaline value of 11.5. However, the powders obtained at pH 13.5 were highly macroporous.

The powders obtained from the less reactive aluminum alkoxide under acidic or neutral pH had higher extents of macroporosity than the powders obtained under alkaline conditions. An increase in pH to alkaline values with this alkoxide led to a decline in the macroporosity in the resulting alumina powder.

Taken together, very consistent behavior was found for this range of alkoxide species with the observation explainable in terms of hydrolytic condensation phenomena. While a rapid hydrolysis process is required for the formation of macropores, the rapid rate of the condensation process is equally important. A faster hydrolyzing aluminum tri \( \text{sec} \)-butoxide did produce macropores over a wide range of pH, however, the highest extent of macroporosity was observed under acidic conditions where the hydrolysis process is favored. This can be attributed to the reactivity of aluminum alkoxide towards hydrolysis which is faster than with silicon alkoxides (which did not produce pattern) but slower relative to the transition metal alkoxides. For aluminum alkoxide, hydrolysis rate enhancement is required to produce the macroporous structure. In contrast, titanium alkoxides hydrolyze much faster, and because of the very dominant hydrolysis process, the macro pattern in the final powders
was either very poor or absent. When the condensation process was enhanced by performing the syntheses at pH 11.5, it resulted in powders with significantly increased extents of macroporosity. A further increase in the condensation rate by performing the synthesis at a higher pH value of 13.5 was actually found to be detrimental to the structure formation. This result was possibly due to slowing down the hydrolysis process due to the presence of a large number of hydroxyl groups, leading to their nucleophilic addition to the central metal atom. However, in the fastest hydrolyzing zirconium alkoxides, a high pH value of 13.5 was necessary to enhance the condensation process relative to hydrolysis in order to obtain powders with improved macroporous structure. In the case of the aluminum alkoxide, the increase in pH to favor the condensation process resulted in powders that appeared to have lesser extents of macroporosity possibly due to the slowing down of the aluminum alkoxide hydrolysis rate, which already is less reactive than the transition metal alkoxides.

Therefore, independently optimizing the synthesis conditions in favor of either hydrolysis or condensation was not sufficient. Instead, the results suggested that there was an optimum window for balancing the contributions from both hydrolysis and condensation, which favored the formation of macropores; this region could be achieved by adjusting the relative rates of these two reactions. For titanium alkoxides with intermediate hydrolysis rates; this window could be approached by enhancing the condensation process relative to hydrolysis when the pH value was increased to 11.5. For more reactive zirconium alkoxides, a higher pH value of 13.5 was required for obtaining the desired balance. The balance was not achieved when the pH was increased for the aluminum alkoxide, which already had insufficient hydrolysis rates comparatively that was further exacerbated under basic
conditions. The balance was realized for the aluminum alkoxide under acidic conditions. The one alkoxide that did not respond as expected to the synthesis pH was titanium \( n \)-butoxide, which although being the least reactive of all titanium alkoxides, still produced the best macroporous product at a pH of 13.5.

The improved formation of macropores with titanium \( iso \)-propoxide and \( tert \)-butoxide at the lower pH value can be understood by considering the molecular structure of these metal alkoxides. As discussed previously, the steric hindrance from the branched alkyl groups in these alkoxides screens the central metal atom and prevents the formation of dimers and trimers to satisfy the unsaturated coordination number. Consequently, these alkoxides are monomeric in their pure form which renders them very reactive due to unsaturated coordination and their hydrolyzed species condense quite rapidly, which would be favorable for creation of the desired morphologies.

The behavior of the different alkoxide precursors in response to pH variation provides some insight into previous literature reports.\(^{20}\) As demonstrated in the current study, the alkoxides of different materials have different optimum pH values for forming these structures. Zirconium alkoxides yielded powders with similar macroporous structure over a wide pH range and a significant improvement was observed only after increasing the pH value to 13.5. The aluminum alkoxide also produced powders with a high extent of macroporosity over a wide range, but high alkalinity led to deterioration in the macroporosity. In contrast, most of the titanium alkoxides produced powders with the desired macroporous structure only for pH values near 11.5. Therefore, titania materials are more sensitive to changes in pH. It appeared that the necessary balance between hydrolysis and
condensation could be maintained for a larger pH range with alumina materials than with titania materials, which is why macroporous powders were obtained by the Su group over a wider range for alumina or aluminosilicates than for titania. Collins and coworkers associated smaller macropore size and more ordered structure with a slower hydrolyzing titanium alkoxide. However in our experiments, we did not observe a consistent trend in the macropore sizes with the hydrolysis rates of the titanium alkoxides. Additionally, zirconium butoxide, which hydrolyzes more slowly than zirconium propoxide, produced powders having macropores with almost twice the size under similar conditions. With the exception of zirconium butoxide, a specific alkoxide precursor did appear to produce smaller macropores for a higher starting pH value of the synthesis solution (Table 1).

Collins et al. proposed a mechanism for the macropore formation in which an outer semi-permeable shell is formed instantaneously after the introduction of an alkoxide droplet into the synthesis solution with the reaction front proceeding inwards. Inside the shell encased droplet, the hydrolysis and condensation were proposed to proceed in concert in such a way as to rapidly produce solid nanoparticles and liquid byproducts which leads to the formation of micro-separated domains that gave rise to the macropore structure. The indispensable need for the rapidity of the process has been highlighted in terms of rapid polymerization. Collins et al. also speculated that rates of hydrolysis/condensation and/or the nature of alcohol byproducts are important in determining the final morphology. The current study demonstrated how this rapid polymerization process is a product of the balance between the constituent hydrolysis and condensation reactions signifying the importance of both acting in a concerted manner. When the balance between these two reactions was maintained, the
proposed mechanism of rapid production of solid and liquid phases could be attained. Unlike aluminum and transition metal alkoxides, silicon alkoxides are not as reactive with water; thus not satisfying the indispensable need of a rapid hydrolysis/condensation process to yield macroporous materials. The attempts to obtain similar patterns using tetramethoxysilane and tetraethoxysilane were made but the syntheses led to the formation of uniform spherical particles of 200 nm diameter and no macropores.  

We found that observing the behavior of the different alkoxides upon introduction to the aqueous medium could provide insight into whether macropores were formed. With the titanium alkoxides, the materials were characterized by a faster transition of the immiscible alkoxide droplets in the synthesis solution to an opaque white solid. These solid particles retained the shape of the original droplets apart from the development of cracks on the surface due to stress. When carefully observed under SEM, these were found to consist of a smooth outer shell and a highly macroporous inner region (Fig. 10). Due to their fragile nature, the powder particles were fragments of these bigger particles and great care was taken while imaging to investigate the individual particles for regions of macroporosity and regions that were macropore free. Such a transition was almost instantaneous for titanium alkoxides in the pH 11.5 solution and was complete in a few seconds, while the process was considerably slower under acidic pH where transparent beads slowly transformed to white solids. At a pH of 13.5, the alkoxide spread upon introduction to the aqueous solution and the final powder had particles with a low quantity of disordered macropores.
For zirconium, the transformation to a white solid, while retaining the shape of droplets, was fastest at a pH of 13.5 and, similar to titanium alkoxides, was completed in a matter of seconds. These materials were observed to be highly macroporous. Conversely for the aluminum alkoxide, which under acidic and neutral conditions took several minutes to transform completely into a solid particle suspension, an increase in pH resulted in longer times for the transformation and the observations revealed that these powders had lower levels of macroporosity. The observations seem to be consistent with the proposed model but questions regarding the true mechanism of pore initiation and microphase separation, and whether the diffusion of water through the resistance of the outer mesoporous shell and
against the counter diffusion of alcohol species is sufficiently fast to match the rapid hydrolysis at the water-alkoxide interface requires further investigation.

Conclusions

Macroporous structures for aluminum oxy-hydroxide, titanium oxides and zirconium oxides were systematically obtained starting from different alkoxide precursors via spontaneous self-assembly in an aqueous medium. The unified synthesis approach in the current work provided a common basis for comparing a variety of macroporous metal oxides synthesized under similar conditions in a single study. This work provided more uniform comparison of these metal oxides than was provided by various independent studies in the literature. The chemistry of the process was investigated for improved understanding of macropore structure formation by examining the effects of sol-gel parameters such as alkyl group of the starting alkoxides, the central metal atom as well as pH of the starting solution. The results suggested that the hydrolysis and condensation rates must be within a certain range for these morphologies to occur; however, these processes cannot be viewed independently as it is the relative rates of these two concerted reactions that dictated the formation of macroporous metal oxides. The synthesis parameters influenced both the extent of the macroporosity and the size of the macropores. For a particular metal oxide, appropriate selection of the precursor alkoxide and solution pH can tune the resulting macropore size. While the work provides a more consistent basis of comparison for the formation of macroporous metal oxides, the precise mechanistic cause of this unique structure formation remains unclear.
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Chapter 3. Investigation of Mesoporous Structure and Crystallinity in Hierarchical Nanoporous Metal Oxides Synthesized via a Spontaneous Self-Assembly

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**Abstract**

Previously, we investigated the formation of macropores in novel hierarchical nanoporous alumina, titania and zirconia materials synthesized via a spontaneous template-free self-assembly process. [Hakim & Shanks, Chem.Mater., 2009] The synthesis conditions and parameters producing a maximum extent of macroporosity and tunable macropore sizes were identified. However, the freshly prepared solids contained amorphous walls and, in many cases, a poor structure at the micro/meso scale. In the current work, the as-synthesized materials were subjected to hydrothermal aging and the influence on textural properties, phase composition and in turn on previously formed macropore structure was investigated under the conditions identified earlier for maximum macroporosity. The results indicated that hierarchical meso-/macroporous materials 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 resulted in the formation of

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crystalline phase for aluminum hydroxides/oxyhydroxides and titania, while the aged zirconia materials were amorphous. Hydrothermal treatment was beneficial for titania and zirconia materials by producing higher surface area and pores with bigger openings while preserving the macropore structure. However, for aluminum hydroxides/oxyhydroxides, there was a relatively smaller increase in surface area, which accompanied deterioration of macropore structure. Thus materials with attractive structural properties have been produced that give them great potential for use in a variety of practical applications.

**Keywords:** hierarchical, macropore, mesopore, micropore, alumina, titania, zirconia, boehmite, pseudoboehmite, bayerite, anatase, rutile, tetragonal, hydrothermal, self-assembly, alkoxide.

**Introduction**

Metal oxides with hierarchical nanoporous structures have attracted great attention because of their capability to offer multiple benefits from pores at different length scales. Mesopores provide high surface area to materials while macropores allow efficient transport of the reactant species to the active sites. Such materials hold great potential in a variety of practical applications such as heterogeneous catalysis, separations and storage materials. A great deal of effort has been made for synthesizing materials that integrate pores at different length scales in the same body.\(^1\) A commonly employed technique is dual templating.\(^2\) However, such methods require post synthesis removal of the templates by heating or extraction and usually the final oxides are contaminated with residual organic matter. Hence, efforts have also been directed towards template-free pathways for obtaining hierarchical
materials. Examples of these include redox cycling producing mesopores in a regenerative way\(^3\), selective leaching of one phase from a two phase composite\(^4\), and coupling of polymer induced phase separation with gelation\(^5\).

Recently, our group 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 the original study, a single surfactant was used.\(^7\) Subsequent to our report, zirconia\(^8\) and titania\(^9\) materials using this technique were also obtained. The formation of patterns in the absence of any surfactant suggested there is no direct role of a surfactant. Thus, this technique offers a very convenient pathway for obtaining hierarchical materials such as alumina, titania and zirconia, which play key roles in industrial processes. The applications of these novel structured materials are emerging but are still in an incipient stage. In order to exploit these architectures in many potential applications, a deeper understanding and control of the structure at individual pore scales is required.

It has been demonstrated that independent mechanisms underlie the formation of macropores and mesopores in hierarchical nanoporous materials obtained by spontaneous self-assembly.\(^6\) 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 is well established to be via a nanoparticle assembly mechanism.\(^10\) According to this mechanism, mesoporosity is created as interstitial spaces
between the aggregating nanoparticles that are formed when precursor species undergo hydrolysis and condensation. The original study by Hicks et al. involved formation of boehmite from aluminum alkoxide and illustrated that the mesoporosity was created as a consequence of scaffold-like aggregation and intergrowth of boehmite nanoparticles. In separate work, the mesoporosity, also due to voids between spherical alumina\textsuperscript{11} and aluminosilicate\textsuperscript{12} nano-particles was observed by Yao et al.

Although individual mechanisms govern the formation of pores at each scale, their formation is closely 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.\textsuperscript{13} The information regarding the formation of macropores in these materials was organized in a consistent manner. Once the synthesis conditions favoring maximum macroporosity were identified, the focus of the current work was to understand and enhance the micro/mesopore structure and the phase transformations in the materials obtained under those conditions. The current work also investigates the influence of manipulation of the structure at the micro- and mesopore scales on the macropore structure.

The textural properties, in terms of surface area, pore size and pore volume, and phase composition, largely determine 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 highly desirable, especially in liquid phase reactions involving bulky molecules.\textsuperscript{14} Additionally,
crystalline frameworks are desirable because the performance of amorphous materials is limited due to concerns such as mechanical strength, chemical stability, and thermal and hydrothermal stability. Crystallinity is a basic requirement in many applications, such as for the use of titania in photocatalysis. Photocatalytic activity of titania is found to be strongly dependent upon its phase structure, crystallite size, specific surface area and pore structure. Thus, synthesis of materials with well defined mesostructure and crystalline walls is highly desirable.

A commonly adopted methodology is hydrothermal aging of the freshly prepared solid. Hydrothermal treatment has been shown to enhance not only the textural properties in terms of higher surface area and larger pores, but also to promote the formation of crystalline phase. The applicability of this method has been illustrated for all the three metal oxides under discussion. Hicks and Pinnavaia demonstrated the structure evolution of boehmite with hydrothermal treatment. Chuah et al. using aluminum nitrate as precursor, obtained hydroxide gels that had very small surface area when freshly prepared but was significantly improved after aging in the mother liquor solution. Digestion also led to an increase in pore diameter and volume, however, with a broader pore size distribution. Bimodal mesoporous and hierarchically structured trimodal macro-/mesoporous titania 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, which yield thermally stable high surface area materials, but also influence the catalytic properties.

Usually crystallization of an amorphous framework is achieved by heating the materials to elevated temperatures that 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 (Ostwald ripening),\textsuperscript{20} which results in strengthening of the network. Such structural rearrangement 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. Chuah and Xu found great improvements in the surface area and phase stability of γ-alumina when the precursor hydroxides were subjected to digestion.\textsuperscript{16}

Efforts have also been made to enhance the mesopore structure in hierarchically porous materials. These methods mostly include classical hydrothermal treatment or its variation. Konishi et al. synthesized hierarchical meso-/macroporous zirconia from a route that coupled phase separation with gelation phenomenon.\textsuperscript{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 in the monoliths. The macropores were unaffected by the solvothermal process. The solvothermal treatment also produced crystalline zirconia walls. Collins et al. stated that by controlled heating of the precipitates, amorphous titania walls could be converted into a mixture of crystalline anatase and rutile phases.\textsuperscript{9} However, there was a tremendous reduction in surface area after calcination that was probably due to disappearance of smaller pores. Ren et al., by employing hydrothermal treatment or microwave heating, synthesized hierarchical meso-/macroporous boehmite and γ-alumina from alkoxide via spontaneous self-assembly in solution in presence of Brij 56 surfactant.\textsuperscript{22} In another work by the same group, the authors suggested that presence of a non-ionic surfactant controls the homogeneity of mesopores that are created as interparticle voids in
hierarchically structured aluminosilicates. Hicks et al. also suggested that an electrically neutral amine surfactant mediates the mesostructure formation by regulating the growth and aggregation of boehmite nanoparticles. Yuan et al. hydrothermally synthesized hierarchically structured high surface area zirconia from zirconium propoxide in the presence of a single surfactant. The group also reported the synthesis in absence of any templating agent. The macrostructure was stable after calcination; however the mesopore structure collapsed due to sintering of the particles.

In the current work, the freshly prepared solids from 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 was studied by using an array of characterization techniques. The influence on the previously formed macropore structure as a result of this treatment was also examined to evaluate the applicability of the method in synthesizing hierarchical meso-/macroporous structures.

**Experimental section**

**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\textsubscript{2} (Acros), titanium iso-propoxide- (98+\%, Aldrich), and zirconium propoxide-70\% sol. in 1-propanol (Aldrich) and 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\textsubscript{4}OH), or sodium hydroxide (NaOH). In
a typical synthesis, 3 ml of alkoxide was introduced into 30 ml of pH-adjusted aqueous solution. A syringe was used to introduce the alkoxides at a rate of about 1ml/min in form of 2.5 mm diameter droplets. All syntheses were performed at room temperature (25°C) and in absence of any stirring. The mixture was allowed to react for 1h. The mixture was then transferred to a round bottom flask and the solids were aged in their mother liquor for 24 hours. The aging temperature was maintained by using a stirred oil bath and a condenser was used to retain the reaction solution. The temperatures studied were 60°C, 100°C, and 120°C. After aging, the solid was retrieved by filtration and washed multiple times with DI water. It was then allowed to dry in air at ambient temperature for 12 hours and at 100°C in vacuum for 5 hours. In order to evaluate the thermal stability, portions of samples were calcined at 500°C – 1000°C in flowing air for 5 hrs with a constant temperature ramp of 5°C/min.

In order to synthesize hierarchical meso-/macroporous materials, the experiments were designed to enhance the mesopores in materials using conditions that produced the maximum macroporosity. The macropores in alumina were obtained over a wide range of pH starting from an acidic value of pH 3 to a highly alkaline value of 13.5. However, the extent of macroporosity in the final alumina powders declined with increasing pH. Thus a pH range of 3 to 11.5 was considered for alumina. Unlike alumina, the macroporosity in titania was a stronger function of pH and a value of 11.5 was found to be optimum for the pattern formation. In our previous study of macropore formation, the pH in the alkaline range was adjusted using NH₄OH. To investigate a possible cation effect, the pH was adjusted using NaOH as a second base catalyst. Although the zirconium alkoxides produced macroporous powders for a wide pH range, the highest macroporosity in resultant powders was observed
only at an extremely alkaline pH value of 13.5. The mesoporosity enhancement was thus studied for materials synthesized under highly alkaline conditions. The indicated pH values are the starting solution pH values in all syntheses.

**Characterization**

The information regarding the micro-/mesostructure in the samples was obtained by nitrogen physisorption using a Micromeritics ASAP-2020 analyzer. The samples were degassed at 100°C for 4 hours prior to analysis. The specific surface area of the materials was obtained from the nitrogen adsorption-desorption isotherm at liquid nitrogen temperature by using the Brunauer-Emmett-Teller (BET) approach. Pore size distribution and pore volume were calculated from the desorption isotherm using the Barret-Joyner-Halender (BJH). The contributions from micropores were evaluated using the t-plots.

The crystallinity in the samples was determined by powder X-ray diffraction (XRD). The diffraction patterns were obtained on a Siemens D-500 XRD operating at 27mA and 50kV and using Cu Ka (λ=0.154 nm) radiation. The sample was prepared in form of a thin coating of powder deposited on a zero background holder of quartz cut in a specific crystallographic direction to avoid diffraction peaks. A 0.15° detector slit and a scan rate of 0.05°s⁻¹ was used to record the pattern in the 2θ range of 10-70°. The average crystallite size was estimated from the X-ray peak broadening by means of the Scherrer equation using LaB₆ (NIST 660) as a standard. The corrections for instrument broadening were made while the microstrain broadening was assumed to be negligible. The analysis was performed using Jade8 software.
Thermal properties of the materials were determined by performing thermogravimetric analysis (TGA) with a Perkin-Elmer TGA7 instrument. The samples were heated in air flow from 50°C to 800°C at a constant heating rate of 10°C/min. Differential thermal analysis (DTA) was performed using a simultaneous DTA-TGA (TA Instruments SDT 2960). The DTA curves were obtained using a heating rate of 10°C/min in flowing air. The calibrations were made using indium and silver.

The influence on macrostructure was analyzed by obtaining electron images using scanning electron microscopy (SEM). Images were taken using a JSM-840 scanning electron microscope (JEOL Inc., Japan). Samples were coated with gold prior to imaging.

Results and Discussions

Alumina

The physical properties of aluminum hydroxide/oxyhydroxide and aluminas are summarized in Table 1. Nitrogen adsorption-desorption isotherms for as synthesized and aged samples are presented in Fig. 1 while the corresponding BJH pore size distributions are shown in Fig. 2. The figures indicate similar physisorption results for samples aged in acidic (HCl) or neutral medium. All the isotherms are type IV, representative of mesoporous materials. The presence of H2 hystereses is indicative of a network of ink-bottle shaped pores. The corresponding BJH pore size distributions calculated using the desorption isotherm indicate a pore neck size of 4 nm or smaller. For alkaline medium (NH₄OH), as-synthesized materials displayed similar structural properties to those of materials prepared in acidic or neutral media. However, the pore structure of the aged materials appeared to consist
of smaller (2.7 nm), irregular shaped mesopores as deduced from the isotherms and pore size distribution plots. The surface area and pore volume in the aged materials were much smaller.

Table 1. Structural characterization results of hierarchical meso-/macroporous aluminum hydroxide/ oxyhydroxide and aluminas.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Textural Properties</th>
<th>XRD</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET SA (m²/g)</td>
<td>BJH PV (cc/g)</td>
<td>Micropore SA (m²/g)</td>
</tr>
<tr>
<td>3-25-1</td>
<td>243</td>
<td>0.35</td>
<td>13</td>
</tr>
<tr>
<td>3-25-24</td>
<td>259</td>
<td>0.26</td>
<td>28</td>
</tr>
<tr>
<td>3-60-24</td>
<td>358</td>
<td>0.32</td>
<td>-</td>
</tr>
<tr>
<td>7-25-1</td>
<td>263</td>
<td>0.36</td>
<td>12</td>
</tr>
<tr>
<td>7-25-1-700</td>
<td>251</td>
<td>0.31</td>
<td>-</td>
</tr>
<tr>
<td>7-25-24</td>
<td>315</td>
<td>0.28</td>
<td>-</td>
</tr>
<tr>
<td>7-60-24</td>
<td>392</td>
<td>0.34</td>
<td>-</td>
</tr>
<tr>
<td>7-60-24-700</td>
<td>411</td>
<td>0.4</td>
<td>-</td>
</tr>
<tr>
<td>11.5-25-1</td>
<td>270</td>
<td>0.3</td>
<td>-</td>
</tr>
<tr>
<td>11.5-25-24</td>
<td>149</td>
<td>0.14</td>
<td>-</td>
</tr>
<tr>
<td>11.5-60-24</td>
<td>115</td>
<td>0.1</td>
<td>-</td>
</tr>
</tbody>
</table>

* pH – temperature(°C) – aging time(h)-calcination temperature(°C)

Boehmite (AlO(OH)) crystallite size is denoted in the mixed phase.

The contribution to the surface area due to microporosity in the system was negligible as calculated using the t-plot (Table 1). An increase in surface area was observed with aging temperature and time for acidic and neutral medium syntheses possibly due to the opening of pores caused by molecular rearrangement and further reactions. Higher temperature and longer aging time did not result in further improvement. An optimum in temperature was also realized by Hicks and Pinnavaia who observed improvement in textural properties when the temperature was increased from ambient to 45°C, but no further improvement was observed after increasing the temperature to 65 or 95°C.10
Fig. 1 Nitrogen adsorption-desorption isotherms of hierarchical porous aluminum hydroxides/oxyhydroxides prepared under (a) pH 3, (b) pH 7, and (c) pH 11.5.

Fig. 2 BJH pore size distribution plots (using desorption branch) of hierarchical porous aluminum hydroxides/oxyhydroxides prepared under (a) pH 3, (b) pH 7, and (c) pH 11.5.

XRD patterns for as-synthesized and aged samples are presented in Fig. 3. The as-synthesized materials were XRD amorphous under all reaction environments. After aging, a mixed boehmite (AlO(OH)) and bayerite (Al(OH)_3) phase was detected in samples under
acidic and neutral medium. Broad peaks indicated a poorly crystalline boehmite with a very small particle size (~2.7 nm). This phase is generally referred to as pseudoboehmite (or gelatinous boehmite) with slightly shifted peaks due to the presence of intercalated water in between the layers. The crystallinity increased and the diffraction peaks became sharper after hydrothermal treatment at 60°C. It also led to the hydrothermal conversion of bayerite to pseudoboehmite. The crystallite size increased to 3.3 nm and 4.8 nm after hydrothermal treatment at 60°C and 100°C, respectively. Hydrothermal aging results in the growth of the particles due to Ostwald ripening, which is seen in terms of higher crystallinity of the aged samples. The samples aged under alkaline conditions displayed exclusively bayerite peaks. The bayerite peaks grew sharper with aging time but after aging at 100°C, the material was hydrothermally transformed into boehmite.

The XRD results were compared to the results obtained in the literature for the hydrolysis of aqueous aluminum chloride salts where the composition of the precipitated hydroxide was defined by the pH of the solution. The composition varied in the order of amorphous aluminum hydroxide, pseudoboehmite and bayerite as the pH of the solution increased. In our experiments we observed stronger pseudoboehmite peaks in neutral medium as compared to acidic medium (pH 3) (Fig. 3) while bayerite was observed when synthesized in the presence of NH₄OH (pH 11.5). The hydrothermal transformation of bayerite to boehmite has also been suggested in the literature. Thus, a similar phase evolution behavior in acidic and neutral medium can be assigned to similarities in textural properties in materials aged under these conditions, which were different than those synthesized in the presence of NH₄OH.
Fig. 3 Wide angle XRD patterns for hierarchical porous aluminum hydroxides/oxyhydroxides/oxides prepared under (a) pH 3, (b) pH 7, and (c) pH 11.5.

TGA results shown in Fig. 4(a) confirmed the findings from XRD. The first weight drop is due to the loss of adsorbed water. The weight loss for dehydration of OH from bayerite takes place between 210-260°C while for pseudoboehmite the weight loss occurs over a broad temperature range and a sharp drop was absent even for a well crystallized
boehmite. The gradual weight loss in pseudoboehmite is due to the presence of a variety of excess water molecules of different binding energy on the surface or in the interlayers.

Fig. 4(b) presents DTA curves for amorphous aluminum hydroxide (as synthesized in neutral medium), pseudoboehmite (after hydrothermally aging at 60°C in neutral medium) and bayerite (after aging at 25°C in alkaline medium). In all curves, the first endothermic peak is due to the release of adsorbed water. For pseudoboehmite, the peak at 423°C indicates the conversion to γ-alumina. The formation of γ-alumina from amorphous hydroxide could not be clearly discerned from the DTA curve. In case of bayerite, a sharp endothermic peak at 295°C suggests the formation of η-alumina. This peak could also indicate the formation of a mixture of boehmite and η-alumina depending on the water trapped in the layers that can create hydrothermal conditions for the conversion of bayerite to boehmite. The weaker peak at 1059°C suggests a θ-alumina phase. The transformation paths from different precursor hydroxides illustrated by the DTA curves were consistent with the literature. All the materials were finally transformed into α-alumina at around 1215°C. The formation of γ-phase was further confirmed by XRD of the calcined samples from both amorphous and pseudoboehmite materials (Fig. 3). The crystallinity of γ-alumina was higher when the starting material was pseudoboehmite which is expected since boehmite is an important precursor for the formation of γ-alumina whereas the conversion to γ alumina from amorphous hydroxides takes place through amorphous alumina. A poorly crystalline boehmite has been reported to produce poorly crystalline γ-alumina. It was previously found that syntheses in presence of NH₄OH resulted in final powders with lower extents of macroporosity; in the current work NH₄OH created smaller surface area, pore volume and
after calcination, \( \gamma \)-alumina was not formed. Thus, alkaline medium synthesis and aging are not recommended for obtaining hierarchically structured alumina materials.

Fig. 4 (a) TGA, and (b) DTA plots for hierarchical porous aluminum hydroxides/oxyhydroxides.

Both freshly prepared and aged samples were thermally stable with no loss in surface area and pore volume after calcination in flowing air at 700\(^\circ\)C for 5 h. To investigate the influence of thermal and hydrothermal treatment on the macroporous structure, SEM images were obtained. Macroporous structure was fully preserved after calcination at 700\(^\circ\)C. However, the structure deteriorated upon hydrothermal aging in all mediums (Fig. 5). The influence on the macroporous structure could be seen even after room temperature aging and the reduction in macroporosity was more severe at elevated temperatures. Macropores
disappeared completely at 100°C. The solubility of alumina increased with temperature and the dissolution-reprecipitation process resulted in pore sealing/filling and reduction in macroporosity.

![SEM images](image)

**Fig. 5** SEM images for hierarchical porous aluminum hydroxides/oxyhydroxides synthesized under neutral conditions in water; (a) as-synthesized, and after aging for 24 h at (b) 25°C, (c) 60°C.

In conclusion, γ-alumina with a hierarchical meso-/macroporous structure was successfully synthesized. Samples aged in acidic/neutral medium produced pseudoboehmite which on calcination resulted in the final materials with higher crystallinity. However, macroporosity deteriorated upon aging. Freshly prepared samples from acidic/neutral medium were also transformed to γ-alumina after calcination. The crystallinity was lower but the macroporosity was completely retained. Samples prepared and aged in presence of NH₄OH contained smaller surface area and pore volume, and could not be transformed to γ-alumina.
Titania

As mentioned earlier in the experimental part, the study for titania materials was performed using two alkoxides to investigate the effect of the linear vs. branched alkoxide. Also, two different bases were used to adjust pH values to investigate the effect of the cation. Due to an analogous nature, the results are presented only for iso-propoxide and those for ethoxide can be found in the supplementary information. Previously, in our macropore structure study, synthesis at pH 11.5, adjusted using NH$_4$OH, was found to produce highest macroporosity in titania powders.$^{13}$ However, alkaline medium synthesis proved detrimental for the micro-/mesopore structure by forming a compact structure. This adverse effect was more prominent when ethoxide was used as starting material (Table 1, supplementary information). Thus, fresh samples prepared under alkaline medium were subjected to hydrothermal treatment to enhance the micro-/mesopore structure in these highly macroporous solids. The results were compared with those of materials aged in absence of any base catalyst as well as in the presence of NaOH as a different base.

The physical characterization results are summarized in Table 2. Fig. 6(a) represents nitrogen adsorption-desorption isotherms for materials aged in neutral media. The isotherm at room temperature is a type IV, representative of mesoporous materials.$^{25}$ The isotherm has two hystereses; first at a partial pressure (p/p$^0$) value between 0.3 and 0.6 which somewhat resembles a type H2 hysteresis, however, with the lower closure point around 0.3.
Table 2. Structural characterization results for hierarchical porous titania materials prepared using titanium iso-propoxide.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Textural Properties</th>
<th>XRD</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET SA (m²/g)</td>
<td>BJH PV (cc/g)</td>
<td>Pore Size (nm)</td>
</tr>
<tr>
<td>7-25-w</td>
<td>431</td>
<td>0.3</td>
<td>3.1</td>
</tr>
<tr>
<td>7-60-w</td>
<td>270</td>
<td>0.31</td>
<td>4.1</td>
</tr>
<tr>
<td>7-100-w</td>
<td>230</td>
<td>0.25</td>
<td>4.3</td>
</tr>
<tr>
<td>7-120-w</td>
<td>225</td>
<td>0.25</td>
<td>4.2</td>
</tr>
<tr>
<td>11.5-25-Na</td>
<td>568</td>
<td>0.38</td>
<td>3.1</td>
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<td>11.5-60- Na</td>
<td>290</td>
<td>0.28</td>
<td>3.9</td>
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<tr>
<td>11.5-100- Na</td>
<td>223</td>
<td>0.28</td>
<td>4.6</td>
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<tr>
<td>11.5-120- Na</td>
<td>220</td>
<td>0.26</td>
<td>4.6</td>
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<td>11.5-25-NH₃</td>
<td>330</td>
<td>0.24</td>
<td>&lt;1.8</td>
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<td>&lt;1.8</td>
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<td>11.5-100-NH₃</td>
<td>476</td>
<td>0.29</td>
<td>1.8</td>
</tr>
<tr>
<td>11.5-120-NH₃</td>
<td>170</td>
<td>0.4</td>
<td>11</td>
</tr>
</tbody>
</table>

* pH – aging temp(°C) – w=water, Na=NaOH, NH₃=NH₄OH.

The pore size estimated from BJH pore size distribution obtained using the desorption branch (Fig. 7) was around 3.1 nm, which was very close to the value obtained using the adsorption branch. This porosity can be assigned to irregularly shaped mesopores created due to intraparticle voids. A second hysteresis present at high p/p° value between 0.8 and 1 is a H3 hysteresis indicative of slit-shaped pores created due to aggregation of plate-like particles. The vertical asymptotic nature at p/p° value of 1 indicates the presence of macropores. Due to the presence of large meso-/macropores, which are outside the range of pore sizes that can be accurately determined by nitrogen physisorption, it was problematic to evaluate the correct pore size using either the adsorption or the desorption branch. From the combined results of nitrogen physisorption and SEM, the interparticle pore size was estimated to range from 50 nm to few hundred nanometers. The samples aged at elevated temperatures produced single well-defined H2 hysteresis with lower closure point at p/p° value of 0.4 indicating ink-bottle
Fig. 6 Nitrogen adsorption-desorption isotherms of hierarchical porous titania prepared from titanium iso-propoxide at (a) pH 7, and pH 11.5 adjusted using (b) NaOH, (c) NH₄OH.

Fig. 7 BJH pore size distribution (using desorption isotherm branch) of hierarchical porous titania prepared from titanium iso-propoxide at (a) pH 7, and pH 11.5 adjusted using (b) NaOH, (c) NH₄OH.

shaped pores. The pore neck size indicated by BJH pore size distribution was around 4 nm or smaller.
The important observation from Fig. 6 and 7 are the structural similarities of the samples synthesized and aged at neutral pH in pure water or in the presence of NaOH, and the very different behaviors for the two bases used to adjust the starting solution pH to an identical value of 11.5. In the presence of NH₄OH, the sample aged at room temperature produced an isotherm that was a combination of types I and IV indicating the presence of pores in both micro- and meso- range. After aging at room temperature or at 60°C, the materials had intraparticle micropores and interparticle meso-/macropores. Aging at 100°C resulted in an isotherm with two hystereses loops similar to the one discussed earlier. Thus, higher temperature hydrothermal aging led to the growth of intraparticle pores from micropores to irregular shaped mesopores (~2 nm). On further increasing the aging temperature to 120°C, the isotherm of the aged sample contained a single hysteresis which resembled an elongated H2 type with large nitrogen uptake. Such an isotherm suggests ink-bottle shaped pores with wide neck. The neck size obtained from BJH pore size distribution was around 11 nm.

Unlike for aluminum hydroxides, aging at room temperature did not lead to the formation of crystalline phase in titania. After performing the hydrothermal treatment at 60°C, anatase phase was detected in materials aged in neutral medium or in presence of NaOH. The diffraction peaks were broad due to small crystallite size (5.3 nm) and weak crystallization of the sample. Higher temperatures promoted the growth of nanocrystalline TiO₂ particles (Table 2). This explains the shift of the intraparticle pore sizes from micro-/smaller meso- to larger mesopores, and the reduction in the surface area. The crystallinity in titania did not appear until aged at 120°C when NH₄OH was present (Fig. 8). Anatase phase
appeared at 120°C and the crystallite size was larger than in materials aged in neutral medium at that temperature (Table 2). A delay in the appearance of anatase phase during calcination when the hydrolysis was performed in presence of NH₄OH has been reported in literature.\textsuperscript{15,31} It is also known that the formation of anatase phase is favored in acidic medium.\textsuperscript{31} The phase transition temperatures for materials in neutral and alkaline medium are illustrated by DTA curves in Fig. 9. It is also important to note that even at identical starting alkaline pH values; results with NaOH were very different than with NH₄OH.

\textbf{Fig. 8} Wide angle XRD patterns for hierarchically porous titania materials prepared in the presence of NH₄OH at pH 11.5.
A study of the influence of hydrothermal treatment time was also performed. The crystalline anatase phase in the presence of NH₄OH also appeared after aging for 48h at 100°C; however, the repeatability was poor. No further improvement in crystallinity/crystallite size was observed after aging for 96 h. The crystallite size was unchanged after aging at 120°C for 48 h. Thus, 24 h was adopted as the hydrothermal aging time in the current study. Other researchers also observed an optimum aging time beyond which either no improvement was observed or led to deterioration of the textural properties.¹⁶

Although hydrothermal treatment produced significant changes in the textural properties and crystallinity, the structure at the macro-scale was fully preserved after aging at 120°C. The walls composed of interconnected titania nanoparticles were observed under SEM. The particulate morphology indicates the presence of interparticle porosity in the size range of few hundred nanometers. The difference between the types of base used to adjust
the starting pH value was observed also in terms of macroporosity. The synthesis in the presence of NaOH resulted in powders with similar extent of macroporosity as with only water. The macroporosity increased tremendously when NH₄OH was used to adjust the pH. This difference was more apparent when ethoxide was used as the starting material since iso-propoxide created macroporous powders even with water. Thus, it can be concluded that the type of base used has important influence on the spontaneous self-assembly at each pore scale. A possible explanation could be the different charge shielding properties of the adsorbed cations and their influence on the intergrowth and aggregation of nanoparticles. In a study with different bases, Chuah found different properties in final materials when NaOH, KOH or NH₄OH was used for the hydrolysis of zirconium chloride. Although the dependence with the digestion for the three series was same, the surface area in the final material was in the order NH₃<K<Na-hydrous oxides. Although acidic medium is known to promote the formation of anatase phase it was not used in the current work because it does not favor macropore formation.

To investigate the thermal stability, both freshly prepared and aged samples were subjected to calcination at 500°C and 1000°C. The crystallite size was in the range 9-11 nm in different samples after calcination at 500°C. The calcination of as-synthesized samples led to a tremendous reduction in surface area. For example, for samples prepared in presence in NH₄OH, the surface area was reduced from 330 to 48 m²/g. Similar reductions were also seen with other freshly prepared samples. However, for the samples aged at 120°C for 24 h, although the surface area was smaller than for the freshly prepared samples, most of it was retained after calcination (140 m²/g in presence of NH₄OH) indicating strengthening of the
network as a result of hydrothermal aging. A mixture of anatase and rutile was formed after calcination at 1000°C (Fig. 8). Due to sintering of particles after high temperature heating, the surface area was reduced to 2.5 m²/g. The macro-structure was retained even after calcination at 1000°C.

Recently, in the study of hierarchical titania materials as photocatalysts, the presence of macropores was found to be highly beneficial. A 10-23% drop in catalytic activity was observed after macrostructure was destroyed. 18,33 Although macropores were found to be beneficial, the photocatalytic activity is defined by the specific surface area and crystallinity. For example, the catalytic activity was highest after calcination of the freshly prepared sample at 300°C, but was greatly decreased after calcination at higher temperatures than 500°C because of a drastic decrease in surface area. 33 Thus, the current methodology is useful in obtaining highly macroporous materials with high crystallinity and no significant loss of surface area. Hydrothermal synthesis of titania have also been reported, however, the authors used titanium butoxide and the synthesis was performed in water. In those cases, the macroporosity in materials could be significantly enhanced in presence of NH₄OH. 13

In conclusion, hierarchical meso-/macroporous titania with crystalline walls can be synthesized by subjecting the freshly prepared solids to hydrothermal treatment. The required hydrothermal conditions are more severe when the synthesis and aging is performed in the presence of NH₄OH. Larger crystallite sizes and larger pore openings were obtained in the presence of NH₄OH. When NaOH was used to adjust the pH value to 11.5, very different behavior was observed. The difference was seen at the micro-/meso scale porosity, phase composition and also in terms of macroporosity. The behavior in the presence of NaOH was
in fact very similar to that in only water. The macropore structure was completely stable after thermal and hydrothermal treatment. Surface area was preserved in aged samples, indicating a greater strength of the network after aging.

**Zirconia**

The physical characterization results of zirconia prepared using zirconium propoxide are presented in Table 3. As seen from the table, freshly prepared samples, irrespective of the presence or type of base catalyst, had very small surface area indicating that the materials were purely macroporous. This result is different from titania materials where the surface area of freshly prepared solids was much higher when prepared in water or NaOH as compared to in NH₄OH. After hydrothermal treatment at 120°C, the surface area increased tremendously for all samples. The results are consistent with the reports in literature where the surface area of zirconia prepared from the hydrolysis of zirconium chloride or using alkoxide precursors increases after hydrothermal treatment. The synthesis of high surface area zirconia after hydrothermal treatment was also demonstrated by Vantomme et al.

**Table 3. Structural characterization results for hierarchical porous zirconia materials.**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Textural Properties</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET SA (m²/g)</td>
<td>BJH PV (cc/g)</td>
<td>Pore Size (nm)</td>
<td>Micropore SA (m²/g)</td>
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<td>5</td>
</tr>
<tr>
<td>7-120-w</td>
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<td>0</td>
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<td>0.03</td>
<td>-</td>
<td>23</td>
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<tr>
<td>13.5-120-NH₃</td>
<td>479</td>
<td>0.33</td>
<td>2.1</td>
<td>17</td>
</tr>
</tbody>
</table>

*pH – w=water, Na=NaOH, NH₃=NH₄OH.

Fig.10 (a) presents the nitrogen adsorption-desorption isotherms of the hierarchical zirconia materials. The isotherms are type IV, characteristic of mesoporous materials. The
shape of the isotherms and hystereses resemble the ones discussed earlier for titania materials. Fig. 10(b) presents the corresponding BJH pore size distributions calculated using the desorption branch. Even after aging at 120°C, small irregular shaped mesopores were formed due to interstitial spaces between the zirconia nanoparticles. The contribution to the surface area from micropores was very small.

![Diagram](image)

**Fig. 10** (a) Nitrogen adsorption-desorption isotherms, and (b) BJH pore size distributions (using desorption isotherm branch) of hierarchical porous zirconia materials.

XRD results indicated that all freshly prepared as well as aged samples were amorphous. After calcination at 500°C, tetragonal phase appeared in the materials (Fig. 11). Higher pH values favored the formation of tetragonal phase. The crystallite sizes calculated using the Scherrer equation indicated formation of smaller crystallites from aged samples (8-10 nm) as compared to those from freshly prepared samples (25-30 nm). This is because after hydrothermal aging, zirconia rearranges itself to a lower energy state making it more stable.
Fig. 11 Wide angle XRD patterns for hierarchically porous zirconia materials prepared in the presence of NH$_4$OH at pH 13.5.

Fig. 12 DTA curves for freshly prepared and hydrothermally treated (120°C, 24h) hierarchically porous zirconia materials.

towards crystallite growth.$^{32}$ DTA curves illustrating the phase transition to tetragonal phase for the as-synthesized and aged samples are presented in Fig. 12.
The mesostructure in the aged samples collapsed after calcination partially at 500°C and completely after calcination at 1000°C. For example, the surface area of zirconia prepared and aged at 120°C in presence of NH₄OH, reduced from 479 m²/g to 136 m²/g after 500°C and to 8 m²/g after 1000°C. The macrostructure was however preserved after hydrothermal aging and also after calcination.

To conclude, hierarchically meso-/macroporous zirconia materials can be synthesized using a combination of spontaneous self-assembly and hydrothermal aging. Crystalline zirconia could not be obtained after aging. After calcination, tetragonal phase appeared but the mesostructure was partially destroyed. Macropore structure was thermally and hydrothermally stable.

Conclusions

The current work investigated the beneficial effects and limitations of hydrothermal aging of macroporous solids obtained using spontaneous self-assembly process on the textural properties and phase composition of the materials. The results illustrate synthesis strategies for obtaining hierarchical meso-/macroporous structures with crystalline framework walls in alumina, titania and zirconia that are known to form such structural patterns.

(1) For alumina materials, hierarchical meso-/macroporous γ-alumina with high surface area can be obtained from both freshly prepared and aged materials after calcination at 500°C. From the former precursor, the highly macroporous final oxide was poorly
crystalline. However, the latter produced oxide with higher crystallinity but the macropore structure deteriorated due to aging. Synthesis in acidic/neutral medium is recommended.

(2) Crystalline titania materials with a hierarchical meso-/macroporous structure were obtained after aging. The appearance of anatase phase was delayed to higher temperatures when aging was performed in the presence of NH$_4$OH. While the surface area in freshly prepared solids could not be retained after calcination at 500°C, the mesopore structure in aged materials was thermally more stable. Macropore structure was thermally and hydrothermally very stable. The type of base used to adjust the starting pH of the solution greatly influenced the structure at both meso- and macropore scale. NH$_4$OH produced powders with better structure.

(3) The surface area of freshly prepared zirconia materials increased tremendously after hydrothermal treatment. However, the resulting materials were amorphous. Calcination at 500°C resulted in the formation of tetragonal phase. The crystallinity was lower when samples were aged prior to calcination. The mesostructure formed during aging, partially collapsed after calcination. The macropore structure was thermally and hydrothermally stable.

**Acknowledgement:** The financial support from Petroleum Research Foundation (American Chemical Society) is gratefully acknowledged.
Supplementary Information

Experimental results for titania obtained using titanium ethoxide:

**Table 1.** Structural characterization results of the hierarchical porous titania from titanium ethoxide.

<table>
<thead>
<tr>
<th>Sample*</th>
<th>Textural Properties</th>
<th>XRD</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>BET SA (m^2/g)</td>
<td>BJH PV (cc/g)</td>
<td>Pore Size (nm)</td>
</tr>
<tr>
<td>7-25-w</td>
<td>403</td>
<td>0.2</td>
<td>&lt;1.8</td>
</tr>
<tr>
<td>7-60-w</td>
<td>280</td>
<td>0.26</td>
<td>3.7</td>
</tr>
<tr>
<td>7-100-w</td>
<td>230</td>
<td>0.24</td>
<td>3.6</td>
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<td>7-120-w</td>
<td>224</td>
<td>0.24</td>
<td>4.1</td>
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<td>11.5-25-Na</td>
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<td>2.6</td>
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<td>11.5-100-Na</td>
<td>230</td>
<td>0.28</td>
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<td>11.5-120-Na</td>
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<td>&lt;1.8</td>
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<td>230</td>
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<td>&lt;1.8</td>
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<td>2.6</td>
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<tr>
<td>11.5-120-NH\textsubscript{3}</td>
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<td>0.4</td>
<td>9.1</td>
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</tbody>
</table>

* pH –aging temp(°C) – w=water, Na=NaOH, NH\textsubscript{3}=NH\textsubscript{4}OH.
Fig. 1 Nitrogen adsorption-desorption isotherms of hierarchical porous titania prepared from titanium ethoxide at (a) pH 7, and pH 11.5 adjusted using (b) NaOH, (c) NH₄OH.

Fig. 2 BJH pore size distribution (using desorption isotherm) of hierarchical porous titania prepared from titanium ethoxide at (a) pH 7, and pH 11.5 adjusted using (b) NaOH, (c) NH₄OH.
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Chapter 4. Synthesis and Characterization of Hierarchically Structured Aluminosilicates

A paper to be submitted to Journal of Catalysis

Sikander H. Hakim* and Brent H. Shanks*

Abstract

Catalytically active aluminosilicate materials with hierarchical porous structures are produced. A spontaneous self-assembly in aqueous solution starting from component alkoxides resulted in patterned powders without the aid of any templating agent. SEM and N₂ adsorption-desorption studies demonstrated regular array of macrochannels connected with micro-mesoporous walls. FTIR of adsorbed pyridine revealed the presence of both Brönsted and Lewis acid sites. Although the synthesis procedure is markedly distinct from sol-gel phenomenon, the structure and acidity in final materials could be manipulated in terms of sol-gel parameters such as composition, pH, temperature, and addition order. Not one parameter set could be identified to provide both best structure and maximum acidity; a compromise between the two was essential. The synthesized aluminosilicate catalysts were active in the esterification reaction of palmitic acid.

Keywords: hierarchical, macropore, mesopore, aluminosilicate, self-assembly, alkoxide, Brönsted acid, Lewis acid.

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Introduction

In the design of novel porous materials for catalysts, the ones with a structural hierarchy are very important and have received great interest.\(^1\) Pores at different length scales exist in hierarchical materials enabling them to offer multiple advantages. The mesopores provide high surface area and the macropores render the mesopores more accessible by reducing diffusion resistance. Such structural pattern can potentially enhance the catalytic performance; especially in applications involving liquid phase reactions. Introduction of secondary macropores in mesoporous framework has been demonstrated to increase the activity of solid catalysts significantly by enhancing the diffusion to and from the active sites.\(^2\)\(^3\) These materials have also been suggested to be a possible replacement of current FCC catalyst composites made up of USY zeolites mixed with a macroporous matrix.\(^4\) Hierarchically porous materials thus avoid the need to physically mix separate materials with pores at different length scales. Introduction of macroporous channels in mesoporous titania framework was found to increase the photocatalytic activity of the catalyst by increasing the photoabsorption efficiency and diffusion of gaseous molecules.\(^5\) Besides their applications in catalysis, hierarchically structured materials have also displayed remarkable properties in separations as a stationary phase of high performance liquid chromatography (HPLC) compared to conventional particle-packed systems.\(^6\) In view of these and multitude of other practical applications, hierarchical porous materials are highly desirable and researchers have adopted a plethora of strategies to incorporate macropores in mesopores material. A review of possible approaches has been recently provided by Yuan and Su.\(^1\) A commonly employed technique is dual-templating where hierarchical structures are created by a combination of surfactant templating and colloidal crystals as macrotemplates.\(^7\) The disadvantage of such a
technique is the post-synthesis treatment step which compromises the purity and stability of the synthesized material. Template-free routes have also been suggested; such as redox cycling producing mesopores in a regenerative process in macroporous materials or selective leaching of one phase from a two phase composite. Nakanishi obtained hierarchical meso-macroporous monolithic materials via a sol-gel route accompanied by polymerization-induced liquid-liquid phase separation. The concurrent phase separation and gelation resulted in the macroporous morphology. The authors were able to control the macropore size depending on the polymer (Polyethylene oxide (PEO)) content while the meso-structure were tailored by solvent exchange and aging.

A simpler template-free technique to obtain mesoporous-macroporous metal oxides is via spontaneous self-assembly in solution. This is a relatively easy one-pot scheme where liquid alkoxides of very reactive metals such as aluminum, titanium and zirconium are allowed to undergo rapid hydrolysis and condensation in presence of excess water. The polymerization reaction results in the formation of metal oxide (oxy-hydroxide) network. The metal oxide nanoparticles organize themselves into walls of macropores and the interstitial spaces between them create the mesoporosity. This technique produces powders with a unique morphology in which parallel macrochannels traverse through the particles. Simulation studies have suggested that not only the presence of macropores but also a well-designed pore arrangement and high connectivity between macro-mesostructure is very effective for high catalytic performance. The structures obtained via self-assembly posses such regularity and interconnectivity and hence holds great potential. For instance, presence
of straight light-harvesting macrochannels with mesoporous walls rather than holes were crucial for improved photocatalytic activity of hierarchical titania.\textsuperscript{5}

Individual mechanisms govern the formation of macropores and mesopores.\textsuperscript{16} In our previous work, we performed a detailed study of macropore formation in different metal oxides and by means of comparative analysis we found that by varying the relative contributions of hydrolysis and condensation reactions by adjusting the parameters such as central metal atom, alkoxy group in the alkoxide or the starting pH of the solution, the macroporosity in the system can be tailored.\textsuperscript{11} Although independent mechanisms govern macropore and mesopore formation, their existence is closely associated to each other. In our experiments, we also found that the mesostructure in hierarchical materials can be manipulated by means of hydrothermal aging without affecting the macrostructure. However, the extent of this manipulation depends on the type of material. An indirect influence of surfactant on mesopore formation in hierarchical materials by affecting the nanoparticle aggregation has also been suggested.\textsuperscript{4,13,17} Surfactant, however, does not affect the formation of macropores.

After obtaining hierarchical structures for a variety of metal oxides employing self-assembly technique and identifying the ways to tailor the pore structure independently at different length scales, the focus in the current work was to synthesize a catalytically active material with hierarchical structure. Towards this aim, hierarchically structured acidic aluminosilicate catalysts were synthesized and characterized. Such a synthesis of aluminosilicates with hierarchical structure has been demonstrated by Su’s research group.\textsuperscript{18} The synthesized aluminosilicates contained a macrostructure as observed under scanning
electron microscope. The meso/micro structure was characterized using nitrogen adsorption-desorption studies and NMR revealed the incorporation of Al in Si network. However, the work focused on only one of the many possible synthesis routes and further work is required to explore these routes defined by various sol-gel parameters. Moreover, surface acidity in the final materials was not characterized. In current work, the challenging synthesis schemes were formulated based on our previous synthesis experience with these materials as well as insights from sol-gel chemistry of mixed metal oxides. It should be made clear that differences exist between a typical sol-gel and the spontaneous self-assembly process. A typical sol-gel process is a multistep process involving a stable sol, gelation and a drying step. Each step plays an important role in determining the properties in resultant oxide. Whereas, in latter, metal oxides in form of solid/ gelatinous precipitates are obtained very rapidly in excess water. The spontaneous self-assembly process can however be viewed as a limiting case of sol-gel process.

A combination of dissimilar oxides presents the potential of creating the surface acid sites that are not present in the pure component oxides is well-known in the sol-gel literature. It has been demonstrated that the textural and acidic properties of the sol-gel derived mixed oxides depend not only on the constituent oxides and their relative amounts but also on the homogeneity of inter-component mixing. A homogeneous molecular level mixing is desired for the creation of acid sites in the system. A uniform mixing of the components takes place when hydrolysis and condensation reactions are slow and are matched for the component alkoxides. The fast hydrolysis reactions are regulated by controlled addition of water. Mismatch in the reactivities of the component metal alkoxides is achieved by either
providing slow reacting component a head start or by chemical modification of the faster reacting component. These routes result in different levels of mixing, the order of which is provided by Miller and Ko.\textsuperscript{19} The authors also suggested many different methods to obtain evidence of mixing. Well mixed samples will result in higher activity in an acid catalyzed reaction. The information regarding the mixing can also be obtained from the XRD patterns where in general, component crystallization is delayed in well-mixed samples. The influence of mixing can also be observed in the textural properties such as specific surface area and pore volume of the mixed oxide pair.

The synthesis control possible for sol-gel cannot be applied to spontaneous self-assembly process which indispensably requires rapid kinetics for pattern formation. This naturally presents a great challenge in synthesizing the materials possessing both hierarchical structure and acidity. A balance can be obtained by studying the synthesis parameters such as constituent composition, addition order of the alkoxide, initial pH and temperature as these are known to change the microstructural distribution of the components in sol-gel process. In aluminosilicates, composition is important because alumina is the structure forming component\textsuperscript{20} while addition of silica is known to create Brönsted acid sites in sol-gel oxides\textsuperscript{21}; a suitable choice of relative amount can provide a best combination of structure and acidity. Whether the premixed alkoxides are allowed to undergo rapid simultaneous hydrolysis, slower component is provided a head start, or structure forming component is introduced in reaction mixture first are different possible methods of precursor addition that can be comparatively evaluated for producing the desired properties in final materials. Additionally, in the reaction system of two components with different reactivities, the initial
pH and temperature influencing the hydrolytic-condensation chemistry can play an important role in influencing the inter-component mixing and defining the textural and acidic properties.

The exact nature of the acidity of aluminosilicates is still under discussion. However, recently Crepeau et al. provided new insights into the nature and structure of acid sites in amorphous silica alumina prepared by methods such as impregnation or cogelification using a combination of double resonance NMR experiments and IR spectroscopic analysis.\textsuperscript{22} The creation of Lewis acid site was explained by elimination of adsorbed water on Al\textsuperscript{3+} sites, while cannot be explained by dehydroxylation via elimination of Al-OH since such species are not detected. To explain the Brönsted acidity, it was proposed that the acidity of silanol groups is modified by the presence of neighboring Al atoms and it cannot be explained by hydroxyl groups bridged between Si and Al since such species were not detected by \textsuperscript{1}H NMR. Thus authors suggested that (SiOH, Al) paired sites generate strongly acidic Brönsted acid sites and that homogeneous amorphous aluminosilicates exhibited strongest Brönsted acidity. The current work investigates homogeneity of mixing in materials via various synthesis routes and provides a comparative analysis by means of a series of structural and acidic characterization techniques.

**Experimental Section**

**Synthesis**

The starting materials were the liquid alkoxides: tetraethoxisilane (TEOS) (Acros, USA) and aluminum tri \textit{sec}-butoxide (TBOA) (97%, Aldrich, USA) and were used as purchased. Deionized water was used in all the synthesis and the pH was adjusted using hydrochloric
acid or a stock solution of aqueous ammonia (>35%). In a typical synthesis, 4 ml of mixed alkoxide in varying atomic ratios of individual component was introduced into 40 ml of pH adjusted aqueous solution. All syntheses were performed in absence of any stirring. The mixture was allowed to react and age in the mother liquor solution for 24 hours. The solid was then retrieved by filtration and washed multiple times with DI water. It was then allowed to dry in ambient temperature for 12 hours and at 100°C in vacuum for 5 hours.

The effect of composition was investigated by synthesizing powders with initial Si/Al atomic ratio of 4, 1 and 0.25. The syntheses were performed using premixed alkoxides at pH 3 and 70°C and the composition yielding a best combination of structural and acidic properties was adopted for subsequent synthesis evaluating the effect of other parameters.

In order to study the effect of the addition order, a first set of samples was obtained from premixed alkoxides. The two alkoxides were allowed to homogenize under stirring for 30 minutes and the mixture was then introduced dropwise into aqueous solution to undergo hydrolysis and condensation as a single solution. Another set of samples was prepared by introducing aluminum alkoxide first dropwise which was then immediately followed by the addition of silicon alkoxide. A third set was obtained by adding silicon alkoxide first and allowing it to prehydrolyze in acidic medium at pH 1.5 for one hour. The pH was then adjusted to neutral before adding the aluminum alkoxide.

The effect of temperature on the properties of the final aluminosilicates was investigated for samples prepared using premixed alkoxides. The synthesis temperatures were chosen to be 40°C, 70°C and 100°C and the one yielding best properties was adopted for subsequent synthesis.
The effect of pH was studied for acidic (pH 3), neutral (pH 7) and alkaline (pH 11.5) values for samples obtained with premixed alkoxides as well as for those obtained by introducing aluminum alkoxide first. For samples prepared by prehydrolyzing silicon alkoxide first, the influence of pH was studied by performing the synthesis as mentioned earlier or by performing the entire synthesis at pH 3.

Portions of samples were calcined for 5h in flowing air at 550°C using a temperature ramp of 5°C/min to evaluate thermal stability.

Characterization

Structural Characterization

The macropores in the resulting aluminosilicate powders were analyzed using scanning electron microscopy (SEM). Images were taken using a JSM-840 scanning electron microscope (JEOL Inc.) with gold coated sample preparation. Morphological information such as the fraction of particles containing macropores and the extent of macroporosity was obtained by acquiring images at various magnifications and by taking into account a large number of particles for minimal error in measurements. Hg-porosimetry was also performed on samples but the results were not informative because the fragile structure could not be preserved under high pressure conditions of Hg-intrusion.

The SEM was equipped with energy dispersive spectrometer - IXRF EDS2004 for elemental analysis on a microscopic scale, with capabilities including quantitative analysis, image analysis, line-scan x-ray profiles and multiple element x-ray maps. Different regions on same particles, regions on different particles of the sample and regions on different
samples were used to confirm the composition of the constituents in the final powder. Dot maps for selected samples were also obtained for evaluating the elemental distribution throughout the sample.

X-ray diffraction patterns were obtained for information regarding the crystallinity of the resultant powders. The measurements were carried out on Siemens D-500 XRD using CuKα radiation.

The micro/meso-structure in the sample was characterized using Micromeritics ASAP-2020 analyzer. The specific surface area of the materials was obtained from the nitrogen adsorption-desorption isotherm at liquid nitrogen temperature by using the BET approach. The pore size distribution and pore volume was calculated using the BJH desorption branch of the isotherm. The contributions of the micropores were evaluated using the t-plots.

**Acidity Characterization**

Analysis of surface acidity in acidic solids using IR spectrum of adsorbed probe molecule has been one of the most common techniques. Some of the early studies were published in 60s.\textsuperscript{23,24} Pyridine as a probe molecule provided unique properties; most important being its ability to differentiate between Brönsted and Lewis acid sites.\textsuperscript{23} The bands in the region 1400-1700 cm\textsuperscript{-1} are due to in-plane vibrations of the C6 ring (modes 8a and 19b). The spectra of pyridine for its different modes of interaction with the surface are remarkably different. Pyridine ion produces a band at approximately 1540 cm\textsuperscript{-1} which is not present in either pyridine or coordinately bonded pyridine. Pyridinium ion on the other hand does not have a band in the 1440-1465 cm\textsuperscript{-1} region but both coordinately and H-bonded pyridine do. It has
been established that a broad band at 1540 cm\(^{-1}\) along with a split band at 1640, 1628 cm\(^{-1}\), and a very strong band at 1490 cm\(^{-1}\) can be used to indicate Brönsted acidity while a band in the region 1140-1465 cm\(^{-1}\) region indicates Lewis acidity. Other properties of pyridine making it a widely used probe include its intermediate basic strength and chemical stability on oxide surfaces.\(^{25}\)

In current work, the IR spectra of pyridine were recorded using a Nicolet 6700 FT-IR spectrometer. The powders were suspended in pyridine at 120°C under reflux for 24 hours, retrieved by filtration and dried at 100°C under vacuum for 5 hours. The powders were then transferred to tubes which were evacuated down to a pressure of 10 \(\mu\)m Hg at 100°C for 5 hours to remove physisorbed and loosely bonded pyridine. The samples were then pelletized using KBr and IR spectra were obtained while purging with nitrogen for removing moisture and carbon dioxide. Data are reported as difference spectra obtained by subtracting the spectrum of KBr pellets without any sample and normalizing to the same weight of catalyst.

To obtain quantitative information regarding the pKa of the acid and the total amount of Brönsted acid sites, potentiometric titrations were conducted on selected samples. An aqueous salt solution of the catalyst was titrated against KOH (0.01M) and the total acid amount was calculated in terms of equivalents per gram. Gran plot method was used to calculate the pKa of the solid acids.

\[
V_b \cdot 10^{-pH} = \frac{\gamma_{HA}}{\gamma_A} K_a (V_a - V_b)
\]

Where \(V_b\) is the volume of the base, \(\gamma\) is the activity.
The synthesized catalysts were tested in the acid catalyzed esterification of fatty acids with methanol. The reagents used for the catalytic test are palmitic acid (PA ≥ 95%, Sigma), refined soybean oil (SBO, Wesson), and methanol (MeOH ≥ 99.9%, Fisher Scientific). A model high free fatty acid oil feed was prepared using 15wt% of PA in SBO. The oil mixture along with MeOH in a ratio of 1:20 w/w was introduced in 100 ml reaction vessel. The reactions were performed in a stainless-steel pressurized batch reactor, Autoclave, USA fitted with mechanical stirrer and sample outlet. The constant temperature in the reaction vessel was maintained with the aid of heating jacket and integrated water cooling system. The range of temperature studied was 100°C - 140°C. Experiments at different stirring speeds were conducted and 500 rpm was found to produce no external mass transfer limitations where all the esterification runs were performed. Activation energies were calculated to investigate internal mass transfer limitations. Samples were drawn every 10 minutes and their acid values were determined using the AOCS method Cd 3a-63. Conversions in the initial linear rate regime were evaluated to compare the performance of catalysts synthesized using different techniques. All experiments were performed at least twice to evaluate reproducibility.

Results and Discussions

Effect of composition

The structural characterization results of the aluminosilicate catalysts synthesized in the current work are summarized in Table 1. SEM images of samples prepared by using premixed alkoxides with different Si/Al atomic ratios are presented and compared with pure alumina in Figure 1.
Table 1. Structural characterization results of the hierarchical porous aluminosilicates.

<table>
<thead>
<tr>
<th>Addition Order</th>
<th>T (°C)</th>
<th>pH</th>
<th>Si/Al atomic ratio</th>
<th>Textural Properties</th>
<th>Acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure alumina</td>
<td>25</td>
<td>3</td>
<td>0</td>
<td>BiSSA (m²/g)</td>
<td>&gt;95</td>
</tr>
<tr>
<td>Premixed</td>
<td>70</td>
<td>3</td>
<td>4</td>
<td>360 (m²/g)</td>
<td>60±10</td>
</tr>
<tr>
<td>Premixed</td>
<td>70</td>
<td>3</td>
<td>0.25</td>
<td>500 (m²/g)</td>
<td>30±10</td>
</tr>
<tr>
<td>Premixed</td>
<td>40</td>
<td>3</td>
<td>4</td>
<td>390 (m²/g)</td>
<td>60±10</td>
</tr>
<tr>
<td>Premixed</td>
<td>100</td>
<td>3</td>
<td>4</td>
<td>210 (m²/g)</td>
<td>0</td>
</tr>
<tr>
<td>TEOS first</td>
<td>70</td>
<td>1.5→7</td>
<td>4</td>
<td>380 (m²/g)</td>
<td>30±10</td>
</tr>
<tr>
<td>TBOA first</td>
<td>70</td>
<td>3</td>
<td>4</td>
<td>560 (m²/g)</td>
<td>&gt;90</td>
</tr>
<tr>
<td>Premixed</td>
<td>70</td>
<td>7</td>
<td>4</td>
<td>310 (m²/g)</td>
<td>60±10</td>
</tr>
<tr>
<td>Premixed</td>
<td>70</td>
<td>11.5</td>
<td>4</td>
<td>280 (m²/g)</td>
<td>60±10</td>
</tr>
</tbody>
</table>

For all the three starting compositions, the particles were found to contain macropores. The percentage of such particles, however, was smaller than in pure alumina (Table 1). The percentage also did not translate completely with Al content in the material. A higher Si content or equimolar amount produced higher extent of macroporosity than samples with higher Al content. A portion of as-synthesized sample was calcined and the macro-structure was found to be intact after calcination at 550°C.

Since not all the particles were found to contain macropores, EDS dot maps were obtained to investigate the possibility of component segregation where the macroporous particles could be predominantly alumina. The results revealed that all the mapped particles contained a homogeneous distribution of both the elements (Figure 2). The dot maps were also obtained at high magnifications of 10kx (not shown here) and homogeneity was observed even at a 100 nanometer scale. Quantitative elemental calculations at different spots (Figure 3) indicated that the ratio in the final aluminosilicate powders was very close to the starting ratio. This suggests that aluminum and silicon alkoxides underwent hydrolysis and
condensation as a single solution rather than individual species to form aluminosilicate nanoparticles. The mixed oxide nanoparticles organized themselves into macroporous walls in a way similar to that in single metal oxides such as alumina, titania, etc.\textsuperscript{11}

![SEM images of hierarchical porous aluminosilicate materials from premixed alkoxides with Si/Al atomic ratio (a)4, (b)1, (c) 0.25, and (d) 0.]

**Fig. 1** SEM images of hierarchical porous aluminosilicate materials from premixed alkoxides with Si/Al atomic ratio (a)4, (b)1, (c) 0.25, and (d) 0.

In order to understand the unexpected behavior observed during the synthesis of aluminosilicates where higher percentage of silica provided better macroporosity, pure alumina was synthesized at 70\textdegree{}C. It was found that the macroporosity in pure alumina was reduced when synthesis was performed at higher temperatures.
Fig. 2 EDS dot map of aluminosilicate particles obtained from premixed alkoxides with Si/Al atomic ratio 4.

Additionally, the ones synthesized at room temperatures were when aged in aqueous solution, contained reduced macroporosity. Such a reduction could be observed after aging even at room temperature; the effect was however more dominant at higher temperatures. The reduction in macroporosity could either be due to dissolution re-precipitation process or the higher synthesis temperature could have driven the reaction rates outside the range that yield macroporous structure or possibly by a combined influence of both. Since the samples synthesized at higher temperature still possessed a high percentage of macroporous particles prior to aging (although with smaller extent than ones synthesized at room temperature), the dissolution re-precipitation process was thought to be the more significant for reduction in macroporosity. It has been observed that the presence of silica can increase the durability of alumina gels in aqueous solution. The opposite effect was also observed where presence of alumina decreased the solubility of silica. This can possibly provide explanation for the current observation. When the percentage of silica was higher, even though the extent of macroporosity was smaller because of smaller percentage of structure forming component; it was mostly retained because of slow rate of dissolution. In alumina rich samples, the small
amount of silica is probably insufficient to reduce the rate of dissolution of alumina and hence very little macroporosity was observed in final powders.

Fig. 3 Quantitative X-ray elemental compositions at various regions of aluminosilicate obtained from premixed alkoxides with Si/Al atomic ratio 4.

<table>
<thead>
<tr>
<th>Region</th>
<th>O (At%)</th>
<th>Si (At%)</th>
<th>Al (At%)</th>
<th>Si:Al</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>59.6</td>
<td>32.6</td>
<td>7.8</td>
<td>4.2</td>
</tr>
<tr>
<td>2</td>
<td>60.9</td>
<td>30.5</td>
<td>8.6</td>
<td>3.5</td>
</tr>
<tr>
<td>3</td>
<td>64.8</td>
<td>27</td>
<td>8.2</td>
<td>3.3</td>
</tr>
<tr>
<td>4</td>
<td>70.2</td>
<td>22.6</td>
<td>7.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>

Nitrogen adsorption-desorption isotherms providing the information regarding the micro/meso-structure in synthesized aluminosilicates are shown in Figure 4. For all samples, a type IV (BDDT classification)\textsuperscript{29} isotherm indicated the presence of mesopores. For a Si/Al ratio of 4, the isotherm plot contained H3 hysteresis indicating open slit-shaped pores.\textsuperscript{29} This is distinct from the H2 (characteristic of ink-bottle shaped pores) hysteresis obtained in pure alumina. Such open pore structure resulted in large uptake of nitrogen and the aluminosilicates had larger pore volume as compared to pure alumina.
Fig. 4 Nitrogen adsorption-desorption isotherms and corresponding BJH pore size distribution plots of hierarchical porous aluminosilicates prepared from premixed alkoxides with different Si/Al atomic ratios.

The powders also contained micropores and their contributions to the surface area as calculated from t-plot analysis are shown in Table 1. For equimolar ratio, the hysteresis appeared to be a combination of type H2 and H3. Finally, for the Si/Al ratio of 0.25, the hysteresis was entirely H2 similar to pure alumina. The corresponding BJH pore size distribution plots were very broad and maximum can barely be seen at around 30-50 nm for Si/Al ratio of 4 which changed into a sharp peak at 3.5 nm for the ratio of 0.25 while the pore size distribution for equimolar ratio appeared to be intermediate between these two scenarios.

The BET surface area increased with percentage of aluminum from 360 to 500 m$^2$/g. The increase in SA with increasing amount of Al was consistent with the observations made with sol-gel derived aluminosilicates by La Parola et al.}$^{21}$
A change in textural properties from the pure oxides suggests interaction between the components. In pure alumina, the interstitial spaces between nanoparticles give rise to ink-bottle shaped mesopores. The neck size of the pores is centered at 3.5 nm. Aluminosilicates with higher percentage of silicon were found to contain open slit-shaped pores which are indicative of aggregates of plate-like nanoparticles. When the percentage of aluminum was increased to make the ratio equimolar, both extra-framework alumina nanoparticles as well as aluminosilicate nanoparticle aggregates appeared to exist resulting in a peak at around 3.5 nm but with a broad tail extending towards greater pore diameter. The isotherm and hysteresis for aluminum-rich samples were very similar to pure alumina. However, presence of silica resulted in increased surface area. Intermixing was also apparent in XRD analysis where boehmite peaks present in pure alumina materials were not detected in any aluminosilicates.

Thus the above structural characterization techniques not only confirmed a hierarchical porous structure but also provided evidence of component intermixing crucial for the creation of surface acid sites. IR spectra of adsorbed pyridine indicated that most of the final aluminosilicates contained both Brönsted and Lewis acid sites. The creation of the surface acid sites in the powders was found to be a strong function of the composition. Figure 5 presents IR spectrum of the adsorbed pyridine on the samples prepared using premixed alkoxides with various Si/Al ratios. The strongest Brönsted peak at 1542 cm$^{-1}$ was obtained for Si/Al atomic ratio of 4. The peak intensity was smaller for equimolar composition while the peak was not detected for Si/Al ratio of 0.25. The peaks corresponding to Lewis acid
sites were found in all samples and the intensity was higher for Si/Al ratio of 0.25 which is typical of aluminum rich samples.

Fig. 5 IR spectra of pyridine on aluminosilicate materials prepared from premixed alkoxides with different Si/Al compositions.

A larger amount of slower reacting TEOS when allowed to hydrolyze simultaneously with a smaller amount of faster reacting TBOA, greater number of hydrolyzed species of silicon results in the incorporation of most of the aluminum into the silica framework providing a molecular scale homogeneity as a result of hetero-condensation between the hydrolyzed species. For equimolar amounts, the hydrolyzed species of aluminum finds equal opportunity to condense with either silicon or aluminum existing in equal amounts. The aluminum species undergoing homo-condensation results in extra-framework domains. A smaller number of silicon interacting with aluminum in turn results in smaller number of hetero-bonds as seen from IR and titration results. When the percentage of Al was further increased, the number of such silanols with adjacent Al was much smaller and the peak was not detected in IR spectrum.
To summarize, a ratio with higher percentage of Si in the precursor solution produced powders with highest acidity in terms of Brönsted acid amount while maintaining a hierarchical structure. Equimolar ratio of silicon and aluminum produced powders with a good macrostructure and similar acid pKa value but the acid amount was lower. Higher percentage of aluminum did not result in good structure or acidity.

**Effect of temperature**

Based on the results from the composition study, the temperature study was performed using premixed alkoxides with Si/Al ratio of 4. The percentage of particles in final aluminosilicate powders that contained macropores decreased with an increase in temperature with no macropores present at 100°C. The samples prepared at 40°C however displayed non-homogeneous distribution of elements as observed by EDS dot maps and the elemental calculations suggested a Si/Al ratio to be around 0.3 rather than 4. At lower temperature, the difference between the reactivities of component alkoxides appeared to be more prominent resulting in homo-condensation of hydrolyzed species of aluminum. The hydrolyzed species of silicon would then have to condense amongst themselves forming smaller silicon oxide oligomers and were unable to get incorporated in the oxide network. The completeness of reaction was studied by thermogravimetric analysis and no unhydrolyzed organic groups existed after one hour of reaction (not shown here). The silicon oxide oligomers did not seem to polymerize further even when the reactions were performed for extended period of 24h.

For the synthesis performed at 40°C, the type IV isotherm consisted of two hystereses, one at a lower partial pressure of 0.45 is of type H2 and second at 0.7 is H3 (Figure 6).
Fig. 6 Nitrogen adsorption-desorption isotherms of hierarchical porous aluminosilicates prepared from premixed alkoxides at temperature (a) 40°C, (b) 70°C, and (c) 100°C.

Such bimodal mesoporosity observed in system usually suggests intra and inter particle porosity. However, present case suggested segregation of the component species at this temperature, where the alumina rich and aluminosilicate domains could possibly result in two independent hystereses. The pore volume was much smaller than that obtained for powders synthesized at 70°C. The individual hystereses were not found in synthesis performed at 70°C and the isotherm had only one elongated H3 hysteresis. There was no enhancement of the textural properties when the synthesis temperature was further increased to 100°C. The smaller specific surface area at 100°C was due to the disappearance of micropores.

The segregation suggested from the nitrogen adsorption-desorption results, if true, would lead to poor/ no creation of acidity in the powders synthesized at 40°C. This was indeed the case as confirmed by IR spectra. No Brönsted peaks were observed for the powders prepared
at 40°C. Thus 70°C was the optimum synthesis temperature. At 70°C, hetero-condensation occurred and because of the molecular scale mixing, all of the introduced silicon retained in the final aluminosilicates. The lower temperature of 40°C although produced powders with higher macroporosity but did not create acid sites. The higher temperature was also discarded in further studies because it did not produce macropores.

**Effect of addition order**

Based on the above two studies, a composition of Si/Al of 4 and a temperature of 70°C was adopted to investigate the effect of addition order. SEM images in Figure 7, presents a general representation of powder particles from three synthesis approaches differing in the addition order. The percentage of particles containing macropores was smallest when TEOS was allowed to pre-hydrolyze before TBOA was added (Table 1). On the other hand most of the particles were found to contain macropores when TBOA was introduced first. Similar to premixed alkoxides, EDS dot maps of aluminosilicate powders from pre-hydrolyzed TEOS revealed a homogeneity in mixing throughout the sample with elemental ratio in the final powder very close to the starting ratio (4.12 as compared to 4). However, when TBOA was introduced first, the final aluminosilicates had non-uniform distribution with most mapped particles having an approximate Si/Al elemental ratio 1.5 suggesting a lack of incorporation of Si. The hydrolysis and condensation of silicon alkoxide lagged behind because of its lower reactivity even though it was added immediately after. This process is very similar to pure alumina and a large number of particles with macroporosity similar in appearance to pure alumina were obtained. For the case where TEOS was allowed to hydrolyze first; the addition of aluminum alkoxide to the hydrolyzed species of silicon presented favorable
Fig. 7 SEM images of hierarchical porous aluminosilicate materials obtained from synthesis techniques differing in addition order of alkoxides: (a) premixed, (b) TEOS first, and (c) TBOA first.
conditions for hetero-bond formation but unfavorable conditions for the pattern formation, resulting in poor macrostructure in the final aluminosilicates.

The nitrogen adsorption-desorption isotherms for above three syntheses are compared in Figure 8. The isotherm for the sample prepared by introducing TEOS first was similar to that prepared using premixed alkoxides, only with a smaller H3 hysteresis. An elongated H2 hysteresis indicating large nitrogen uptake was obtained for samples produced by introducing the TBOA first; the corresponding pore size distribution was centered at 10 nm. All three cases were distinct from pure alumina providing evidence of some level of inter-component mixing.

![Fig. 8](image)

**Fig. 8** Nitrogen adsorption-desorption isotherms and corresponding BJH pore size distribution plots of hierarchical porous aluminosilicates prepared from techniques differing in addition order of alkoxides.
Providing slow reacting TEOS a head start by allowing it to hydrolyze before introducing faster reacting aluminum alkoxide matches the reactivity resulting in a better inter-component mixing as seen by the presence of strong Brönsted peak in IR spectra (Figure 9).

![IR spectra of pyridine on aluminosilicate materials prepared from synthesis techniques differing in addition order of alkoxides.](image)

Identical Brönsted peak intensities in FTIR plots suggested comparable acidities in aluminosilicates synthesized by both premixing and silicon alkoxide first techniques. The results were confirmed quantitatively by titrations (Table 1). Very similar pKa values and acid amounts were seen in both samples. For third technique where TBOA was introduced first, peaks representing both Brönsted and Lewis acidity were present but the Brönsted peaks appeared to be of smaller intensity suggesting smaller number of acid sites. The smaller acid amount for these samples was further confirmed with titrations. The pKa value was similar to the ones in aluminosilicates obtained via other methods. Similar pKa values for samples irrespective of the synthesis route indicate similar acid strengths and suggest identical nature of acid sites in all solid acids. The smaller Brönsted acidity could be
attributed to the less reactive silicon alkoxide lagging behind when introduced after TBOA which resulted in homo-condensation rather than hetero-condensation. This was also evident from EDS results which revealed incomplete retention of silicon in final aluminosilicate powders which would in turn imply formation of a fewer number of inter-component bonds.

Thus premixed alkoxide resulted in highest Brönsted acid amount while maintaining a good hierarchical structure. Prehydrolyzing silicon alkoxides produced acidity comparable to premixed alkoxides but with a lower extent of macroporosity. Aluminosilicates obtained by adding aluminum alkoxide first resulted in highly macroporous materials but possessed lower amount of acid sites.

**Effect of pH**

**Premixed alkoxides & TBOA first**

To investigate the effect of pH, the syntheses were performed at pH values of 3, 7 and 11.5. These values were selected based on the results from pure alumina where a pH value less than 2 resulted in the formation of gel because of slow condensation process in highly acidic medium while alkaline pH values, especially higher values such as pH 13, led to a decrease in the macroporosity. The structural as well as acidic properties in final aluminosilicates synthesized at initial pH 2 were very similar to those synthesized at pH 3. Thus pH 3 was selected as the lower limit. Although acidic and neutral medium is better, a pH value of 11.5 still produced high percentage of particles with macropores. Thus the pH value of 11.5 was chosen to be the upper limit in current study.
The influence of starting pH on the formation of macropores in aluminosilicates obtained by introducing TBOA first was not apparent since all syntheses resulted in powders with large number of macroporous particles. For samples obtained with premixed alkoxides, macroporosity increased with an increase in pH. This observation is not consistent with pure alumina. The explanation can be provided in terms of the influence of pH on the hydrolytic-condensation chemistry of mixed alkoxide system. A higher pH enhances the condensation, thereby consuming the hydrolyzed species of aluminum as soon as they are produced and not allowing them enough time to form hetero-bonds with hydrolyzed silicon alkoxide. Thus, a faster homo-condensation of structure forming component results in increased macroporosity at higher pH values. This segregation at a pH value of 11.5 was evident in EDS analysis where sample obtained by introducing aluminum alkoxide first resulted in a non-homogeneous distribution. The elemental compositions varied from a Si/Al ratio of 23 (silica rich) to 0.7 (alumina rich) with most particles having the compositional ratio of around 1.5. FTIR spectra, shown in Figure 10 further confirm the results where acidity in the samples prepared at alkaline values of pH was significantly smaller.

The results are consistent with $^{27}$Al NMR study performed by Leonard and Su which revealed that a neutral or alkaline medium did not favor the incorporation of Al within Si framework, while acidic medium promotes the incorporation as evident by dominant tetrahedral Al species. This segregation of the components at higher pH also explains the formation of crystalline boehmte domains observed by the authors which were not detected under acidic conditions.
For aluminosilicates synthesized using premixed alkoxides, the nitrogen adsorption-desorption isotherms appeared similar for all three syntheses with a type IV isotherm and H3 hysteresis. The SA decreased from 360 m$^2$/g to 270 m$^2$/g as the pH increased from 3 to 11.5. This decrease was mostly due to no contribution from micropores at higher pH values. Similar trend was observed for powders obtained from TBOA first where the BET SA decreased from 560 m$^2$/g to 380 m$^2$/g as the pH increased from 3 to 11.5. Thus to summarize the effect of pH, hierarchical structure was obtained for all pH values studied. Alkaline value of pH promoted the formation of macropores but resulted in decreased amount of acidity due to segregation of the components in mixed oxide aluminosilicate.

**TEOS allowed to prehydrolyze first**

The values of pH in the two steps were chosen based on the sol-gel chemistry of silica$^{31}$ and pure alumina results. Iso-electric point of silica is around 1.5 - 2. The rate of acid catalyzed hydrolysis of TEOS is higher for lower values of pH and is slowest at neutral pH.
The condensation rate on the other hand, is maximum at pH 7 and minimum at iso-electric point. For aluminosilicates prepared by introducing silicon alkoxide first, a very acidic pH of 1.5 was chosen to favor the hydrolysis of silicon alkoxide and also to prevent the condensation of hydrolyzed species. After prehydrolysis, the pH was adjusted to neutral value before the addition of aluminum alkoxide to enhance the condensation reaction. Thus the faster reacting aluminum alkoxide finds enough opportunity to form hetero-bond with the hydrolyzed species of silica. As mentioned earlier, this technique did create strong Brönsted acidity in final powders but produced poor macroporous pattern. The influence of pH was then studied by performing the entire synthesis at pH 3. A similar structure but lower acidity was observed in final materials. The lower acidity can be due to fewer hetero-bonds as a result of homo-condensation between hydrolyzed silicon species prior to addition of TBOA at higher pH value of 3.

Catalytic activity

High activity can be associated with high density of active sites, thus to characterize Brönsted acidity in the materials further, synthesized aluminosilicates were used for acid catalyzed esterification reaction of palmitic acid with methanol. Conversions of palmitic acid in the initial linear rate regime were evaluated as a measure of catalytic activity to compare different catalysts (Figure 11). The activation energies were calculated by performing the reactions at different temperatures and were found to be consistent with the value 48 kJ/mol obtained for homogeneous catalyst H$_2$SO$_4$. Similar activation energy of esterification of palmitic acid with alcohol has been reported. This suggests involvement of a similar mechanism of protonic species catalyzing the reaction. The activity results were
consistent with other characterization results where aluminosilicate catalyst obtained from premixed alkoxides or by hydrolyzing TEOS first resulted in a higher conversion than the catalysts prepared when TBOA was introduced first.

![Graph showing catalytic results for palmitic acid conversion at 140°C.](image)

**Fig. 11** Catalytic results for palmitic acid conversion at 140°C.

### Conclusions

Catalytically active hierarchically structured aluminosilicates from spontaneous self-assembly without the aid of any templating agents were successfully synthesized and characterized. The synthesis parameters studied were initial composition, addition order of the alkoxides, reaction temperature and starting solution pH. A Si/Al atomic ratio of 4, acidic pH and synthesis temperature of 70°C made the best choice for obtaining the hierarchical structures with maximum acidity. A good percentage of particles in final powders from premixed alkoxides were macroporous whereas the macroporosity in powders obtained by prehydrolyzing TEOS before the addition of TBOA was poor. Both these methods produced best acidity in final aluminosilicates. Introducing TBOA first provided
best hierarchical structure with highest extent of macroporosity but with lower acidity in final powders. The synthesized materials were found to be catalytically active in acid catalyzed esterification reaction of palmitic acid with methanol.

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Chapter 5. General Conclusions and Future Direction

General Conclusions

Hierarchically structured meso-/macroporous alumina, titania and zirconia materials were synthesized from a spontaneous self-assembly in aqueous solution. The study of these porous structures was performed separately at individual pore scales. The results illustrated that the tunable pore sizes in materials resulting from a spontaneous self-assembly process can be obtained by regulating the reaction chemistry and the nanoparticle aggregation and growth process. A deeper understanding and higher level of control of the porous properties was demonstrated, which is crucial for emerging applications of these materials.

The macropore study provided an exhaustive set of data for these materials synthesized by a common technique under similar conditions. A comparative analysis of alumina, titania and zirconia, which are known to produce these structural patterns because of the high reactivity of their chemical precursors, was possible due to the different characteristic chemistries of their corresponding alkoxides. The analysis provided insights into the formation of the macroporous structure. The results indicated that it is the relative contribution of hydrolysis and condensation reactions that dictates the formation of macropores in the resultant powders and that these processes cannot be viewed independently. It was observed that an optimum balance of these reactions is required for maximum macroporosity, which was identified for each material. Due to lower reactivity of aluminum alkoxides, enhancement of hydrolysis rates in acidic medium (pH 3) resulted in maximum macroporosity. An alkaline pH value of 11.5 was required by titanium alkoxides.
to increase the contribution of condensation reaction relative to rapid hydrolysis to create macroporous powders. Most reactive zirconium alkoxides required even higher alkaline conditions of pH 13.5 to arrive at the proper balance, which produced highly macroporous zirconia powders. It was also demonstrated that by means of sol-gel parameters such as the central metal atom, type of alkoxide and pH of the solution, the size of macropores can be tuned. Thus, the study not only unified and explained the existing data in the literature but also provided essential guidelines for the choice of materials and synthesis conditions for future studies and development these materials for specific applications.

The freshly prepared samples after spontaneous self-assembly were amorphous in nature, a property that can limit their applications. Moreover, for titania materials, the conditions that resulted in maximum macroporosity proved to be detrimental for mesostructure. In zirconia materials, freshly prepared samples were essentially purely macroporous irrespective of the synthesis conditions and starting materials. Thus, in order to obtain hierarchical materials with high surface area and crystalline walls, the influences of hydrothermal aging and thermal treatment of the materials prepared under conditions for maximum macroporosity were investigated. The results indicated that such materials can be synthesized for all the three materials; however, the required procedure depends upon the type of material. For alumina materials, there was a trade-off associated with aging. Aged samples, after calcination, resulted in final γ-alumina with higher crystallinity. However, the macroporosity was deteriorated by dissolution-reprecipitation in solution during aging. Macro-structure was fully preserved when freshly prepared samples were directly subjected to calcination, but the resultant materials had lower crystallinity.
For titania materials, anatase phase was formed after hydrothermal treatment. Aged samples also contained well-defined mesopores with larger pore sizes. While the mesostructure in freshly prepared samples collapsed during calcination, the structure was more stable after aging due to a strengthened network. Macropore structure was thermally and hydrothermally very stable. A cation effect was observed by using different types of bases to adjust the starting pH of the solution, which was found to greatly influence the structure at both meso- and macropore scales. Use of ammonium hydroxide required more severe hydrothermal conditions, but produced powders with better structure. The surface area of freshly prepared zirconia materials increased tremendously after hydrothermal treatment. Aged samples were amorphous. Calcination at 500°C resulted in the formation of tetragonal phase. The crystallinity was lower when samples were aged prior to calcination. Although the mesostructure that was formed during aging collapsed partially after calcinations, the macropore structure was thermally and hydrothermally stable.

In the last part of the project, using the insights from sol-gel chemistry and the previous synthesis experience from the macropore and mesopore studies, catalytically active hierarchical porous aluminosilicate materials were synthesized via spontaneous self-assembly and characterized for their structural and acidic properties. The synthesis parameters studied were: initial solution composition, addition order of the alkoxides, reaction temperature and starting solution pH. The results indicated that not one particular parameter set could be identified to provide both best structure and maximum acidity; a compromise between the two was essential. Introducing aluminum alkoxide first produced the best hierarchical structure with the highest extent of macroporosity but resulted in lower acidity of the final
powders. Premixing alkoxides or introducing the silicon alkoxide first produced maximum acidity but the macroporous structure was inferior as compared to those obtained by introducing the aluminum alkoxide first. Final powders from premixed alkoxides displayed a good combination of both structural and acidic properties. The macroporosity in powders obtained by prehydrolyzing the silicon alkoxide before the addition of the aluminum alkoxide was poor. Irrespective of the addition order, a Si/Al atomic ratio of 4, acidic pH and synthesis temperature of 70°C made the best choice for obtaining the hierarchical structures with maximum acidity. The synthesized materials were found to be catalytically active in acid catalyzed esterification reaction of palmitic acid with methanol. The catalytic activity of the hierarchical aluminosilicate demonstrated the successful application of knowledge gained from the mesopore and macropore studies in synthesizing active materials with hierarchical nanoporous structure.

**Future Direction**

The current work was critical in providing a deeper understanding of the structure formation as well as in demonstrating the ways to independently manipulate and control the porous structure at individual length scale. The understanding of the formation of macropores, however, still remains limited and there is a great desire to understand the formation mechanism. Insights can be obtained from an analogy with the ordered macroporous structure formed in porous anodic alumina (PAA), a system that has been studied in much greater detail. PAA is produced by electrochemical oxidation of aluminum in acidic solution. On application of electric current, aluminum in acidic solution serve as
anode (positive electrode). $\text{O}^{2-}$ and $\text{Al}^{3+}$ ions are produced as a result of the interfacial reactions as shown in Fig. 1, which migrate in the electric field and combine to form an oxide barrier film. When this barrier layer grows to a certain thickness, scalloped depressions are formed at the metal-film interface. Pore growth then occurs by the accumulation of oxide in the pore walls and aluminum metal is consumed in the process. A representative SEM image of ordered porous structure in anodic alumina is shown in Fig. 2.\(^1\)

**Fig. 1** Pore formation and growth in anodic alumina

Recently, Houser and Hebert modeled the steady state growth of porous anodic alumina films.\(^2,3\) They demonstrated that the oxide flow is driven by stress gradients as well as electric field. The flow is produced by high deposition rate of $\text{O}^{2-}$ ions at the pore bottom, and is driven by locally elevated compressive stress near the film-solution interface (Fig. 3).

**Fig. 2** Porous Anodic Alumina (PAA) \(^1\)
The authors suggested that the possible source for the generation of stress was the adsorption of acid anions, such as sulfate groups, on the surface Al-OH$_2^+$ sites.$^4$ Such ligand exchange between SO$_4^{2-}$ and –OH$_2^+$ has been demonstrated by quantum chemical calculations.$^5$ The adsorption of these anions at film-solution interface of pore base blocks the film growth, causing O$_2^-$ ions to migrate into the oxide and combine with interstitial Al$_3^{3+}$ to form new oxide in the relatively open areas within the amorphous film. This would result in the compressive interfacial stress which is relieved by Newtonian viscous flow of the oxide into the more stationary pore walls.

A similar stress driven oxide flow could be responsible for the macropore formation in spontaneous self-assembly process. An oxide film is formed as soon as the immiscible droplets come in contact with water (Fig. 4). This outer shell is clearly visible under SEM as shown in Fig. 10 (Pg. 48) in Chapter 2. This oxide film prevents further hydrolysis and condensation reactions and the water must diffuse in through the semi-permeable oxide film to come and contact with the shell-encased liquid alkoxide for further reaction to proceed.
When the oxide layer reaches a certain thickness, scalloped depressions are formed at the alkoxide-film interface and the shortest path for the unreacted alkoxide to contact the water will be at the pore base. However, the process is possibly diffusion limited due to the rapid rates of hydrolysis and condensation as compared to the rate of diffusion of water through the semi-permeable shell, which prevents the water to reach the alkoxide-film interface at the pore base. The alkoxide and water meet inside the oxide layer near the pore base and as a result of hydrolysis-condensation reaction, new oxide is formed in the open areas of amorphous film (Fig. 4). This results in the generation of compressive stress and to relieve the stress, the oxide flows from the pore base into the pore walls. This results in the pore growth and the process continues until the entire alkoxide is consumed.

![Diagram](image)

**Fig. 4** Macropore formation via spontaneous self-assembly in aqueous solution

The modeling of such a system requires estimates of hydrolysis and condensation rates which are very difficult to obtain for the rapid spontaneous self-assembly process. Using FTIR and SAXS, reaction times of 80 milliseconds have been investigated for the controlled hydrolysis of zirconium and titanium alkoxides in ethanol. However, no
quantitative information on the reaction rates could be obtained because of the complexity of
the hydrolysis-condensation reactions. In the absence of such critical data, modeling of the
pore growth in spontaneous self assembly remains a challenge. However, an analogy with
PAA offers a reasonable starting point. Based on this analogy, other alternative approaches
can be explored. For instance, the relationship between the size of hydrolysis-condensation
products and the generation of compressive stress can possibly provide evidence of the oxide
flow. A critical size could be important for the generation of stress; smaller sized products
would be incapable of generating the stress whereas the transport becomes less feasible for
relatively larger hydrolysis products.

References

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