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CONTROLLED CERAMIC POROSITY AND MEMBRANE FABRICATION
VIA ALUMOXANE NANOPARTICLES

by

CHRISTOPHER D. JONES

A THESIS SUBMITTED
IN PARTIAL FULFILLMENT OF THE
REQUIREMENTS FOR THE DEGREE
DOCTOR OF PHILOSOPHY

APPROVED, THESIS COMMITTEE

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ABSTRACT

Controlled Ceramic Porosity and Membrane Fabrication
via Alumoxane Nanoparticles

by

Christopher D. Jones

Carboxylate-alumoxanes, \([Al(O)_x(OH)_y(O_2CR)_z]_n\), are organic substituted alumina nano-particles synthesized from boehmite in aqueous solution which are an inexpensive and environmentally-benign precursor for the fabrication of aluminum based ceramic bodies. The carboxylate-ligand on the alumoxane determines the morphology and the porosity of the derived alumina. Investigations of A-, MA-, MEA-, and MEEA-alumoxanes were undertaken to determine the effects of these organic peripheries on the properties of the alumina at different sintering temperatures including the morphology, surface area, pore volume, pore size, pore size distribution, and crystal phase. The effects of physically or chemically mixing different carboxylate-alumoxanes were also investigated.

The alumina derived from the thermolysis of the carboxylate-alumoxanes exhibits small pore diameters and narrow pore size distributions that are desirable for use in ceramic ultrafiltration membranes. In addition, it is possible to form alumina membranes with a range of pore sizes and porosity by changing the organic periphery. This lead to investigating the ability to produce asymmetric alumina filters with characteristics that at the lower end of the ultrafiltration range. The flux, permeability, molecular weight cut-off, roughness, and wettability of the asymmetric alumina membranes derived from carboxylate-alumoxanes are determined. Comparisons of these filters are made with commercially available filters.
The ability to dope carboxylate-alumoxanes via a transmetallation reaction followed by thermolysis has previously shown to result in catalytically active alumina based materials. This lead to investigations into forming catalytically active membranes. Dip-coating aqueous solutions of the doped carboxylate-alumoxanes onto porous alumina supports, followed by thermolysis, resulted in the formation of doped-alumina asymmetric filters. In addition, a novel method to form surface-modified carboxylate-alumoxanes and their application as catalytic materials was determined.
Show me a man who lives alone and has a perpetually clean kitchen, and 8 times out of 9
I'll show you a man with detestable spiritual qualities.

Charles Bukowski
Acknowledgements

When I look back at my time here at Rice University, there are many people to whom I will be forever greatful. First, I would like to thank my parents, Don and Joanne, for always supporting and encouraging me in all my pursuits in life. It was they who first gave me a chemistry set at the age of nine and allowed me to conjure up great odors in the house while trying to determine what would happen if I burnt sulfur. This influence continued through my educational endeavors by having my father as a chemistry teacher in high school. He is indeed a great teacher. My brother, David, and sisters, Angela and Melissa, have also had a great influence on my life and I am very proud of their own accomplishments.

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I never really thought that lab work could be so much fun, but as it turns out, it is if you are surrounded by friends. The Barron research group, past and present, made it possible to wake up and actually look forward to going into lab. Thanks for all the great insights, ideas, shoulder tapping, breaks, BBQ, and conferences. It will be a time that I will never forget.

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was very enjoyable working for a person who makes his students lives his top priority, and I consider him not only a great person to work for, but also as a friend. There have been so many great times, it is hard to mention them all, but I think that Spectra (finally! 10-0, 8:45 p.m., April 24th, 2000) and sitting on a balcony in Florence drinking grappa soaking in the wonderful view must be at the top of the list. Thanks for everything Andy.
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<tr>
<td>A-A</td>
<td>acetic-alumoxane</td>
</tr>
<tr>
<td>A-H</td>
<td>acetic acid</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscopy</td>
</tr>
<tr>
<td>$a_g$</td>
<td>average radius of gyration of a geometric chain</td>
</tr>
<tr>
<td>$a_r$</td>
<td>average radius of gyration of a real chain</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>avg.</td>
<td>average</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer, Emmett, and Teller method</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett, Joyner and Holenda method</td>
</tr>
<tr>
<td>°C</td>
<td>degrees centigrade</td>
</tr>
<tr>
<td>cf</td>
<td>solute concentration in the filtrate</td>
</tr>
<tr>
<td>ct</td>
<td>solute concentration in the test solution</td>
</tr>
<tr>
<td>ca</td>
<td>approximately</td>
</tr>
<tr>
<td>ccp</td>
<td>cubic close-packed</td>
</tr>
<tr>
<td>CMR</td>
<td>catalytic membrane reactor</td>
</tr>
<tr>
<td>CVD</td>
<td>chemical vapor deposition</td>
</tr>
<tr>
<td>CY</td>
<td>ceramic yield</td>
</tr>
<tr>
<td>Da</td>
<td>Daltons</td>
</tr>
<tr>
<td>$d_s$</td>
<td>solute diameter</td>
</tr>
<tr>
<td>$\Delta$</td>
<td>change, or difference</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>surface porosity</td>
</tr>
<tr>
<td>Eq.</td>
<td>equation</td>
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<tr>
<td>EDX</td>
<td>energy dispersive X-ray spectrometry</td>
</tr>
<tr>
<td>FBR</td>
<td>fixed bed reactor</td>
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<td>grams</td>
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GC  gas chromatography
GPC  gel permeation chromatography
hcp  hexagonal close-packed
HPLC  high pressure liquid chromatography
IMRCF  inert membrane reactor with catalyst on the feed side
IR  infrared spectroscopy
J  flux
JCPDS  Joint Committee on Powder Diffraction Standards
k  permeability
l  thickness of a membrane
L  liters
MA-A  methoxyacetic-alumoxane
MA-H  methoxyacetic acid
MEA-A  methoxyethoxyacetic-alumoxane
MEA-H  methoxyethoxyacetic acid
MEEA-A  methoxyethoxyethoxyacetic-alumoxane
MEEA-H  methoxyethoxyethoxyacetic acid
μm  micron, 10⁻⁶ m
mL  milliliters, 10⁻³ L
mm  millimeter, 10⁻³ m
min  minutes
mol  mole
M_w  molecular weight
MWCO  molecular weight cut-off
nm  nanometer, 10⁻⁹ m
NMR  nuclear magnetic resonance spectroscopy
P  pressure
PEG  polyethylene glycol
ppm  parts per million
PCS  photon correlation spectroscopy
r  radius
rsolute  solute radius
r_pore  pore radius
%R  rejection coefficient
R  alkyl
R_m  resistance of a membrane
rpm  revolutions per minute
SHOP  Shell higher olefin process
SEM  secondary electron microscopy
µ  viscosity
τ  tortuosity
T_α  α-alumina phase transformation temperature
TG  thermogravimetric analysis
TOC  total organic carbon
XRD  powder X-ray diffraction

agglomerate  Clustering of small particles through electrostatic attraction to form larger particles
alumina  Al₂O₃ in any phase
alumoxane  An oligomeric or polymeric material consisting of an Al-O backbone and containing various pendant groups
amorphous  Lacking in crystallinity
boehmite  γ-alumina, AlO(OH), a naturally occurring mineral
ceramic A class of inorganic, non-metallic material which is subjected to temperatures in excess of 500 °C for the purposes of manufacture or use
contact angle The interior angle formed between the edge of a solvent “bubble” and the surface on which it rests. Angles are measured either advancing or receding; low numbers indicate hydrophilic surfaces (“wetting”) while high numbers represent hydrophobic surfaces (“non-wetting”)
crossflow filtration filtration utilizing tangential flow of the permeate
dead-end filtration filtration when the permeate is forced perpendicular through the filter
macropores pores larger than 50 nm
mesopores pores between 2 and 50 nm
micropores pores less than 2 nm
microfiltration filtration pertaining to macropores
morphology the characteristic shape or contour of a surface
nanofiltration filtration pertaining to micropores
pore a small opening, void, interstice, or also channel within a consolidated solid mass or agglomerate
pore size the characteristic or equivalent dimensions or range of same (e.g., diameter) of a pore or family of pores in a material
pore size distribution the specific pore volume of all measurable pores in each of a set of equivalent diameter increments from the smallest to the largest present in a material
pore volume the porosity of a solid
pyrolysis decomposition of a material by heat
reverse osmosis filtration due to osmonic pressure gradient through pores < 1 nm
seeded growth  particle size growth that occurs as a result of small particles
  serving as nucleation sites rather than through the simple
  agglomeration of particles
sintering  general term for densification of a powder compact or solid by
  heating to produce crystallinity
sol-gel  solution-gelation
surface area  the area, per unit weight of a granular or powdered or formed
  porous solid, of all external plus internal surfaces that are
  accessible to a penetrating gas
thermolysis  heating or dissipation of heat
transition aluminas  a family of metastable crystalline aluminas, including γ, δ, and θ
  phases, containing minor but detectable OH⁻ as well as O⁻² ions.
topotactic  change in crystal structure without changes in morphology
ultrafiltration  filtration pertaining to mesopores
vermicular  worm-like
Introduction

Aluminum is the most abundant metal in the earth's crust (ca. 8%)\(^1,2\) and is a major constituent of many terrestrial minerals including feldspars, micas, spinels, and garnets. Although it derives its name from alum, K[Al(SO\(_4\)]_{2}.12(H\(_2\)O), which was known throughout the world in ancient times, it was not until the isolation of aluminum in the late eighteenth century by the Danish scientist H. C. Ørsted that research into the chemistry of aluminum began in earnest. Initially, metallic aluminum was isolated by the reduction of aluminum trichloride with potassium or sodium; however, with the advent of inexpensive electric power in the late 1800's, it became economically feasible to extract the metal via the electrolysis of alumina (Al\(_2\)O\(_3\)) dissolved in cryolite, Na\(_3\)AlF\(_6\), (the Hall-Heroult process).\(^3\)

Production of aluminum today is primarily prepared by the Bayer process, in which the mineral bauxite (named for Les Baux, France, where it was first discovered by P. Berthier in 1821) is dissolved in aqueous hydroxides, and the solution is filtered and treated with CO\(_2\) to precipitate alumina. This is followed by electrolysis of the alumina dissolved in Na\(_3\)AlF\(_6\) at 940 – 980 °C, yielding aluminum metal. As a general rule, 4 tons of bauxite are required to produce 2 tons of alumina, which, in turn, provide 1 ton of aluminum metal. It follows that the primary commercial considerations are availability of bauxite and, more importantly, inexpensive electric power. The largest producers of aluminum are the United States, Japan, Canada, and the former Soviet Union.\(^1\)

The aluminum compounds of greatest importance are the oxides and hydroxides, due to a combination of excellent physical and chemical properties and the relatively low cost of raw materials.\(^1,4\) With a combined annual production of over 30 million tons, applications include abrasives, refractories, catalysts, catalyst supports, ion exchangers, and a diverse range of advanced, technical and fine ceramic materials.\(^5\) The principal structural types of aluminum oxides and hydroxides are corundum (\(\alpha\)-Al\(_2\)O\(_3\)), diasporo (\(\alpha\)-AlO(OH)), bayerite (\(\alpha\)-Al(OH)\(_3\)), boehmite (\(\gamma\)-AlO(OH)), and gibbsite (\(\gamma\)-Al(OH)\(_3\)).\(^1,4,5\)
In addition, numerous transitional phases and structural modifications have been characterized during partial dehydration.\textsuperscript{4,5,6}

The many crystalline forms of aluminum oxides and hydroxides are linked by complex structural relationships. For example, the mineral bauxite has the formula $\text{Al}_x(\text{OH})_{3-2x}$ ($0 < x < 1$) and is a mixture of $\alpha$-$\text{Al}_2\text{O}_3$, $\gamma$-$\text{Al(OH)}_3$, and $\gamma$-$\text{AlO(OH)}$.\textsuperscript{1} Diaspore, $\alpha$-$\text{AlO(OH)}$, is a polymorph of boehmite, has an ideal structure comprising a hexagonal close-packed (hcp) array of oxygen atoms with continuous chains of edge-shared octahedra stacked in layers and further interconnected by hydrogen bonds, with aluminum atoms in certain octahedrally coordinated sites.\textsuperscript{4} The structure of boehmite differs in that it is not close-packed overall, but within each layer of $\text{AlO}_6$ octahedra the oxygen atoms are arranged in cubic-close packing (ccp). The structure of boehmite is shown in Figure I.1.

\textbf{Figure I.1.} The topographic structure of boehmite, $\gamma$-$\text{AlO(OH)}$, showing the continuous chains of edge-shared octahedra stacked in layers and the interconnecting hydrogen bonding (double lines).
Dehydration of boehmite and diaspore by calcination up to 450 °C yields forms of alumina which have structures related to their oxide-hydroxide precursors; i.e., boehmite produces cubic γ-alumina, while diaspore yields hexagonal α-alumina. Upon further heating, γ-alumina converts to the α-alumina hcp structure through other transitional aluminas. There is yet another form of alumina that exists as a protective layer on the surface of the clean aluminum metal. This thin, tough, transparent oxide skin is rapidly self-repairing because of its large heat of formation (Eq. I.1) and is the reason for much of the usefulness of aluminum.

\[
4 \text{Al} + 3 \text{O}_2 \rightarrow 2 \text{Al}_2\text{O}_3 \quad \Delta H = 3351.4 \text{ kJ.mol}^{-1}
\]  

(I.1)

In common with the majority of oxide ceramics, two primary synthetic processes are employed for the preparation of alumina and doped alumina materials: (a) the traditional ceramic powder approach and (b) the solution-gelation, or "sol-gel" process.

Traditional ceramic powder processing involves physically mixing separate oxides or oxide precursors (such as oxalates and carbonates), sintering at high temperatures for extended times, grinding, and resintering. This method consists of three basic steps generally referred to as powder-processing, shape-forming, and densification, often with a final mechanical finishing step. The powders are obtained by extraction from naturally occurring minerals, recovered as by-products of mining operations, or chemically synthesized. These powders are mixed, blended, granulated, and crushed. Crushing is generally done in a ball mill and may be wet or dry. The ground particles are combined with a variety of additives, including dopants, binders, plasticizers, deflocculents, lubricants (e.g., for mold release) and wetting agents. The component chemicals are mixed to a slurry, cast, then dried and fired.

Whereas the traditional ceramic powder process is used primarily for the manufacture of dense parts, the solution-gelation (sol-gel) process has been applied
primarily for the production of ceramic coatings and porous solids. Sol-gel involves a four stage process: dispersion, gelation, drying, and firing. A stable liquid dispersion or sol of the colloidal ceramic precursor is initially formed in a solvent with appropriate additives. By changing the concentration (aging) or pH, the dispersion is "polymerized" to form a solid phase or gel. The excess liquid is removed from this gel by drying and firing at higher temperatures produces the final ceramic. The typical sol-gel route to aluminum oxides employs aluminum hydroxide or hydroxide-based material as the solid phase, the liquid phase being water and/or an organic solvent. A common problem with this approach is that the strong interactions of the freshly precipitated alumina gels with ions from the precursor solutions makes it difficult to prepare pure materials. To avoid this complication, gels are also prepared from the hydrolysis of aluminum alkoxides, Al(OR)₃ (i.e., Eq. 1.2).

\[
\begin{align*}
\text{H}_2\text{O}/\text{H}^+ & \quad \Delta \\
\text{Al(OR)}_3 & \rightarrow \text{Al-gel} \rightarrow \text{Al}_2\text{O}_3 \\
\end{align*}
\] (I.2)

Although the exact composition of the gel in commercial systems is ordinarily proprietary, however, a typical composition will include an aluminum compound, a mineral acid, and a complexing agent, e.g., Table I.1.

Table I.1. Typical composition of an alumina sol-gel for green bodies.

<table>
<thead>
<tr>
<th>Function</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boehmite Precursor</td>
<td>ASB [aluminum sec-butoxide, Al(OCH₉₉)₃]</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>HNO₃ 0.07 mole/mole ASB</td>
</tr>
<tr>
<td>Complexing agent</td>
<td>glycerol ca. 10 wt.%</td>
</tr>
</tbody>
</table>
The sol-gels formed during the hydrolysis of aluminum compounds belong to a general class of inorganic-organic hybrid compounds known as alumoxanes. First reported in 1958 by Andrianov, and were proposed to consist of linear (I) or cyclic (II) chains (i.e., analogous to that of poly-siloxanes). Research by the Barron group has since redefined the structural view of alumoxanes, revealing that they are not chains but three-dimensional cage compounds. For example, siloxy-alumoxanes, \([\text{Al(O)(OH)}_x\text{(OSiR}_3\text{)}_{1-x}]_n\), consist of an aluminum-oxygen core structure (III) analogous to that found in boehmite, \([\text{Al(O)(OH)}]_n\), with a siloxide substituted periphery.

![Diagram](image)

The hydrolysis of aluminum alkoxides can be considered a “bottom-up” synthetic approach in that it consists of reacting small inorganic molecules to form larger oligomeric and polymeric materials (for example, see Eq. I.2). This route has met with varied success due to the difficulties in controlling the reaction conditions and therefore the solubility, stoichiometries, and processability or the resulting gel. Based on investigations of the boehmite-like core structure of hydrolytically stable alumoxanes, the following question was posed: Can alumoxanes be prepared directly from the mineral boehmite? Such a “top-down” approach represented a departure from the traditional synthetic methodologies.

Previous work in the Barron research group had shown that the “organic” unit itself in the siloxy-alumoxanes contained aluminum, i.e., IV. In order to similarly prepare an alumoxane with a siloxide substituted periphery, the anionic moiety \([\text{Al(OH)}_2\text{(OSiR}_3\text{)}_2]\)
would be required as a bridging group; adding this unit clearly presented a significant synthetic challenge. However, the carboxylate anion, \([\text{RCO}_2]^−\), is an isoelectronic and isostructural analog of the organic periphery found in the previously reported siloxy-alumoxanes, (IV and V).

Following this rational, a "top-down" approach was developed based upon the reaction of boehmite, \([\text{Al(O)(OH)}]_n\), with carboxylic acids (Eq. I.3).\(^{21}\) This reaction resulted in the formation of carboxylate-alumoxane nanoparticles, \([\text{Al(O)}_x\text{OH}_y\text{(O}_2\text{CR})_z]_n\), (V).

\[
\text{HO}_2\text{CR} \quad \xrightarrow{\text{[Al(O)(OH)]}_n} \quad [\text{Al(O)}_x\text{OH}_y\text{(O}_2\text{CR})_z]_n \\
(\text{I.3})
\]

It was determined that the solubility of these carboxylate-alumoxanes are dependent on the identity of the carboxylic acid. It was also found that water soluble alumoxanes may be prepared by the use of polyether substituted ligands, leading to hope of an environmentally benign precursor for alumina ceramics. However, as reported, these carboxylate-alumoxanes were prepared in xylene thereby nullifying their environmentally benign nature. Research was undertaken to investigate methods for aqueous processing of the carboxylate-alumoxanes.

Pseudoboehmite and the appropriate carboxylic acid were reacted in water to yield the respective carboxylate-alumoxane, see Figure I.2.\(^{22}\) The carboxylate-alumoxanes prepared in aqueous solution are spectroscopically similar to their analogs prepared in
xylene: the solution $^{27}$Al NMR spectra is indicative of aluminum in an octahedral AlO$_6$ coordination environment and the IR spectra is consistent with a bridging mode of coordination of the carboxylate to the boehmite-like core.

\[
\text{RCO}_2\text{H} \rightarrow \text{H}_2\text{O}
\]

**Figure I.2.** Pictorial representation of the reaction with boehmite and carboxylic acids to form carboxylate-aluminoxanes. The shaded triangles represent a side view of the aluminum-oxygen fused octahedra, while the carboxylate groups are represented by a semicircle with bar.

A wide range of carboxylate aluminoxanes may be prepared using a catholic range of acids, including, methoxyethoxyethoxyacetic acid [HO$_2$CCH$_2$(OCH$_2$CH$_2$)$_2$OCH$_3$, MEEA-H], methoxyethoxyacetic acid [HO$_2$CCH$_2$OCH$_2$CH$_2$OCH$_3$, MEA-H], methoxyacetic acid [HO$_2$CCH$_2$OCH$_3$, MA-H], acetic acid [HO$_2$CCH$_3$, A-H], gluconic acid [HO$_2$(CHOH)$_4$CH$_2$OH, glu-H], para-hydroxybenzoic acid [HO$_2$CC$_6$H$_4$OH, p-HB-H], and lysine [HO$_2$CCH(NH$_2$)(CH$_2$)$_4$NH$_2$, lys-H].$^{20,21,22,23,24}$ For simplicity throughout
this discourse, the alumoxanes will be referred to by the acronym of the acid, i.e., MA-alumoxane rather than methoxyacetate-alumoxane.

Solution particle size measurements were performed in water on some carboxylate-alumoxanes by photon correlation spectroscopy (PCS), see Figure I.3.22 The particle size number average follows the order MEEA-alumoxane (67 nm) > MEA-alumoxane (50 nm) > A-alumoxane (28 nm), consistent with their formation via the cleavage of the significantly larger boehmite starting material (30 - 100 μm).

The particle size distribution follows the same order. Gel permeation chromatography (GPC) measurements in HOCH₂CF₃ for the samples of MEEA-

![Graph showing particle size distribution](image)

MEA-, and MA-alumoxane, are consistent with the PCS data. The pH dependence of each of the previously mentioned alumoxanes has been determined and shows that particle size increases with increasing pH. In all cases, the particle size increases linearly to a pH of 6 after which point the size increase become exponential. Based upon the spectroscopic characterization the carboxylate-alumoxanes are best considered to be nano-particles of aluminum oxide hydroxide (or boehmite) which are capped with carboxylate residues.

The physical properties of the carboxylate-alumoxanes are dependent on the identity of the carboxylate substituent, see Table I.2. The alumoxanes are indefinitely stable under ambient conditions and are adaptable to a wide range of processing techniques e.g., infiltration, dip-coating, spin coating, and spray-coating onto various substrates.

<table>
<thead>
<tr>
<th>Alumoxane</th>
<th>Gel point in water (g.mL(^{-1}))</th>
<th>Refractive indexes (n(_D))</th>
<th>Decomp. Temp.(^d) (°C)</th>
<th>Ceramic yield (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MEEA-alumoxane</td>
<td>0.30</td>
<td>1.5</td>
<td>142/370</td>
<td>20</td>
</tr>
<tr>
<td>MEA-alumoxane</td>
<td>0.95</td>
<td>1.5</td>
<td>160/370</td>
<td>27</td>
</tr>
<tr>
<td>MA-alumoxane</td>
<td>0.11</td>
<td>c</td>
<td>230/360</td>
<td>30</td>
</tr>
<tr>
<td>A-alumoxane</td>
<td>0.20</td>
<td>1.5</td>
<td>155/520</td>
<td>76</td>
</tr>
</tbody>
</table>


\(^b\) Defined as the mass of alumoxane required to form a solid gel in 1.0 mL of water.

\(^c\) Sample too opaque.

\(^d\) Temperatures at which alumoxane starts to decompose and at which decomposition is complete.
Thermogravimetric /differential thermal analysis (TG/DTA) of the carboxylate-alumoxanes indicates that they all decompose above 180 °C, and as may be expected, the ceramic yield is conditional on the identity of the carboxylic acid: greatest for A-alumoxane (ca. 75 %), lowest for MEEA-alumoxane (ca. 20 %), see Table I.2.

It has previously been reported that the carboxylate-alumoxanes may be used as precursors to ternary and doped alumina ceramics.25,26 A simple and rapid process has been developed that allows the formation of highly crystalline main group, lanthanide, and transition metal aluminates, including: CaAl12O19 (hibonite), Y3Al5O12 (YAG), LaAl11O18, LaAlO3, Ce2Al3O8, NdAlO3, Er6Al10O24, and Al2TiO5. Carboxylate-alumoxanes are reacted with the appropriate metal acetylacetonate complexes to form metal-doped carboxylate-alumoxanes and aluminum acetylacetonate via a facile transmetalation reaction. Thermolysis of the metal-doped carboxylate-alumoxanes, up to 1400 °C, yields the crystalline aluminates as confirmed by XRD, elemental microprobe analysis, and SEM. The synthesis of different phases (i.e., LaAl11O18 versus LaAlO3) is controlled by the stoichiometry of the transmetalation reaction. It is significant that the carboxylate-alumoxane methodology results in multicomponent aluminate materials that are obtained in shorter processing times and with higher phase purity than previously reported. This is undoubtedly due to the atomic scale mixing inherent in the alumoxane nanoparticle approach.

The synthetic methodology of carboxylate-alumoxanes would impact the release of contaminants to the environment on at least two distinct levels. First, the new synthetic methodology for producing these ceramic materials will eliminate the use of toxic solvents and reduce energy consumption (due to a lowering of the sintering temperatures), especially in the case of tape casting. With respect to the use of the carboxylate-alumoxanes as binders in green body processes, byproducts formed from the combustion of plasticizers and traditional binders will be minimized, and with regard to sol-gel synthesis, the use of mineral acids may be eliminated. Thus, the process will reduce the potential for
environmental release through the use of more environmentally benign feedstocks and an alternative synthetic procedure that will improve energy efficiency. Second, due to the very versatile nature of the process, the carboxylate-alumoxane process holds the potential for fabricating new ceramic ultrafiltration membranes.

Membrane processes can be classified according to the driving force and the physical sizes of the separated species. Driving forces include pressure, concentration, or a voltage difference across the membrane. Membranes generally fall into four categories, see Figure I.4. (1) Microfiltration membranes contain the largest pores (macropores) which are greater than 50 nm. (2) Ultrafiltration membranes contain mesopores in the range of 2 nm to 100 nm in diameter. (3) Nanofiltration membranes contain micropores that are less than 2 nm in diameter. (4) Reverse osmosis membranes contain pores less than one nanometer in diameter. As will be discussed in Chapter 1,

![Diagram showing types of filtration and related particle sizes.](image)

**Figure I.4.** Chart showing types of filtration and related particle sizes.
alumina derived from the thermolysis of carboxylate-alumoxanes exhibit pore sizes at the lower end of the ultrafiltration range.

Filtration using ceramic membranes may be performed using either dead-end or crossflow configurations (Figure I.5). In dead-end filtration, the permeate is forced perpendicular through the filter, while particles are retained. The retained particles

(a)

Figure I.5. Illustration of (a) dead-end and (b) crossflow filtration. Adapted from R. R. Bhave, Inorganic Membranes: Synthesis, Characteristics, and Applications, Van Nostrand Reinhold, New York, 1991.
eventually concentrate on the membrane surface forming a cake layer, which increases the resistance to filtration and hence, decreases flux.\textsuperscript{28} This is a major problem with dead-end filtration because the process must be stopped periodically to remove this cake layer. The crossflow filtration configuration (Figure I.5b) utilizes tangential flow to reduce caking. The feed flow brings both liquid and solid particles to the membrane surface, where they are rejected or allowed to cross to cross the membrane. These particles begin to make a thin cake layer, however, it does not build up indefinitely. The high sheer exerted by the suspension flowing tangential to the membrane surface removes the particles forming the cake layer toward the exit.\textsuperscript{28} This allows for continuous processing and thus crossflow filtration is increasingly being used for industrial applications.

An ideal ceramic membrane must be highly selective, permeable, and durable. For aqueous applications it is desirable for the ceramic to be hydrophilic to maximize flow and decrease fouling.\textsuperscript{31} The membrane selectivity is primarily dependent upon the pore-size distribution: a narrow distribution contributes to a highly selective membrane. Membrane permeability is a function of global porosity, connectivity, and pore-size distribution. Mechanical integrity is enhanced in such applications by slip-casting a relatively thin selective membrane onto a larger, durable support with large pores and high permeability, see Chapter 2.

The sol-gel technique is presently the only feasible route to making commercial alumina ultrafiltration membranes.\textsuperscript{29,30,39,40} Lennears, Keizer, and Burgraaf first developed the technique of using sol-gel processes to make alumina ultrafiltration membranes,\textsuperscript{32,33,34,35} which lead to an explosion of research in ceramic filters. These filters were made by the controlled hydrolysis of aluminum alkoxides to form alumina of the boehmite structure, based on the technique by Yoldas.\textsuperscript{12} The conventional method of forming sol-gel membranes consists of the controlled hydrolysis of aluminum sec-butoxide at 80 – 90 °C, see Figure I.6.\textsuperscript{36} Nitric acid is added to the mixture to peptize the sol particles formed. Aging is allowed to occur to allow for the formation of a stable sol, which
may take up to 48 hours at reflux temperatures. After cooling, the sol is poured into molds to slowly dry under carefully controlled conditions (i.e., temperature and humidity).

Figure I.6. Typical fabrication of an alumina membrane formed by the sol-gel process. Adapted from M. A. Anderson, M. J. Gieselmann, and Q. Xu, J. Memb. Sci., 1988, 39, 243.
Bodies formed by conventional drying are referred to as xerogel, while those dried by supercritical methods are known as aerogels. Cracking may be a problem, so drying control agents such as glycerol, formamide, or oxalic acid may be added.\(^8\)

While the sol-gel process currently used to produce commercially available ceramic membranes are suitable for producing ceramic ultrafiltration membranes, they are energy and time intensive, and there is no other method to control pore size except by thermal treatment (i.e., pore growth during sintering). In addition, the starting materials are expensive and usually require special handling methods. Thus, it is desirable to have a sol-gel style technology without the disadvantages based on nano-particle precursors to allow for small pore sizes.

Membrane technologies play an increasingly important role in pollution prevention, resource recovery, process development, water purification, and waste treatment activities.\(^{28,30,37}\) Due in large part to cost considerations, polymeric membranes dominate these applications,\(^{38}\) however, the use of polymeric membranes in separations involving aggressive materials such as many organic solvents, acids, bases, and oxidants is often limited by the tolerance of the polymeric material to extreme conditions.\(^{39}\) Ceramic membranes are noted for their excellent mechanical strength and tolerance to solvents, as well as pH, oxidation, and temperature extremes.\(^{28,40}\) In addition, the amphoteric properties of ceramic surfaces result in uniquely versatile membranes for water and wastewater treatment.

Ultrafiltration membranes can be used for a broad field of applications involving situations where species with high molecular weight need to be separated from low molecular weight species. Table 1.3 displays just a fraction of the many applications with respect to the treatment of industrial effluent, food and dairy, biotechnology, water purification, and the petroleum and specialty chemical industries.\(^{28,29,30,38,39}\) New applications for ultrafiltration membranes are emerging each year, and the industry is continually growing.
<table>
<thead>
<tr>
<th>Industry</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Treatment of industrial effluent</td>
<td>Automotive (E-coat paint recovery)</td>
</tr>
<tr>
<td></td>
<td>Oil and water separations</td>
</tr>
<tr>
<td></td>
<td>Textile, pulp and paper</td>
</tr>
<tr>
<td></td>
<td>Nuclear isotope separation</td>
</tr>
<tr>
<td>Food and dairy</td>
<td>Whey and skim milk processing</td>
</tr>
<tr>
<td></td>
<td>Cheese manufacturing</td>
</tr>
<tr>
<td></td>
<td>Recovery of proteins</td>
</tr>
<tr>
<td></td>
<td>Clarification of fruit juice</td>
</tr>
<tr>
<td></td>
<td>Meat industry</td>
</tr>
<tr>
<td>Biotechnology</td>
<td>Virus/Bacteria removal and/or concentration</td>
</tr>
<tr>
<td></td>
<td>Concentration of enzymes</td>
</tr>
<tr>
<td></td>
<td>Antibiotic recovery</td>
</tr>
<tr>
<td>Water purification</td>
<td>Desalinization of sea water</td>
</tr>
<tr>
<td></td>
<td>Electronics industry</td>
</tr>
<tr>
<td></td>
<td>Pharmaceutical industry</td>
</tr>
<tr>
<td>Petroleum and specialty chemicals</td>
<td>Recovery of catalysts</td>
</tr>
<tr>
<td></td>
<td>Catalytic membranes</td>
</tr>
<tr>
<td></td>
<td>Catalytic membrane reactors</td>
</tr>
</tbody>
</table>


As may be expected from the foregoing discussion, it is increasingly recognized that the development of novel ceramic precursors, such as carboxylate-alumoxane nanoparticles, enhances our ability to create carefully tailored compounds by designing them at the molecular level which will inevitably lead to materials with better-controlled properties. The focus of my graduate research has involved extensive preparation and characterization studies on the chemical control of porosity using carboxylate-alumoxanes as precursors for alumina. In particular, the application of carboxylate-alumoxanes as precursors to ultrafiltration membranes and filters was evaluated. These studies are considered in detail in subsequent chapters. As part of this work, carboxylate-alumoxanes as materials and related methodologies were evaluated as precursors to heterogeneous catalysts and catalytic membranes.

References


(b) P. H. Hsu, and T. F. Bates, Mineral Mag., 1964, 33, 749.


R. H. Green, S. L. Hem, J. Pharm. Sci., 1974, 63, 635.

(a) A. Adkins, J. Am. Chem. Soc. 1922, 44, 2175.


The aluminum compound was traditionally assumed to be the direct precursor to pseudo-boehmite. However, the gel is now known to consist of aluminum-oxygen macromolecular species with a boehmite-like core: alumoxanes, see A. R. Barron, Comm. Inorg. Chem., 1993, 14, 123.

The term alumoxane is commonly used to describe a species containing an oxo (O²⁻) bridge binding (at least) two aluminum atoms, i.e., Al-O-Al.


S. Pasynkiewicz, Polyhedron, 1990, 9, 429.


Chapter 1

Chemical Control of Alumina Porosity, Crystal Phase, and Morphology using Carboxylate-Alumoxanes

Introduction

Knowledge of microstructural evolution in ceramic systems is important because the chemical and thermal properties greatly affect the uses of the final product.\textsuperscript{1,2} Alumina systems (solid, CVD, and sol-gel) have been the subject of many studies due to the economic value of alumina based ceramics.\textsuperscript{1,2,3}

The phase, morphology, porosity, and crystallinity of alumina changes according to the method of preparation, chemical treatment of the precursors, particle size and shape, degree of agglomeration, and thermal treatment.\textsuperscript{4,5,6,7,8,9} The properties of the resulting alumina after thermal treatment is very crucial because of the many uses of alumina that include coatings, catalyst supports, co-catalysts, adsorbents, abrasives, thin films, composites, lenses, filters, membranes, etc.\textsuperscript{1,2}

The transformation from boehmite ($\gamma$-AlOOH) to corundum ($\alpha$-Al$_2$O$_3$) has been well characterized and is known to go through the following sequence: $\gamma$-AlOOH $\rightarrow$ $\gamma$-$\rightarrow \delta$ $\rightarrow \theta$ $\rightarrow \alpha$-Al$_2$O$_3$.\textsuperscript{1,2,5,8,9,10,11,12} The phase changes from boehmite through $\theta$-alumina are known to be topotactic (i.e., changes in crystal structure are accomplished without changes in crystalline morphology) and are known collectively as the transition aluminas.\textsuperscript{4,5,8} However, each phase does have changes in the morphology of the porosity due to changes in the microstructure. The temperatures at which these transitions occur are variable, however boehmite fired to 500, 850 and 1000 °C usually exhibit the $\gamma$-, $\delta$-, and $\theta$- alumina phases, respectively.\textsuperscript{1,2} However, the temperature at which certain phases occur greatly vary according to how the precursors were prepared.
The θ- to α-alumina phase transition occurs through nucleation and growth of the θ-alumina crystallites.1,6,7,9 The θ-alumina grows until the crystallites exceed a critical size needed for the formation of an α-alumina nucleus, and nucleation of α-alumina occurs.8,13 The critical size of the θ-alumina crystallites have been extensively investigated, however these results range widely between 50 and 1000 nm.8 Once nucleation starts, growth of α-alumina occurs rapidly until all of the θ-alumina been converted. The α-alumina phase transition also varies on the precursors used, but is usually over 1100 °C,1 although temperatures between 1000 and 1200 °C have been reported under standard conditions.5,8,11,12,14 The α-alumina phase transition temperature can be altered by the addition of certain additives. For example, because the α-alumina phase occurs by nucleation, the addition of small α-alumina seed crystals can lower the transition temperature between 100 and 200 °C.7,10,15 The addition of certain transition metals (chromium, manganese, iron, cobalt, nickel, and copper) has shown to decrease the α-alumina transition temperature, while lanthanum or other rare earths tend to increase the temperature.16,17,18,19 Finally, the addition of metal oxides has also shown to affect the growth rate in α-alumina.20

Earlier studies on the carboxylate-alumoxanes revealed that the carboxylate substituent determines the ceramic yield of the nanoparticles.21 It was also realized that pyrolysis to 500 °C results in γ-alumina. Further studies on thin sections have shown that the γ-alumina is transformed into α-alumina at higher temperatures with the carboxylate substituent having a direct effect on the final microstructure and temperature of phase conversion.22,23 However, these previous studies did not investigate the porosity, phase, or grain growth of bulk ceramics derived from carboxylate-alumoxanes, during the thermolysis and sintering to α-alumina.

As discussed above, it is desirable to know the microstructural evolution of ceramic systems. This study will investigate the phase, morphology, porosity, and crystallinity of A-, MA-, MEA-, and MEEA-alumoxane during thermolysis and sintering.
It is known that the overall ceramic microstructure is dependent on how the precursors have been chemically treated. For this reason, special attention will be given to the control of ceramic porosity by the carboxylate substituent.

**Results and Discussion**

The morphology, porosity, and crystal phase of alumina samples formed during the thermolysis and sintering of carboxylate-alumoxanes have been investigated. The physical conditions (drying method, grinding, thermal environment, etc.) were consistently maintained in order to eliminate physical processing as a variable. Scanning electron microscopy (SEM) was used to provide information about the size and shape of the microstructural constituents of the ceramic material. Porosity, surface area, pore volume, and pore size distributions were obtained using nitrogen adsorption techniques. Surface area was calculated using the BET (Brunauer, Emmett and Teller) equation and pore size distribution was determined by the BJH (Barrett, Joyner and Halenda) technique. Crystalline phase identification was determined by powder X-ray diffraction (XRD). The following discussion is divided with respect to the carboxylate-alumoxane ceramic precursor.

**A-Alumoxane.** Heating a sample of A-alumoxane to 600 °C yields a material that is composed of uniform particles approximately 10 – 50 nm in diameter, see Figure 1.1a. Continued firing through 800 °C does not change the morphology significantly, however at 900 °C the texture appears to be coarser, see Figure 1.1b. Analysis at higher magnification reveals that the particles are larger at 900 °C and more void space is present between the particles see Figure 1.2. This trend is continued through 1000 °C, however, 5 µm features are observed throughout the material upon heating to 1100 °C, see Figure 1.1c.
Figure 1.1: SEM images of A-alumoxane fired to (a) 600, (b) 900, (c) 1100, (d) 1200, (e) 1300, and (f) 1400 °C for 3 hours.
These features account for approximately 65% of the material and as may be seen from Figure 1.3, they are not evenly distributed. At higher magnification (Figure 1.4) these features appear to be crystalline material where smaller particles have sintered together causing a collapse in the small pores resulting in the formation of larger, less dense pores. The center of these features exhibits an intricate network of material that is vermicular in morphology, with no distinct grain boundaries within the crystallized area.

![SEM images](image_url)

**Figure 1.2.** SEM images of A-alumoxane fired to (a) 600 °C and (b) 900 °C for 3 hours.
There are two types of pores are visible in the SEM image shown in Figure 1.4b: small circular pores, approximately 50 nm in diameter and larger elongated pores several hundred nanometers in length. The smaller pores appear to be mostly intra-granular (where the pores are found within individual grains), while the elongated pores are a mix of intra- and inter-granular pores (where the pores are found between the grains). At the edge of these crystalline areas (Figure 1.4a), it can be observed that the boundaries between crystal zones are quite distinct. Pores near the boundary of the large crystal domains are smaller than the pores at the center. The formation of these crystalline domains probably occurs through a seed crystal first forming at the center of each area (nucleation). Crystallization then proceeds outward to form near perfect circles (growth). The nucleation and growth mechanism is known to accompany the onset of the α-alumina phase.

Further firing the A-alumoxane derived alumina to 1200 °C results in sintering of all the small individual particles, see Figure 1.1d. Crystal grains are now clearly evident with sizes between 0.5 and 2 µm. The resulting material has two distinct morphologies: high pore density and low pore density.
Figure 1.4. SEM images of A-alumoxane fired to 1100 °C for 3 hours showing grain growth at edge (a) and center (b).

The areas with high pore densities contain mainly elongated pores, which are mostly inter-granular. These areas are very similar to the crystallized regions at 1100 °C, see Figure 1.1c. Most likely, this occurs from freshly sintered small particles that have not yet had enough time to sinter into larger grains. Some of the elongated pores have lengths up to 1 μm and diameters of 100 nm. The areas of low pore density are mostly composed of intra-granular porosity. Pores in these areas range from 18 to 85 nm in size (by SEM analysis).
Firing to higher temperatures (> 1200 °C) results in the pore density decreasing, see Figure 1.1e, as a result of grain growth closing off the inter-granular pores. This effect has two consequences. First, a decrease in the size of pores, and second, a decrease in the number of pores. It should be noted, however, that there are still large elongated pores found within the material. Although there has been plenty of time (and high enough temperature) for sintering to occur, most likely these pores are still present because of shrinkage upon phase transformation from the less dense transitional aluminas (\( \rho = 3.2 - 3.6 \text{ g.cm}^{-3} \)) to the more dense \( \alpha \)-alumina (\( \rho = 3.98 \text{ g.cm}^{-3} \)). After 36 hours at 1400 °C the material is composed entirely of large grains (0.5 – 3 \( \mu \text{m} \)) with very little intra-granular porosity (Figure 1.1f). The pores between the grains are generally large (0.5 – 1 \( \mu \text{m} \)) and few in number. The morphology is vermicular in structure.

The surface area of alumina formed from A-alumoxane is high at 600 °C (> 200 \( \text{m}^2 \cdot \text{g}^{-1} \)), but decreases as the firing temperature increases, see Figure 1.5a. The largest decrease occurs between 1000 and 1100 °C, which corresponds to the formation of large crystallites within the material as shown by SEM analysis (Figures 1.1c and 1.1d). Pore volume generally follows a similar trend, except that the pore volume increases between 600 °C and 800 °C, corresponding to the opening of pores between the particles as noted in the discussion relating to Figures 1.1a and 1.1b (also see discussion about Figure 1.7 below).

To determine the effect of sintering temperature on alumina formed from A-alumoxane, BJH pore distributions were calculated from the nitrogen adsorption isotherm, see Figure 1.6. The pore distribution reveals that at 600 °C the alumina contains no pores greater than 8 nm in diameter. As the firing temperature is increased, the average pore diameter increases and the pore size distribution broadens (Figure 1.6a). At 1100 °C (Figure 1.6b) the smaller pores have decreased in number, and a second distribution of pores begin to emerge around 100 nm. This corresponds to the larger crystallites forming in the material due to sintering reducing the number of smaller
Figure 1.5. Effect of sintering temperature on (a) surface area and (b) pore volume for A-alumoxane.

particles and the formation of larger pores (growth of α-phase). At temperatures above 1100 °C, the small pores around 20 nm collapse and only large pores remain until at 1400 °C no pores under 150 nm are found. The nitrogen adsorption measurements are consistent with the SEM image analysis described above, where the generation of small pores is noticed at low temperatures (600 – 1000 °C), and the collapse of these pore at higher temperatures (> 1100 °C).

X-ray diffraction shows that alumina formed from A-alumoxane sintered to 600 °C the contains both γ- and δ-alumina phases (JCPDS # 23-1009 and 16-0394,
Figure 1.6. BJH Pore Volume distribution for A-Alumoxane during firing (a) below 1100 °C and (b) above 1100 °C. Note the different y axis scale in (b).
Figure 1.7. X-ray diffraction patterns for alumina samples formed from firing A-alumoxane to (a) 600, (b) 1000, and (c) 1100 °C.
respectively), see Figure 1.7a. This is a low temperature for which the δ-phase is present. The γ- and δ-alumina phases are retained at 800 °C and the θ-alumina (JCPDS # 35-0121) phase appears. The appearance of the θ-alumina phase coincides with the pore volume increasing between 600 and 800 °C. This may be due to the smaller alumina crystallites coalescing into larger particles. The surface area decreases (Figure 1.5a), but the spacing between the particles increases. This increase may allow for more nitrogen to absorb, thereby increasing the pore volume. At 900 °C only δ- and θ-alumina phases are present and continued firing to 1000 °C shows a more dominant θ-alumina phase, see Figure 1.7b. As expected, at 1100 °C, the dominant phase is α-alumina (JCPDS # 42-1468), although small traces of the θ-alumina phase are observed. The appearance of α-alumina corresponds with the crystallized features occurring in the SEM images and the decrease in surface area, as discussed earlier. Above 1200 °C, only the α-phase is present.

A summary of surface properties and crystal phase of alumina formed by the thermolysis of A-alumoxane determined at different temperatures are given in Table 1.1.

**MA-Alumoxane.** The thermolysis of MA-alumoxane to 600 °C yields alumina that appears quite smooth and uniform, see Figure 1.8a. Higher magnification reveals that the material is composed of textured particles up to 45 nm in size (Figure 1.9a). The larger particles appear to be aggregations of smaller particles. The material as a whole does not appear to be highly porous since there are many areas that do not appear to contain pores at all. There is some formation of more elongated pores between the particles at 900 °C, however for the most part the material still has the same appearance. Continued firing to higher temperatures does not change the appearance of the material all that much until 1100 °C.

At 1100°C, the surface has become embedded with pits (Figure 1.8b), between 250 and 400 nm in diameter which do not appear to penetrate into the bulk material. With
Table 1.1. Characteristics of alumina formed by the thermolysis of A-alumoxane.

<table>
<thead>
<tr>
<th>Temp.(^a) ((^\circ)C)</th>
<th>Phase (XRD)</th>
<th>Average pore diameter (nm)</th>
<th>Surface area (m(^2).g(^{-1}))</th>
<th>Pore volume (mL.g(^{-1}))</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>(\gamma,\delta)</td>
<td>5.9</td>
<td>229</td>
<td>0.3351</td>
<td>52</td>
</tr>
<tr>
<td>800</td>
<td>(\gamma,\delta,\theta)</td>
<td>9.9</td>
<td>172</td>
<td>0.4264</td>
<td>58</td>
</tr>
<tr>
<td>900</td>
<td>(\delta,\theta)</td>
<td>10.6</td>
<td>156</td>
<td>0.4170</td>
<td>57</td>
</tr>
<tr>
<td>1000</td>
<td>(\delta,\theta)</td>
<td>12.2</td>
<td>109</td>
<td>0.3314</td>
<td>51</td>
</tr>
<tr>
<td>1100</td>
<td>(\theta,\alpha)</td>
<td>24.4</td>
<td>24</td>
<td>0.1461</td>
<td>51</td>
</tr>
<tr>
<td>1200</td>
<td>(\alpha)</td>
<td>n/a</td>
<td>5.7</td>
<td>0.0396</td>
<td>32</td>
</tr>
<tr>
<td>1300</td>
<td>(\alpha)</td>
<td>n/a</td>
<td>4.1</td>
<td>0.0149</td>
<td>14</td>
</tr>
<tr>
<td>1400</td>
<td>(\alpha)</td>
<td>n/a</td>
<td>3.8</td>
<td>0.0095</td>
<td>6</td>
</tr>
<tr>
<td>1400(^b)</td>
<td>(\alpha)</td>
<td>n/a</td>
<td>1.0</td>
<td>0.0045</td>
<td>2</td>
</tr>
</tbody>
</table>

\(^a\) Dwell time 3 hours unless otherwise noted.

\(^b\) Dwell time 36 hours.

the exception of these pits, the surface is still quite uniform. However, closer analysis reveals that the particles that were present up to 900 \(^\circ\)C, have started to sinter together but the vermicular structure present in A-alumoxane at this temperature is not evident MA-alumoxane. The surface pores appear to be approximately 10 nm in diameter and they are inter-particle.

As may be seen in from Figure 1.8c, grain growth occurs 1200 \(^\circ\)C due to sintering. The grains are observed to be between 1 and 5 \(\mu\)m. There are elongated pores that appear to be inter-granular that are approximately 50 nm in diameter and several
Figure 1.8. SEM images of MA-Alumoxane fired for 3 hours to (a) 600, (b) 1100, (c) 1200, (d) 1300, (e) 1400, and (f) 1400 °C (36 hours).
Figure 1.9. SEM image of MA-Alumoxane fired to (a) 600 and (b) 1200 °C for 3 hours. Microns in length. Intra-granular pores are abundant and range between 10 and 50 nm in diameter, see Figure 1.9b.

Continued firing to 1300 °C does not appear to change the size of the grains, however, the elongated inter-granular pores start to close, and now form smaller pores (Figure 1.8e). The intra-granular pores have also begun to close, as evidenced by the absence of pores around 50 nm in diameter that were present at 1200 °C. Firing to 1400 °C for 36 hours results in the formation of densely packed large grains (1 – 10 µm), see Figure 1.8f.
Both inter- and intra-granular porosity has disappeared, and the grains have a textured appearance that appears highly crystalline and exhibits a step-like layered structure at higher magnification, see Figure 1.10.

![Figure 1.10: SEM image of MA-alumoxane fired to 1400 °C for 36 hours.](image)

Surface area and pore volume of alumina formed from MA-alumoxane is less than that of A-alumoxane, see Figure 1.11a and 1.11b, respectively, which is consistent with SEM image analysis. A gradual decrease in surface area is observed between 600 and 1100 °C, see Figure 1.11a. Pore volume remains essentially constant between 600 and 900 °C; this is followed by a rapid decrease above 900 °C. An interesting point to note is that while the surface area has collapsed at 1100 °C, the pore volume is still approximately 50% that of the sample at 600 °C.

BJH pore distribution of alumina formed from MA-alumoxane (Figure 1.12) reveals a broader range of pores at 600 °C than for A-alumoxane (most likely due to a broader particle size of the agglomerates). At 800 °C the pore distribution is actually narrower than at 600 °C. The pore distribution broadens through 1000 °C where some
Figure 1.11. Effect of sintering temperature on (a) surface area and (b) pore volume on alumina formed from MA-alumoxane.

...pores are up to 80 nm in diameter. At 1100 °C all the small pores have closed and only pores greater than 80 nm are formed. By 1200 °C there does not appear to be any micropores, which is consistent with SEM image analysis.

The X-ray diffraction patterns show that at 600 °C, γ- and δ- alumina phases are present. At 800 °C the γ-alumina phase has disappeared and the growth of the θ-alumina phase is evident. A mixture of δ- and θ- alumina phases exist at 900 °C, see Figure 1.13a. Surprisingly, by 1000 °C the α-alumina phase is observed with a trace of...
Figure 1.12. BJH pore size distribution for alumina derived from MA-Alumoxane during firing to 1100 °C.

the θ-alumina phase still present (Figure 1.13b). This accounts for why the BJH pore distribution is so large at 1000 °C (due to the onset of α-alumina). This is an interesting property because the SEM image analysis did not show any morphology change until 1100 °C, indicating that the formation of α-alumina has occurred topotactically. At 1100 °C only the α-alumina phase is present (Figure 1.13c). The transformation to α-alumina at 1100 °C also corresponds to the collapse of the small pores in the BJG distribution (see Figure 1.12b). It should also be noted that the total pore volume of α-alumina at 1100 °C is approximately 0.08 mL·g⁻¹, corresponding to a porosity of 25% which is very high for pure α-alumina.

A summary of surface properties and crystal phase of alumina formed from the thermolysis of MA-alumoxane determined at different temperatures are given in Table 1.2.
Figure 1.3. X-ray diffraction patterns of alumina derived from MA-alumoxane fired to (a) 900, (b) 1000, and (c) 1100 °C.
Table 1.2. Characteristics of alumina formed by the thermolysis of MA-alumoxane.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Phase (XRD)</th>
<th>Average pore diameter (nm)</th>
<th>Surface area (m².g⁻¹)</th>
<th>Pore volume (mL.g⁻¹)</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>γ,δ</td>
<td>6.7</td>
<td>115</td>
<td>0.1924</td>
<td>38</td>
</tr>
<tr>
<td>800</td>
<td>δ,θ</td>
<td>7.3</td>
<td>100</td>
<td>0.1836</td>
<td>37</td>
</tr>
<tr>
<td>900</td>
<td>δ,θ</td>
<td>8.7</td>
<td>83</td>
<td>0.1819</td>
<td>37</td>
</tr>
<tr>
<td>1000</td>
<td>θ,α</td>
<td>13.4</td>
<td>44</td>
<td>0.1506</td>
<td>33</td>
</tr>
<tr>
<td>1100</td>
<td>α</td>
<td>n/a</td>
<td>7.2</td>
<td>0.0857</td>
<td>25</td>
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<tr>
<td>1200</td>
<td>α</td>
<td>n/a</td>
<td>4.8</td>
<td>0.0173</td>
<td>6</td>
</tr>
<tr>
<td>1300</td>
<td>α</td>
<td>n/a</td>
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<tr>
<td>1400</td>
<td>α</td>
<td>n/a</td>
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</tr>
<tr>
<td>1400b</td>
<td>α</td>
<td>n/a</td>
<td>0.5</td>
<td>0.0045</td>
<td>2</td>
</tr>
</tbody>
</table>

a Dwell time 3 hours unless otherwise noted.
b Dwell time 36 hours.

**MEA-Alumoxane.** Heating MEA-alumoxane to 600 °C results in alumina that is very similar to A-alumoxane, see Figure 1.14a. Closer magnification reveals that the material is composed of small uniform particles between 10 and 50 nm in diameters, see Figure 1.15a. The pores on the surface are highly dense and are inter-particle. The material appears to have more pores than A-alumoxane at this temperature (compare to Figure 1.2a). Continued firing to 900 °C (Figure 1.15b) results in a material that appears to be more porous, but no other change is evident until 1200 °C (Figure 1.14b), where circular features with larger pores are present.
Figure 1.14. SEM images of MEA-Alumoxane fired for 3 hours to (a) 600, (b) 1200, (c) 1300, (d) 1400, and (e) 1400 °C (36 hours).
Figure 1.14. cont’d.

These features appear to be similar to the vermicular crystallization areas in A-alumoxane at 1100 °C (compare to Figure 1.1c), although visibly not as distinct. Closer analysis of the center of these crystal domains reveal that the small particles have sintered and well-defined grain boundaries are present, see Figure 1.15c. Pores are larger in this region and both inter- and intra-granular porosity is present. These crystal domains exhibit grain growth through 1300 °C, until all the small particles have sintered together, see Figure 1.14c. As with A-alumoxane, there are areas of high and low pore density resulting from
when sintering occurred (i.e. the longer the sintering time, the lower the pore density). The pores are not as large as in A-alumoxane.

SEM imaging reveals that firing to 1400 °C for 3 hours results in continued grain growth, an increase in pore size of the elongated inter-granular pores (some are over 1.5 μm in length), and a decrease in the number of intra-granular pores, see Figure 1.14d. The increase in size of the inter-granular pores is probably due to shrinkage upon transformation from the transitional aluminas to the denser α-alumina (see discussion of A-alumoxane, above). Grain growth continues at this temperature and by 36 hours, grains (between 0.2 and 2 μm) are very distinct with very little intra-granular porosity, see Figure 1.14e. Inter-granular pores (as large as 1 μm in diameter) are more plentiful than other carboxylate-alumoxanes fired to this temperature. Figure 16 displays that the grains are textured and the large range of inter-granular pores (between 60 and 500 nm in diameter). The vermicular morphology is still present.

The surface area of alumina derived from MEA-alumoxane after heating to 600 °C is high (above 200 m².g⁻¹), see Figure 1.17a. There is a gradual decrease in surface area through 1000 °C. At 1000 °C the surface area is still quite high (>100 m².g⁻¹). Surface area decreases to 60 m².g⁻¹ at 1100 °C, then at 1200 °C the surface area collapses. The pore volume is also very high for alumina between 600 and 900 °C, corresponding to porosity over 65 %, see Figure 1.17b. Pore volume decreases rapidly between 900 °C and 1200 °C, however at 1100 °C the pore volume is 0.30 mL.g⁻¹, corresponding to a porosity of 49 % which is still extremely high for alumina at this temperature.

The BJH pore size distribution generally follows the same trend as other carboxylate-alumoxanes with both pore distribution and average pore diameter increasing with increasing temperature, see Figure 1.18. One exception is noted however: there is
Figure 1.15. SEM images of MEA-Alumoxane fired for 3 hours to (a) 600, (b) 900, and (c) 1200 °C.
Figure 1.16. SEM image of MEA-alumoxane fired to 1400 °C for 36 hours.

(a)

(b)

Figure 1.17. Effect of temperature on (a) surface area and (b) pore volume for MEA-A.
Figure 1.18. BJH pore size distribution for MEA-alumoxane during firing to 1100 °C.

still a significant number of pores around 20 nm at 1100 °C, while hardly any large pores have formed around 100 nm, which is consistent with SEM analysis. By 1200 °C, the pore structure has completely collapsed.

The X-ray diffraction patterns of the alumina formed from MEA-alumoxane are consistent with the other carboxylate-alumoxanes discussed at 600 °C with γ- and δ-alumina phases present. An interesting exception occurs at 900 °C, where γ-alumina is still present at this temperature along with δ- and θ-alumina phases, see Figure 1.19a. This may explain the high pore volume at these temperatures. Continued firing to 1000 °C shows only δ- and θ-alumina phases (Figure 1.19b) and by 1100 °C the alumina is a mixture of the θ- and α- phases (Figure 1.19c). It is interesting to note that the α-alumina phase is not as dominant at this temperature and this could explain why the surface area and pore volume is so high for this sample at 1100 °C. The presence of nucleation and growth sites of α-alumina is not visible by SEM at 1100 °C, and only start to appear at
Figure 1.19. X-ray diffraction patterns of alumina derived from MEA-alumoxane fired to (a) 900, (b) 1000, and (c) 1100 °C.
1200 °C, where the only phase present is α-alumina. This indicates that the formation of α-alumina is topotactic. These α-alumina sites then become nucleation sites for further growth.

A summary of surface properties and crystal phase of alumina formed from the thermolysis of MEA-alumoxane determined at different temperatures are given in Table 1.3.

### Table 1.3. Characteristics of alumina formed by the thermolysis of MEA-alumoxane.

<table>
<thead>
<tr>
<th>Temp. (°C)</th>
<th>Phase (XRD)</th>
<th>Average pore diameter (nm)</th>
<th>Surface area (m².g⁻¹)</th>
<th>Pore volume (mL.g⁻¹)</th>
<th>Porosity (%)</th>
</tr>
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<tbody>
<tr>
<td>600</td>
<td>γ,δ</td>
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<td>207</td>
<td>0.6198</td>
<td>66</td>
</tr>
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<td>800</td>
<td>γ,δ</td>
<td>14.6</td>
<td>159</td>
<td>0.5795</td>
<td>65</td>
</tr>
<tr>
<td>900</td>
<td>γ,δ,θ</td>
<td>16.2</td>
<td>141</td>
<td>0.5709</td>
<td>65</td>
</tr>
<tr>
<td>1000</td>
<td>δ,θ</td>
<td>13.0</td>
<td>116</td>
<td>0.3771</td>
<td>55</td>
</tr>
<tr>
<td>1100</td>
<td>θ,α</td>
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<td>60</td>
<td>0.3015</td>
<td>49</td>
</tr>
<tr>
<td>1200</td>
<td>α</td>
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<td>9</td>
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<tr>
<td>1300</td>
<td>α</td>
<td>n/a</td>
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<td>α</td>
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<td>α</td>
<td>n/a</td>
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ᵃDwell time 3 hours unless otherwise noted.

ᵇDwell time 36 hours.
MEEA-Alumoxane. Heating MEEA-alumoxane to 600 °C results in alumina that is composed of large particles with many void spaces, see Figure 1.20a. Closer analysis reveals that the particles are between 0.5 and 1 μm in size, see Figure 1.21a. The particles are very textured and appear to be agglomerations of well packed smaller particles less than 50 nm in size, similar to MA-alumoxane. There are large void spaces up to 500 nm in size due to irregular packing of the agglomerates.

Firing the samples to higher temperatures (< 1100 °C) results in more ordering and there appears to less void space on the surface, see Figure 1.20b. At 1100 °C there is a remarkable change in the texture of the material, see Figure 1.20c. The particles have sintered together to form a continuous material with two pore types: smaller circular pores and larger elongated pores. Interestingly, the elongated pores all seem to be orientated along the same axis (this is not observed with the other carboxylate-alumoxanes). Higher magnification reveals that the small circular pores are actually quite irregular in shape and appear to be mostly intra-granular, see Figure 1.21c, although here are no distinct grain boundaries observed. The elongated pores do not appear to be inter-granular or inter-particle but this is difficult to determine with certainty due to the lack of defined grains and particles.

At 1200 °C the interesting features observed at 1100 °C have disappeared due to further sintering resulting in a material exhibiting vermicular texture that contains larger pores, see Figure 1.20d. These pores are between 50 and 500 nm in size, see Figure 1.21c. Grain boundaries are very distinct, and the pores are both inter- and intra-granular. It is interesting to note that while this material (Figure 1.20d) looks very similar to A-alumoxane at 1200 °C and MEA-alumoxane at 1400 °C (Figures 1.1d and 1.13e, respectively), MEEA-alumoxane does not exhibit any large irregular inter-granular pores or cracks due to shrinkage from the θ- to α-alumina phase transformation. The material has very uniform pores.
Figure 1.20. SEM images of MEEA-Alumoxane fired for 3 hours to (a) 600, (b) 1000, (c) 1100, (d) 1200, and (e) 1400 °C (36 hours).
Continued firing of MEEA-alumoxane at 1400 °C for 36 hours results in a material with large grains (1 – 5 μm) and decreased porosity, see Figure 1.20e. It is obvious that the material contains both inter- and intra-granular porosity, although they are few in number and are quite large (0.5 – 1 μm). These grains are highly textured and appear to have formed a step-like layered structure along several different axes, see Figure 1.22.
Figure 1.21. SEM images of MEEA-Alumoxane fired for 3 hours to (a) 600, (b) 1100, and (c) 1200 °C for 3 hours.
The surface area of alumina derived from MEEA-alumoxane is lower than other carboxylate-alumoxanes at 600 °C. The surface area displays a gradual loss of surface area through 1200 °C, see Figure 1.23a. This is different than other carboxylate-alumoxanes because there is no sudden increase in the loss of surface area over this temperature range. Pore volume also decreases with increasing temperature, however the pore volume increases between 800 and 900 °C, see Figure 1.23b. The pore volume continues to decrease through 1200 °C.

BJH pore size distribution shows the same trend for all the other carboxylate-alumoxanes discussed: pore size distribution and average pore size increases with increasing temperature, see Figure 1.24. At 1100 °C, significant pores still remain at the smaller pore sizes (below 50 nm), however larger pores have also started to form near 100 nm.
Figure 1.23. Effect of sintering temperature on alumina formed from MEEA-alumoxane on (a) surface area and (b) pore volume.

X-ray diffraction patterns show that the $\gamma$- and $\delta$- alumina phase is present up to 800 °C. At 900 °C the $\gamma$-alumina phase has disappeared and the ceramic is now composed of only the $\delta$- and $\theta$- alumina phases. The appearance of $\theta$-alumina coincides with the pore volume increasing between 800 and 900 °C. This may be due to the coalescing of smaller crystallites, as discussed earlier. At 1000 °C a mixture of $\delta$-, $\theta$-, and $\alpha$-alumina phases exist, see Figure 1.25a. This is the first time that all three of these phases have co-existed with one another during the calcination of the carboxylate-alumoxanes. The
Figure 1.24. BJH pore size distribution for alumina formed from MEEA-alumoxane during firing to below 1100 °C.

The presence of the δ-phase may inhibit the growth of α-alumina, resulting in the lack of large crystals which are absent in the SEM images (Figure 1.20b), once again indicating that the phase transformation to α-alumina is topotactic. At 1100 °C the δ-alumina phase has disappeared leaving only θ- and α-alumina (Figure 1.25b), leading to the interesting texture noticed at this temperature. At 1200 °C the material is pure α-alumina.

A summary of surface properties and crystal phase of alumina formed from the thermolysis of MEEA-alumoxane determined at different temperatures are given in Table 1.4.

Comparison of Alumina Formed from the Thermolysis of A-, MA-, MEA-, and MEEA-Alumoxane. The morphology of the carboxylate-alumoxanes fired to 600 °C show two distinct patterns: particles and agglomerates. Alumina derived from A- and
MEA-alumoxane are composed of small particles between 10 and 50 nm in diameter, while alumina derived from MA- and MEEA-alumoxane are composed of agglomerations of smaller particles. Previous studies have shown MA-alumoxane to be an aggregate, or colloid in aqueous solution, however MEEA-alumoxane did not exhibit this quality. During the drying stage the removal of water causes shrinkage, which may

Figure 1.25. X-ray diffraction patterns of alumina derived from MEEA-alumoxane fired to (a) 1000 and (b) 1100 °C.
Table 1.4. Characteristics of alumina formed by the thermolysis of MEEA-alumoxane.

<table>
<thead>
<tr>
<th>Temp.(^{\circ}\text{C})</th>
<th>Phase (XRD)</th>
<th>Average pore diameter (nm)</th>
<th>Surface area (m(^2).g(^{-1}))</th>
<th>Pore volume (mL.g(^{-1}))</th>
<th>Porosity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>600</td>
<td>(\gamma,\delta)</td>
<td>7.6</td>
<td>161</td>
<td>0.3042</td>
<td>49</td>
</tr>
<tr>
<td>800</td>
<td>(\gamma,\delta)</td>
<td>8.7</td>
<td>115</td>
<td>0.2506</td>
<td>45</td>
</tr>
<tr>
<td>900</td>
<td>(\delta,\theta)</td>
<td>11</td>
<td>95</td>
<td>0.2637</td>
<td>46</td>
</tr>
<tr>
<td>1000</td>
<td>(\delta,\theta,\alpha)</td>
<td>11</td>
<td>68</td>
<td>0.1816</td>
<td>37</td>
</tr>
<tr>
<td>1100</td>
<td>(\theta,\alpha)</td>
<td>24</td>
<td>27</td>
<td>0.1599</td>
<td>34</td>
</tr>
<tr>
<td>1200</td>
<td>(\alpha)</td>
<td>n/a</td>
<td>4.9</td>
<td>0.0172</td>
<td>6</td>
</tr>
<tr>
<td>1300</td>
<td>(\alpha)</td>
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<td>3.9</td>
<td>0.0155</td>
<td>6</td>
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<tr>
<td>1400</td>
<td>(\alpha)</td>
<td>n/a</td>
<td>3.2</td>
<td>0.0104</td>
<td>4</td>
</tr>
<tr>
<td>1400(^{b})</td>
<td>(\alpha)</td>
<td>n/a</td>
<td>0.06</td>
<td>0.0035</td>
<td>1</td>
</tr>
</tbody>
</table>

\(^{a}\) Dwell time 3 hours unless otherwise noted.

\(^{b}\) Dwell time 36 hours.

cause the MEEA-alumoxane to aggregate. This may not occur with A- or MEA-alumoxane due to the shorter organic periphery attached to the nanoparticles. This anomaly also follows that MEA-alumoxane is more soluble in water than MEEA-alumoxane.\(^{22}\)

Average pore diameters at 600 \(^{\circ}\text{C}\) for the carboxylate-alumoxanes are between 5.9 and 12 nm exhibiting the following sequence: A- < MA- < MEEA- < MEA-alumoxane, see Figure 1.26. As discussed above, the carboxylate-alumoxanes are either particulate or aggregates after drying. When broken into this series, the trend is A- < MEA- and MA- < MEEA-alumoxane. This trend follows the same trend as the length of
the organic periphery. At this temperature, the pores are formed from the void space between the particles. As the organic periphery becomes larger, particles cannot pack as close together as at shorter lengths. However, it is interesting to note that by 1000 °C, all the carboxylate-alumoxanes contain average pore diameters between 11 and 13 nm.

The porosity of the carboxylate-alumoxane samples also show trends relating first to morphology of the particles and secondly to the organic periphery. The overall trend of the porosity is MA- < MEEA- < A- < MEA-alumoxane. The carboxylate-alumoxanes that are particulate have the greatest porosity, compared to those that are agglomerate, which have the lowest. Within each of these categories, the carboxylate-alumoxane with the longest organic periphery have the greatest porosity, hence, A- < MEA-alumoxane and MA- < MEEA-alumoxane.

It is interesting that none of the carboxylate-alumoxanes studied here exhibit any

![Figure 1.26](image.png)

**Figure 1.26.** Pore size growth of the carboxylate-alumoxanes with increasing temperature: A-alumoxane (■), MA-alumoxane (■), MEA-alumoxane (■), and MEEA-alumoxane (■).
Figure 1.27. Phase changes of the carboxylate-alumoxanes compared to boehmite with increasing temperature.

pure transitional alumina phases, see Figure 1.27. While the rational of this observation is unknown at present, it may be as a result of the carboxylate ligands bound to the aluminum cations on the surface of the nanoparticles. The phase changes between γ- and θ-alumina are a result of cation movement, and the effect of the carboxylate ligands may effect this migration by constraining or ordering the aluminum cations.
The \( \alpha \)-alumina phase transformation temperature \( (T_\alpha) \) is also dependent on whether the material is composed of particles or agglomerates. For MEEA- and MA-alumoxane the \( T_\alpha = 1000 \, ^\circ C \), while for A- and MEA-alumoxane the \( T_\alpha = 1100 \, ^\circ C \). The appearance of the \( \alpha \)-alumina phase is topotactic for all carboxylate-alumoxanes except for A-alumoxane. The reason for A-alumoxane not exhibiting the topotactic \( \alpha \)-alumina phase transformation is unknown, and there is a good possibility that it actually occurs this way, but attempts to capture the transformation (at temperatures at 1030, 1050, and 1090 \( ^\circ C \)) were unsuccessful. It is also interesting to note that alumina derived from MA-alumoxane is pure \( \alpha \)-alumina at 1100 \( ^\circ C \) and it does not exhibit any vermicular morphology. This may be due to the low porosity, and hence the high density packing of the nanoparticles.

Firing MEEA- and MA-alumoxane at 1400 \( ^\circ C \) for 36 hours results in the formation of highly textured grains. The particulate carboxylate-alumoxanes (A- and MEA-) still exhibit the vermicular structure at this temperature. This is most likely due to the lower porosity of the agglomerated carboxylate-alumoxanes.

**Mixtures of Carboxylate-Alumoxanes.** While it is clear that the pore size and pore size distribution is controlled by the choice of carboxylate group, it would be desirable to prepare ceramics with a broader range of pore sizes. The simplest method by which this may be accomplished is through physically mixing two (or more) different carboxylate-alumoxanes.28,29 Mixed solutions of MEA- and A-alumoxane were prepared with MEA-alumoxane:A-alumoxane ratios of 1:0, 1:0.5, 1:1, 1:2, 1:4, and 0:1. These physical mixtures were used to form alumina bodies and the pore sizes measured. Figure 1.28 shows a plot of average pore size as a function of the fraction of MEA-alumoxane. It appears that at high A-alumoxane content the pore size remains essentially unchanged, however, above a threshold value (MEA-alumoxane:A-alumoxane = 1:2) the average
pore size varies linearly with the relative ratio of the two different carboxylate-alumoxanes.

It may be expected that a physical mixture of two carboxylate-alumoxanes would yield alumina with a broad pore size distribution, similar to that which would be observed for a physical mixture of aluminas prepared from the two carboxylate-alumoxanes. However, as can be seen from Figure 1.29, the pore size distribution of a 1:1 physical mixture of MEA- and A-alumoxane is actually surprisingly narrow. This suggests that the carboxylate-alumoxanes are intimately mixed in solution rather than segregated.\textsuperscript{28}

As an alternative to physically mixing carboxylate-alumoxanes with different substituents, it is possible that different porosity results may be obtained if individual alumoxane nano-particles are derivatized with a mixture of two or more carboxylic acids, i.e., \([\text{Al(O)}_x(\text{OH})_y(\text{O}_2\text{CR})_z(\text{O}_2\text{CR'})_z']_n\), where \(R \neq R'\). In this regard, a hybrid

![Graph showing the relationship between average pore size and fraction of MEA-alumoxane.](image)

**Figure 1.28.** Plot of the average pore sizes of alumina derived from the physical mixing of MEA- and A-alumoxane (1:1).
carboxylate-alumoxane (MEA/A-alumoxane) was prepared by reaction of an equimolar mixture of MEA-acid and acetic acid with boehmite, see Experimental.\textsuperscript{28}

The average pore size for alumina prepared from MEA/A-alumoxane is comparable to the physical mixture of the similar MEA:A composition.\textsuperscript{28} Thus, chemical mixing appears to have little difference in effect as compared to physical mixing. However, further study is required to demonstrate that the MEA/A-alumoxane is indeed distinct from a simple physical mixture. Physical mixing of two (or more) carboxylate-alumoxanes has the advantage of simplicity in preparation and processing. Another benefit of the carboxylate-alumoxane methodology with respect to large scale processing is their relatively low cost.

Conclusions

The carboxylate-alumoxanes are a novel, environmentally benign precursor for developing alumina bodies and films with controlled porosity. The methodology of the
carboxylate-alumoxane system allows for chemical control over the precursors to alumina ceramics. The choice of the carboxylate periphery determines the properties of the alumina formed during thermolysis. Alumina derived from A- and MEA-alumoxane have a particulate morphology, while alumina derived from MA- and MEEA-alumoxane are composed of aggregates of smaller particles. The properties of the alumina at higher temperatures are dependent on the type of morphology and on the length of the carboxylate periphery. Also, average pore sizes may be altered through either physical or chemical mixtures of the carboxylate substituents. Physical mixing of two (or more) carboxylate-alumoxanes has the advantage of simplicity in preparation and processing.

**Experimental**

Pseudoboehmite was provided by the CONDEA Vista Company. All carboxylic acids were obtained commercially (Aldrich) and were used as received. SEM studies were performed on a Phillips XL-30 ESEM scanning microscope. The samples were attached to a metal mount using carbon tape. Due to the insulating nature of the materials, a thin layer of gold was applied as a coating to provide a conducting surface. Surface area, pore size distribution, pore volume, average pore size, and porosity were obtained using gas sorption techniques using a Coulter™ SA3100™. Helium was used to determine the free space in the sample tube and nitrogen as the absorbate gas. Calculations were based on the cross sectional area of nitrogen using the value of 0.162 nm². Surface area was calculated using the BET (Brunauer, Emmett, and Teller) equation with 5 data points. Pore size distributions were determined using the BJH (Barrett, Joyner, and Halenda) method with 65 data points. Pore volume calculation was performed at a relative pressure of 0.9814. Porosity and average pore diameter were calculated based on surface area, pore volume, and density of alumina (dependent on the alumina crystal phase determined by XRD). All samples were outgassed at 300 °C for 2 hours under a stream of dry nitrogen using a Coulter™ SAPrep™. To enable XRD
analysis, samples were lightly ground using a mortar and pestle and attached to plexiglass mounts using Scotch™ brand double stick tape. Data were collected on a Seimens Diffractometer (B).

**Synthesis of A-Alumoxane.** Pseudoboehmite (100.0 g, 1.66 mol) was slowly added to a vigorously stirring mixture of acetic acid (80 mL, 1.4 mol) in water (800 mL). The resulting slurry was decanted after 20 minutes and then centrifuged at 4900 rpm for 1 hour to yield a clear viscous solution. Removal of the volatiles in vacuo (10⁻² Torr) at 80 °C, results in white granules. The solid yield was 92.4 g and had a ceramic yield of 78 %. The granules were ground to a fine while free flowing powder and stored until further use.

**Synthesis of MA-Alumoxane.** Pseudoboehmite (80.0 g, 1.33 mol) and methoxyacetic acid (169.2 mL, 2.66 mol) were refluxed in water (800 mL) for 36 hours, which resulted in a clear white solution. The volatiles were removed in vacuo (10⁻² Torr) at 80 °C to yield a white waxy solid. The solid was stirred overnight in diethyl ether. The powder was collected by filtration, ground, and stirred in Et₂O for 1 hour (4-x 150 mL). After drying overnight at 50 °C the solid yield was 151 g and had a ceramic yield of 29.4 %.

**Synthesis of MEA-Alumoxane.** Pseudoboehmite (80.0 g, 1.33 mol) and methoxyethoxyacetic acid (193.0 mL, 1.69 mol) were refluxed in water (900 mL) for 48 hours, which resulted in a clear brown solution. The water was removed in vacuo (10⁻² Torr) at 80 °C resulting in a brown gel. The gel was dissolved in ethanol (500 mL) and MEA-alumoxane was precipitated via the addition of diethyl ether, as a white powder. The MEA-alumoxane was washed with Et₂O, collected by filtration and dried overnight at 50 °C. The resulting solid yield was 164 g and had a ceramic yield of 48 %.
Synthesis of MEEA-Alumoxane. Pseudoboehmite (80.0 g, 1.33 mol) and methoxyethoxyethoxyacetic acid (260 mL, 1.69 mol) were refluxed in water (900 mL) for 48 hours, which resulted in a clear light brown solution. The water was removed in vacuo (10^-2 Torr) at 80 °C resulting in a brown gel. The gel was dissolved in ethanol (500 mL) and MEEA-alumoxane was precipitated via the addition of diethyl ether, as a white powder. The MEEA-alumoxane was washed with Et_2O, collected by filtration and dried overnight at 50 °C. The resulting solid yield was 181 g and had a ceramic yield of 46 %.

Synthesis of Mixed Ligand MEA/A-Alumoxane. Acetic acid (19.0 mL) and methoxy(ethoxy)acetic acid (152.0 mL) was dissolved in 500 mL of water and Vista Catapal B boehmite (20 g) was slowly added and refluxed for 72 hours. The white solution was filtered and the filtrate was evaporated under reduced pressure to yield an off-white gel. The gel was dissolved in ethanol (100 mL) and the white powder product was obtained by the addition of Et_2O. The MEA/A-alumoxane was dissolved in water and allowed to evaporate to a thin glass-like membrane.

Physical Mixing of MEA-Alumoxane and A-Alumoxane. MEA-alumoxane (1.0 g) and A-alumoxane (1.0 g) were dissolved in about 20 mL of water. After stirring for approximately 0.5 hours the solutions were poured into drying containers. After approximately 36 hours, the solutions had evaporated to leave a thin glass-like membrane.

Fabrication of Carboxylate-Alumoxane Green Bodies. Each carboxylate-alumoxane (10 g) were separately dissolved in water (100 mL) and stirred overnight. The solutions were centrifuged at 4900 rpm and poured into Teflon™ drying molds. The
solutions were dried at room temperature in the atmosphere, yielding films approximately 1 – 2 mm thick.

**Conversion of the Carboxylate-Alumoxanes to Alumina.** In order for a comparison of the effects of chemical substitution, processing was kept consistent for all experiments. All of the carboxylate-alumoxane green bodies were heated from 25 °C to 600 °C over 4 hours, then held at 600 °C for 3 hours. This alumina separated into sets containing four samples dependent on the precursor (i.e., A-, MA-, MEA-, and MEEA-alumoxane). Each set was then subjected to further firing to temperatures of 800, 900, 1000, 1100, 1200, 1300, or 1400 °C over 4 hours and held at the respective temperature for 3 hours. Additionally, another set of samples was fired to 1400 °C over 4 hours, then held for 36 hours.

**References**

therein.


Porosity (%) = 100 (ρ_{alumina}V_{pore})(1 + ρ_{alumina}V_{pore})

Average pore diameter = (4V_{pore})(surface area)^{-1}
Chapter 2

Formation of Asymmetric Ultrafiltration Filters Using Carboxylate-Alumoxane Nanoparticles

Introduction

Materials that exhibit small pores and narrow pore size distributions may be used to form a barrier for separation, see Introduction. Ultrafiltration filters are used for many applications in water purification, wastewater treatment, food and beverage industry, industrial waste separation, and solvent recovery. Currently, most ultrafiltration separations utilize polymeric filters because of their low cost; however, ceramic filters contain many desirable properties such as thermal stability, high chemical resistance, pH stability, and high flow rates.

The sintering of ceramic particles is perhaps the simplest approach to forming a porous ceramic filter, however, the starting particles are usually quite large and non-uniform resulting in pores that also have these characteristics. The sintering of bulk ceramics is also very expensive due to the high temperatures required. The pore size is controlled by the starting particle size and the sintering time and temperature. Due to the large size of the starting particles, it is extremely difficult, and not very efficient, to make ultrafiltration filters by this method because of grain growth during sintering, resulting in low porosity and large pores. This method is generally used to produce alumina microfiltration filters, which contain larger pores and supports for ultrafiltration membranes, which contain smaller pores.

At present, ceramic membranes are typically produced by slip casting a colloidal suspension of ceramic particles or precursors (i.e., sol-gel process) onto a pre-formed porous ceramic support. Control of the colloidal suspension and limitations on the size of colloids have constrained the range of membrane types that can be produced. In
addition, cost is a key obstacle to overcome in advancing the use of ceramic membranes for pollution prevention applications.\textsuperscript{5} The sol-gel process currently used to produce commercially available ceramic membranes is energy and time intensive, and difficult to control. Alternative approaches for manufacturing ceramic membranes include the anodic oxidation of aluminum metal or chemical vapor deposition (CVD) onto pre-formed supports. During the anodic oxidation of aluminum the applied voltage controls the pore size, while the current governs the film thickness.\textsuperscript{3} Commercial Anodisc\textsuperscript{TM} membranes have a uniform pore size available between 0.02 and 2 \( \mu \text{m} \) in diameter, however strong dielectric solutions of various acids must be employed, and the method of preparation leads to low porosity, which results in low flux. Membranes prepared by CVD are generally contain pores less than 1 nm in diameter, and are usually used for nanofiltration or reverse osmosis applications.\textsuperscript{19,20} Additionally, the CVD method is used to fill in larger pores, however this results in decreased porosity, which reduces flux.

Due to the small pore sizes of ultrafiltration membranes, the flow of water (flux) through the membrane is very slow due to the high amount of resistance. For this reason, it is necessary to have the membrane layer to be as thin as possible. However, very thin membranes are usually unable to withstand the high pressures necessary to drive the liquid through the pores. This problem is may be overcome by the use of supports with little resistance compared to the membrane. The resistance through a filter is determined by the resistance through the support and the membrane, see Eq. 2.1, where \( R_{\text{filter}} = \text{resistance through the entire filter, } R_{\text{support}} = \text{resistance through the support, and } R_{\text{membrane}} = \text{resistance through the membrane.} \)

\[
\frac{1}{R_{\text{filter}}} = \frac{1}{R_{\text{support}}} + \frac{1}{R_{\text{membrane}}} \tag{2.1}
\]
As the resistance through the support becomes small, the resistance, and hence the flux, of the filter is only dependent on the membrane. Supports for ultrafiltration should have large pores and have a high physical strength, to withstand high pressures. The large pores in the support should decrease the resistance within this part of the filter. Casting a thin layer of the membrane material on top of these supports result in an asymmetric filter, see Figure 2.1. \(^2,^3\)

Of the present technologies, sol-gel is the best method for making ceramic ultrafiltration membranes.\(^5\) As noted above, the pore size is generally limited to the sizes of the ceramic precursor particles prior to sintering. For sol-gels, the particle size distribution is difficult to control, and they must be used immediately after preparation or aggregation and precipitation can occur. Thus, it is desirable to have a sol-gel style technology without the disadvantages based on nano-particle precursors to allow for small pore sizes. We have previously reported that aluminum-oxide nanoparticles (5 – 80 nm) may be prepared by the reaction of the mineral boehmite with carboxylic acids.\(^21,^22\) The identity of the carboxylic acid appears to control the size of the nanoparticles. These nanoparticles, carboxylate-

(a)

(b)

Membrane

Support

Figure 2.1. Schematic of a symmetric membrane (a), and an asymmetric membrane (b).
alumoxanes, are readily processed to alumina bodies and coatings.\textsuperscript{22,23} As discussed in Chapter 1, the alumina nanoparticles formed from the thermolysis of carboxylate-alumoxanes exhibit pore diameters below 13 nm (\(\leq 1000^\circ\text{C}\)), i.e., the ultrafiltration range. Carboxylate-alumoxane derived alumina also contains narrow pore size distributions,\textsuperscript{23} which is a characteristic of highly selective membranes. Given these results, it was proposed that carboxylate-alumoxanes should be good precursors for the fabrication of ultrafiltration membranes. This Chapter reports the fabrication techniques investigated to make ultrafiltration filters using several different support types and different methods of forming the alumina membrane layer.

Results and Discussion

Three classes of supports have been investigated: (a) silica glass, (b) silica/alumina, and (c) alumina. The initial choice of glass supports was made because of the easy availability in a wide range of pore sizes that allowed for exploratory investigation of the slip casting technique. The ceramic supports were chosen based on the higher thermal resistance to glass supports and the availability of lower pore sizes. The following discussion is separated into the three classes of supports.

Silica Glass Supports. Silica supports were first utilized in the first attempts to produce a ceramic filter. Coarse (pore size 40 – 60 \(\mu\text{m}\)) and medium (pore size 10 – 16 \(\mu\text{m}\)) glass fritted discs were used as supports. Both fritted discs illustrated similar properties, and therefore are presented throughout this discussion. A summary of experiments is shown in Table 1.1.

SEM images of the surface and cross-section of the untreated supports are shown in Figure 2.2. The glass supports are composed of silica rods that have been pressed and fused together to form a porous network. On the surface the glass rods lay horizontal along
Table 2.1. Summary of techniques used to form alumina coatings derived from A-alumoxane on silica glass supports.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Coating/ infiltration method</th>
<th>Aqueous conc. wt %</th>
<th>Firing temp. (°C)</th>
<th># Repeated coatings</th>
</tr>
</thead>
<tbody>
<tr>
<td>2.1</td>
<td>1</td>
<td>10</td>
<td>350</td>
<td>0</td>
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<td>2.2</td>
<td>1</td>
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<td>5</td>
</tr>
<tr>
<td>2.3</td>
<td>1</td>
<td>10</td>
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<td>10</td>
</tr>
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<td>15</td>
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<td>2.10</td>
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<td>10</td>
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</tr>
<tr>
<td>2.11</td>
<td>3</td>
<td>10</td>
<td>1100</td>
<td>2</td>
</tr>
</tbody>
</table>

a See Experimental Section.

their long axis (Figure 2.2a). When the filter is broken, it is the cleaved ends of the rods that are viewed (Figure 2.2b).

We were interested in filling the pores with A-alumoxane and effectively closing off the pores to make a smaller pore size. Initial attempts to infiltrate/coat the support were made by dropping a 10 % wt A-alumoxane aqueous solution onto the filter (Method 1, see
Figure 2.2. SEM images of the silica glass support surface (a) and cross-section (b).

Experimental). The A-alumoxane solution becomes trapped between the glass rods. Drying in air at room temperature followed by firing to 350 °C results in the formation of alumina. Figure 2.3 show SEM images of the surface of the treated support (2.1). In comparison with Figure 2.2a, it appears that the alumina has been infiltrated within the pores. Closer analysis reveals that the alumina is broken into small fragments (Figure 2.3b).
Figure 2.3. SEM images of a silica glass support coated once with A-alumoxane and then heated to 350 °C (2.1).

Based upon the forgoing results, it was determined that repeated dips and fires were needed to achieve a better coating. As expected, each time the dip/fire process was repeated, more alumina was found between the silica rods (2.2 – 2.4). From the SEM images,
(e.g., Figure 2.4) it may be seen that while there is more alumina present than in sample 2.1, there is not a continuous coating and furthermore, where there is a coating there are many cracks. These cracks could cause the alumina coating to flake off, and allow for chemical degradation of the glass support.

Figure 2.4. SEM image of a silica glass support coated 10 times with A-alumoxane and heated to 350 °C (2.3).

In order to gain insight into why the A-alumoxane was not forming a continuous coating, samples were studied prior to thermal decomposition of the A-alumoxane. Figure 2.5a shows a SEM image of the surface of silica support after coating with A-alumoxane (2.5). It is clear that significant cracking has occurred during the drying stage. This cracking is most likely caused by the amount of void space between the glass rods, and the roughness of the surface. 19,20,24 Clearly any cracking of the A-alumoxane is passed on to the final fired product, i.e., sample 2.6 (Figure 2.5b). It would appear that the alumina
derived from A-alumoxane is not physically bound to the support, which could result in the alumina flaking off the support.

Figure 2.5. SEM images of coatings derived from A-alumoxane on a silica glass support (a) unfired (2.5) and (b) fired to 350 °C (2.6).
These initial experiments showed that it was not possible to form a continuous coating on the top of the silica. Even the best sample showed many cracks and some lifting of the coating away from the surface, which would decrease the efficiency of the filter. The failure to form asymmetric filters on the glass supports prompted us to investigate the full infiltration of the support. The concept being that if a sufficient fraction of the pores inside the sample were filled with the alumina then a hybrid symmetrical filter could be produced, see Figure 2.6. It was hoped that as we continually filled the cracks and pores with A-alumoxane, the cracks would fill in and the surface would become smooth.

![Figure 2.6. Schematic of a hybrid alumina-glass symmetrical filter. The large gray circles represent the glass support while the small black circles represent alumina derived from carboxylate-alumoxanes.](image)

The glass supports were vacuum infiltrated by A-alumoxane solution (see Experimental). SEM images of the surface of the support and cross-section after vacuum infiltration with A-alumoxane solution heated to 350 °C (2.7) are shown in Figure 2.7. The surface of the support appears to be similar to sample 2.3 (Figure 2.4). However, the cross-section image clearly shows that the alumina has reached the center of the support and appears to be filling in the bulk of the void space, thus decreasing the macroscopic porosity. While previous samples prepared by Methods 1 and 2 (2.1 - 2.6), showed
some carboxylate-alumoxanes in the center of the supports, the vacuum infiltration technique had a larger quantity.

Figure 2.7. SEM images of the top (a) and cross-section (b) of the silica support after vacuum infiltration with A-alumoxane and heated to 350 °C (2.7).
The extent of infiltration at the center of the support is readily observed by microprobe analysis (Figure 2.8). The SEM image (Figure 2.8a) shows the cross-section of the filter (2.7) after cleavage. The X-ray elemental map of aluminum shows that the particles between the silica rods are composed of alumina, and that there is a thin coating of alumina around each glass rod. As shown in Figure 2.8c, the alumina coats the glass rods uniformly, even in places where there is no bulk alumina.

![Image](image_url)

**Figure 2.8.** SEM image (a) and associated Si (b) and Al (c) X-ray elemental maps of the silica support cross-section after vacuum infiltration of A-Alumoxane and heating to 350 °C (2.7).

We were interested in studying the effect of heating on the coated supports. For this purpose, a glass support was infiltrated with A-alumoxane and heated to various temperatures. The glass supports melt at approximately 700 °C. SEM images of the surface of the treated supports are shown in Figure 2.9 at various temperatures between 350 °C and 1000 °C. There is not much difference on the top surface of the filter up to 900 °C. At this temperature, it appears that the glass filter does not exhibit as much open porosity as at lower temperatures, and there are areas in which the glass rods (coated) are connected. As the temperature is increased to 1000 °C, this effect is more prevalent.
Figure 2.9. SEM images of the top of a silica support after vacuum infiltration with A-alumoxane and heating to (a) 350 \(2.7\), (b) 700 \(2.8\), (c) 900 \(2.9\), and (d) 1000 °C \(2.10\).
Figure 2.9. cont’d.

To understand what is occurring during the firing sequence, it is necessary to look at the cross-sections of the glass filters during this firing sequence, see Figure 2.10. The samples fired to 350 °C and 700 °C (2.7 and 2.8, respectively) are very similar in appearance (silica rods with alumina between them). However, upon firing to 900 °C
(2.9), the macrostructure of the silica rods is no longer visible because they have melted. Continued firing to 1000 °C (2.10) shows a much smoother appearance.

Figure 2.10. SEM images of the cross-section of a silica support after vacuum infiltration with A-alumoxane and heating to (a) 350 (2.7), (b) 700 (2.8), (c) 900 (2.9), and (d) 1000 °C (2.10).
Figure 2.10. cont’d

To determine what happens to the alumina during this melt microprobe analysis was performed, see Figure 2.15. The analysis shows that the aluminum and silicon are intimately mixed at this temperature (as at 900 °C, not shown), and there are no agglomerations of alumina or silica within the matrix. This is quite interesting because
before these samples were fired to over 900 °C, there was bulk alumina found between the glass rods, and it was expected that this alumina would form "pockets" of alumina within the melted silica matrix.

Figure 2.11. SEM image (a) and associated Si (b) and Al (c) X-ray elemental maps of a cross-section of a silica support after vacuum infiltration of A-alumoxane and heating to 1000 °C (2.10).

It is interesting to note that while the uncoated silica support melts at 700 °C, the alumina coating on the glass rods prevents the rods from melting together, see Figure 2.12. At 900 °C the forces during the melt break apart the alumina coatings, allowing the silica to melt together with intimate mixing of the alumina occurring. The top surface of the support when coated retains the macroscopic shape of the glass rods to 1100 °C (2.11), probably due to less force on the surface than in the center of the support due to melting silica. A SEM image of a cross-section from a support showing the edge of the top and the interior fired to 1100 °C is shown in Figure 2.13. Note that it is only the outer surface that has retained the shape of the glass rods.
Figure 2.12. SEM images of cross-sections of a silica support fired to 700 °C uncoated (a) and after vacuum infiltration (b) of A-alumoxane (2.8).

An interesting feature of the carboxylate-alumoxane infiltrated glass supports is that they retain their macroscopic shape during heating. Even after heating to 1100 °C, the shape of the glass support appears to be the same as before heating. The untreated supports melt, as expected, and does not retain their shape.
Figure 2.13. SEM image of a cross-section of an A-alumoxane infiltrated support fired to 1100 °C (2.11) showing both the surface of the support (right side) and the interior (left side).

While the glass supports were interesting to study, they did not make very good supports for ceramic membranes. The knowledge gained from the infiltration studies led us to look for a support that would allow us to form thin membranes and greater thermal stability, namely ceramic microfiltration filters.

Alumino-Silicate Supports. The ceramic microfiltration filter that was tested as a support was a SiO₂-Al₂O₃ composite (Refractron Technologies Corp.) with pore sizes around 25 μm. This support was chosen because it is more stable to higher temperatures (1200 °C) than the silica filter supports. The mixture of alumina and silica also allows for microprobe analysis of silicon and aluminum, so it could be determined how the carboxylate-alumoxanes interacted with the support.
The Refractron support is commercially formed by pressing and sintering bulk SiO₂-Al₂O₃ particles. The particles are not uniformly shaped and appear as jagged chunks that have grown together due to sintering. The outer surface (top) and the cross-section are very similar due to the irregular shapes of the particles, see Figure 2.14 and Figure 2.15a. The overall porosity of the support is 40 – 45%. Microprobe analysis of the particles show that the alumina and silica are not intimately mixed, but rather each particle is mostly alumina with regions of silica, see Figure 2.15. According to the aluminum X-ray elemental map, it may be possible that the silica regions are actually a mix of Si-Al oxides, however, it is possible that the surrounding alumina is appearing through the silica.

Several methods were used to try and form a coating of carboxylate-alumoxanes on the surface of this support, see Table 2.2.

![SEM image of cross-section of SiO₂-Al₂O₃ ceramic support.](image)
Figure 2.15. SEM image (a) and associated Al (b) and Si (c) X-ray elemental maps of a SiO2-Al2O3 ceramic support.

The first method consisted of the dropping various concentrations of A-alumoxane onto the support and allowing it to dry. The coated support is then fired to burn out the organics. The image in Figure 2.16 is a result of five such dip and firings. Once again cracking is a problem as in the silica supports, however there is much better coverage over the area of the support. The cracking is most likely caused by shrinkage within the film during drying. A type of defect not observed in the glass supports is noticed using this support and technique. There are holes approximately 40 μm in diameter throughout the top layer. This size corresponds quite well with the size of the void spaces on the surface of the support. It is possible to decrease the number of holes with more coatings, as illustrated in Figure 2.17, where the support was repeatedly coated with A-alumoxane and fired to 1000 °C a total of ten times (2.13). It should be noted however, that even after this many coatings, cracking is still a major problem.

The second technique investigated was to make a thick gel out of the A-alumoxane with higher concentrations and smooth this gel on the surface using a razor blade (like the doctor blade process). The gel is then allowed to dry at room temperature and the technique
Table 2.2. Summary of techniques used to form alumina coatings derived from carboxylate-alumoxanes on SiO$_2$-Al$_2$O$_3$ ceramic supports.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carboxylate-alumoxane</th>
<th>Coating/infiltration method$^a$</th>
<th>Aqueous conc. wt %</th>
<th>Firing temp. (°C)</th>
<th># Repeated coatings</th>
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</table>

$^a$ See Experimental Section.

is repeated. It was hoped that by using a razor blade to scrape off any excess carboxylate-alumoxane, the cracking of the coating would be minimized. Also, by running the razor blade across the surface, carboxylate-alumoxanes should be forced to enter any void spaces on the surface of the support. The results of this experiment are shown before (2.14) and after firing to 1000 °C (2.15) in Figure 2.18. The cracking of the coating is still present, and it can be seen that the cracking occurs during the drying stage since it is present in the
unfired sample. It appears that during the drying stage of the gelled carboxylate-alumoxane, the coating shrinks and cracking occurs. During heating to higher temperatures, these cracks widen (and some new ones may occur) due to further shrinkage during burnout of the organic ligands. The crack widths are smaller than the samples treated by Method 1 (2.12 and 2.13). It should also be noted, however, that the holes that were present by just dropping the solution on the surface have mostly disappeared.

Figure 2.16. SEM images of SiO$_2$-Al$_2$O$_3$ ceramic support coated with A-alumoxane and fired to 1000 °C five times (2.12).
Figure 2.17. SEM image of a SiO$_2$-Al$_2$O$_3$ coated with A-alumoxane and fired to 1000 °C ten times (2.13).

It was decided to try and use MEA-alumoxane to decrease the cracking on the top surface because it was noted that during drying symmetric membranes the MEA-alumoxane cracked less than A-alumoxane. This is probably due to more organic content, allowing for more "give" during drying.

A thick gel of MEA-alumoxane was placed on the surface of the support and the excess was scraped away using a razor blade and dried at room temperature (2.16). The result of this experiment is shown in Figure 2.19a. As the SEM image shows, the extent of cracking is much less than in the A-alumoxane samples, see Figure 2.16a. There also appears to be pinholes along some of the crack lines. The unfired results seemed to be an improvement over using A-alumoxane for a coating material (2.14), however, after firing the MEA-alumoxane coated support (2.17) coating this was not true. Due to the larger amount of organic content in the MEA-alumoxane it shrinks more than the A-alumoxane during firing. The MEA-alumoxane coating fired to 1000 °C is shown in Figure 2.19b. The shrinkage of the MEA-alumoxane was so significant during firing that the cracks became
Figure 2.18. SEM images of a SiO$_2$-Al$_2$O$_3$ support coated with gelled A-Alumoxane (a) unfired (2.14) and (b) heated to 1000 °C (2.15).

quite large (some cracks being up to 100 μm across). The cracks are so large that it is possible to see the support through the cracks in this image.

Another coating applied in the same manner (2.18) was then attempted over the existing coating (2.17). This layer was applied to try and fill in the void spaces left by the cracking of the first layer. Unfortunately, the second layer did not appear to fill in the cracks, but rather just made another layer on top of the first one with just as many cracks.
Figure 2.19. SEM images of a SiO₂-Al₂O₃ support coated with MEA-alumoxane and scraping away the excess with a razor (a) unfired (2.16) and (b) heated to 1000 °C (2.17).

Figure 2.20 shows a SEM of sample 2.18 looking through a crack in the second layer viewing the first cracked layer. Cracks in this second layer appear to be the same size as the cracks in the first layer.

The final method used to try and obtain a membrane layer on top of the ceramic support was spin coating. Different concentrations of A- and MEA-alumoxanes were dropped on top of a spinning ceramic support (2.19 – 2.23), however, cracking also
Figure 2.20. SEM image of the second coating of MEA-alumoxane on a SiO$_2$-Al$_2$O$_3$ support heated to 1000 °C (2.18) showing the first cracked layer (2.17) below.

occurred in this technique during the drying and firing stages. It was determined that the higher the concentration of the alumoxanes, the better the coating. The edge of one of these samples (2.19) shows how the alumina layer formed from the thermolysis of the carboxylate-alumoxanes interacts with the support. Figure 2.21 shows a MEA-alumoxane derived alumina finger and the surrounding area at the edge of the support produced from the spin coating technique. The finger is much thicker than the thin layer of alumina surrounding it, and the cracks are larger. As the layer thins out, the cracks are smaller, but more common. Beyond these two layers, it is possible to view the uncoated support.

Attempts to form a thin uniform layer on the SiO$_2$-Al$_2$O$_3$ porous support was not successful. Cracks were predominant throughout the membrane layers irrespective of the techniques employed. From experience with sol-gel techniques, it is known that thick (< 20 μm) membrane layers crack due to the stresses involved during drying and subsequent firing. $^{25}$ Also, due to the large amount of void space on the surface of the support, holes
Figure 2.21. SEM image of a SiO$_2$-Al$_2$O$_3$ support spin coated with MEA-alumoxane solution and fired to 1000 °C (2.21).

that had similar dimensions were transferred to the membrane layer. In other words, we required a support that had less void space on the surface, and one that would allow a thinner membrane layer to be cast.

The alumina derived from carboxylate-alumoxanes fired to 1000 °C contains pores less than 13 nm in size, see Chapter 1. As mentioned earlier, it is desirable to have a support with larger pores so that the flow through the filter is only dependent on the membrane. Because our attempts at coating rough supports with very large pores (> 10 μm) did not allow us to form a perfect membrane layer, we decided to try and coat a support with a much smaller pore size and a smoother surface. This reasoning lead us to choose a commercially available α-alumina filter with much smaller pores.

α-Alumina Supports. The final support tested for making an asymmetric filter with carboxylate-alumoxanes was a pure alpha-alumina ceramic filter. This support was obtained from a commercial source (Refractron Technologies Corp.) made by sol-gel synthesis and calcined at 1400 °C. As can be seen from Figure 2.22, the surface of the
support is still quite rough, although not as rough as earlier supports tested. There appears to be void spaces on the top surface of the support.

A closer view of the support (Figure 2.22b) shows that the support is composed of alumina particles sintered together with particle sizes ranging from 1 μm to 0.05 μm, with many surface defects. These defects do not appear to continue through the support, as can be seen by the cross section of the support, see Figure 2.23. This support is composed of much smaller particles than the previous supports tested.

The cross-section shows that the particles are sintered together and that pore channels exist between sintered particles. The surface area (4.1 m².g⁻¹) and pore volume (0.0244 mL.g⁻¹) are quite low on the support indicating that the particles composing of the support are not porous. Nitrogen absorption reveals that there is a broad distribution of pores with a maximum pore size over 180 nm, see Figure 2.24. The large distribution of pore is to be expected, considering that the support itself is composed of particles with a large distribution of sizes.

A summary of the different techniques used to form alumina membranes on the α-alumina support is given in Table 2.3.

Following previous attempts to cast thin membranes onto silica glass and SiO₂-Al₂O₃ supports, two different techniques using A- and MEA-alumoxane aqueous solutions at different concentrations were applied to the α-alumina support (2.24 – 2.35). By SEM investigations, it was determined that the membranes formed were very thick and had many cracks.

A new method was tried: dip coating, see Experimental. First, the α-alumina support was dip coated with a 10 %wt aqueous solution of A-alumoxane (2.36). After drying in at room temperature, the filter was heated to 1000 °C. As shown in Figure 2.25, there are islands of alumina on the surface of the support. Closer magnification revealed that the support was much smoother and the alumina derived from the A-alumoxane was
Figure 2.22. SEM image of the top surface of a commercial $\alpha$-alumina support (Refrectron Technologies Corp.).

starting to form a coating. However, many problems were still evident with this membrane such as cracks, agglomerates, bare patches, curling, etc.
Figure 2.23. SEM image of the cross-section of an α-alumina support (Refractron Technologies Corp.).

Figure 2.24. Nitrogen adsorption BJH pore volume distribution of the α-alumina support.
Table 2.3. Summary of techniques used to form alumina coatings derived from carboxylate-alumoxanes on α-Al₂O₃ ceramic supports.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Carboxylate-alumoxane</th>
<th>Coating/infiltration method⁴</th>
<th>Aqueous conc. wt %</th>
<th>Firing temp. (°C)</th>
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</table>

⁴ See Experimental Section.
It was then decided to try less concentrated solutions for dip coating. While this methodology did not work well with the glass or SiO\textsubscript{2}-Al\textsubscript{2}O\textsubscript{3} supports, we reasoned that it may work with the \(\alpha\)-alumina support. We believed this would work because the pores in the support are smaller, and capillary action should draw the solution into the pores. The particles of the carboxylate-alumoxanes are too large to pass into many of the pores and agglomerate on the surface of the support. For pores that are larger, the particles travel into the support, but are eventually trapped by smaller pores. This technique should result in thin membranes that are well packed on the support.

Attempts to dip coat lower concentrations of A-alumoxane aqueous solutions were made with 5, 4, 3, 2, 1, and 0.5 \% wt. The 5, 4, and 3 \% wt (2.37, 2.38, and 2.39) solutions did not make perfect membranes, because cracking and excess carboxylate-alumoxanes were still found on the support. However, these attempts were greatly improved over the membranes formed from 10 \% wt solutions. The membranes formed from the 2 and 1\% wt (2.40 and 2.41, respectively) solutions appeared to form good

\textbf{Figure 2.25.} SEM image of alumna derived from a 10 \% wt A-alumoxane solution coated on an \(\alpha\)-alumina support (2.36).
uniform membranes, see Figure 2.26. There are no cracks, surface defects, or pin holes found within the membranes. Closer magnification (Figure 2.26b) reveals that the surface is composed of tightly packed spherical particles, consistent with alumina derived from A-alumoxane, see Chapter 1. The packing of the particles is very important if membrane integrity is to be maintained. If the membrane is merely sitting on the surface, it would be quite easy to break or remove under high-pressure conditions.

When comparing the $\alpha$-alumina support to the others studied (*vida supra*), this support works better for two reasons. The first advantage of this support is due to the smoothness of the surface. The lack of (or minimized) void spaces on the surface allows the carboxylate-alumoxanes to be physically supported by the $\alpha$-alumina support. The second improvement is a result of its small pores. Using smaller pores not only traps the carboxylate-alumoxane particles on the surface, but also the capillary action from the pores packs the particles tightly.

To have a robust membrane, the particles should be strongly attached to the support. To investigate how the particles are attached to the support, part of a membrane was scratched off using a razor blade, then cleaned with high-pressure air. If the particles were not physically attached to the surface, they should easily be removed under the high-pressure air stream. As seen in Figure 2.27, once the membrane is removed and cleaned there are still many pieces of the alumina derived from A-alumoxane attached to the support, leading to the conclusion that the membrane is physically attached to the support.

The thickness of membranes formed by using a 1 wt% aqueous solution of A-alumoxane (2.41) were approximately 2 $\mu$m thick, see Figure 2.28. Doubling the concentration of the carboxylate-alumoxane (2.40) resulted in membranes approximately 3 – 4 $\mu$m thick. These membranes are very homogeneous throughout with no obvious defects. This is crucial to forming an asymmetric membrane that does not have any leaks. Another important feature is to have a membrane that casts well to the support without any
Figure 2.26. SEM images of the A-alumoxane membrane cast on top of an α-alumina support heated to 1000 °C (2.41).

... sign of breaking away from the support. Figure 2.28a shows that the membrane conforms to the curves of the support.

As discussed above, the membranes derived from using dilute solutions combined with the dip-coating technique appears to be fairly defect free (Figure 2.26), however, even if there are just a few defects on the surface it can ruin a membrane. If these defects go
Figure 2.27. SEM image showing the removal of part of the A-alumoxane derived alumina membrane (2.41) (lower left) by a razor blade and exposing the support (upper right).

throughout the membrane into the support, the whole asymmetric filter will be compromised because any defects that are large enough will act as “sink-holes” for the particles being separated. An investigation into the defects of carboxylate-alumoxane membranes was performed by SEM. As seen in Figure 2.29, a scratch or surface defect present in the membrane does not travel throughout the membrane’s thickness. This will not interfere with the membrane’s functions. It can also be seen in Figure 2.30 that a pinhole does not travel throughout the membrane. During the SEM investigations, not one defect was found that could be considered fatal for the asymmetric filter.

The above discussion has focused around a casting technique (dip coating) that worked very well to make an ultrafiltration membrane on top of an alumina support, however, there were some experimental errors during casting that did lead to fatal defects. Pinholes are caused by air bubbles in solution, or by air getting trapped between the support and the solution during dip-coating, see Figure 2.31. This type of defect can be corrected by ensuring that the surface of the support is clean (removal of any grease) by
heating to 600 °C before dip coating it and by removing any air bubbles trapped in the carboxylate-alumoxane solution.

Another type of defect observed in some samples are hairline fractures or cracks, see Figure 2.32. This type of crack is due to shrinkage either during the drying stage or during organic burn out when transforming into alumina. This type of defect can be

![SEM images of cross-sections of an A-alumoxane derived alumina membrane (top layer) cast on an alumina support (bottom) fired to 1000 °C (2.41).](image)

Figure 2.28. SEM images of cross-sections of an A-alumoxane derived alumina membrane (top layer) cast on an alumina support (bottom) fired to 1000 °C (2.41).
Figure 2.29. SEM image of a surface defect in an A-alumoxane derived alumina membrane fired to 1000 °C.

Figure 2.30. SEM image of a pin hole defect in an A-alumoxane derived alumina membrane fired to 1000 °C.
Figure 2.31. SEM image of pinhole defects in an A-alumoxane derived alumina membrane caused by air bubbles in the alumoxane casting solution.

Figure 2.32. SEM image of hairline fracture or crack in an A-alumoxane derived alumina membrane caused by too concentrated alumoxane solution (2.37).

avoided if dilute solutions are used so that the coating on the surface of the support is limited by the capillary action of the support. If there is excess carboxylate-alumoxane on
the surface, cracking can occur upon drying which will subsequently cause the active
membrane layer to also crack.

It is also possible to have an area on the support that did not get covered by any
carboxylate-alumoxane solution during dip coating. This can be caused by not ensuring that
all the support was covered with carboxylate-alumoxane solution or by using a solution that
is too dilute, Figure 2.33. This was a problem with the membranes coated with the 0.5
%wt A-alumoxane solution (2.42).

Figure 2.33. SEM image of a defect in an A-alumoxane derived alumina membrane
(2.42) caused by using an insufficient concentrate of the alumoxane.

Conclusions

Carboxylate-alumoxanes are ideal precursors for the formation of asymmetric
ultrafiltration membranes. Several different supports and methods were investigated for the
formation of alumina membranes, and it was determined that a smooth support surface,
combined with small pores makes the ideal support for these membranes. It is also
necessary to use dilute solutions (< 2% wt) of the carboxylate-alumoxanes to obtain a thin
coating. Asymmetric membranes formed by one dip-coat of carboxylate-alumoxane
solutions were approximately 2 μm thick, and did not appear to contain any defects that
would be detrimental during ultrafiltration processes. This is a great improvement over sol-
gel methods because usually multiple dip-coatings are required to form defect free coatings.
Compared to the traditional sol-gel method, carboxylate-alumoxanes are an inexpensive,
stable, and much less time and energy intensive precursor to use for the fabrication of
alumina ultrafiltration membranes.

Experimental

General characterization and carboxylate-alumoxane synthesis were prepared per
Chapter 1. Silica glass supports were obtained from Chemglass (Vineland, NJ) with
porosity grades of medium and coarse with ASTM Designation of M and C, correlating to
pore sizes of 10 – 16 and 40 – 60 μm, respectively. SiO₂-Al₂O₃ composite ceramic
supports were obtained from the Refractron Technologies Corp. (Newark, NJ) and were
reported to have a 25 μm pore size. SEM studies were performed on either a Phillips XL-
30 ESEM, or a JEOL JSM-5300 scanning microscope. To form the solutions for coating
the supports, carboxylate-alumoxanes were added to water and stirred until completely
dissolved. The solutions are centrifuged at 4000 rpm to remove any insoluble particles,
then stored until time of use.

General Techniques of Coating and Infiltrating Membrane Supports
with Carboxylate-Alumoxanes. Summaries of reaction conditions are given in Table
2.1 (silica glass supports), Table 2.2 (SiO₂-Al₂O₃ ceramic supports), and Table 2.3 (α-
alumina ceramic supports).
**Method 1.** An aqueous solution of carboxylate-alumoxanes was dropped using a pipette onto the top of a support until complete coverage was obtained. The support was then dried at room temperature and heated to the indicated temperature.

**Method 2.** A thin layer of an aqueous solution of carboxylate-alumoxanes was placed into a Teflon dish and a support was placed into the solution so that half of the support was covered by the solution. This set-up was allowed to dry at room temperature, then heated to the indicated temperature.

**Method 3.** The supports were placed in a Schlenk flask and evacuated (1 Torr) for 10 minutes. An aqueous solution of carboxylate-alumoxanes was added through the rubber septum using a cannula, such that the support was completely immersed. The support was removed from the Schlenk flask and placed in a drying oven (60 °C) for one hour, fired to the appropriate temperature using a furnace.

**Method 4.** A gelled aqueous carboxylate-alumoxane solution was spread over a support. After 10 min., a razor blade is used to scrape off excess carboxylate-alumoxane gel. The coated support is allowed to dry at room temperature. This process is repeated 3 times, then fired to the appropriate temperature.

**Method 5.** A support was rotated between 2000 and 2500 rpm using a spin coater. The aqueous carboxylate-alumoxane solution was dripped onto the center of the support while spinning until the entire support appeared to be wet. The coated support is dried at room temperature, then fired to the appropriate temperature.

**Method 6.** A support was brought into contact with a carboxylate-alumoxane solution so that only the top surface is touching the solution for approximately 2 – 5 seconds. The support is then shaken to remove any excess solution, and dried at room temperature. The coated support is then fired to the appropriate temperature.
References


Chapter 3

Characterization of Alumina Ultrafiltration Membranes derived from Carboxylate–Alumoxanes

Introduction

Membrane technologies play an increasingly important role in pollution prevention, resource recovery and waste treatment activities.\(^1\) Due in large part to cost considerations, polymeric membranes dominate these applications\(^2\), however, the use of polymeric membranes in separations involving aggressive materials such as many organic solvents, acids, bases, and oxidants is often limited by the tolerance of the polymeric material to extreme conditions, see Table 3.1.\(^3\) Ceramic membranes are noted for their excellent mechanical strength and tolerance to solvents, as well as pH, oxidation, and temperature extremes.\(^4,5\) In addition, the amphoteric properties of ceramic surfaces result in uniquely versatile membranes for water and wastewater treatment.

An ideal ceramic membrane must be highly selective, permeable and durable.\(^2,3,4\) For aqueous applications, or aqueous/organic separations it is desirable for the ceramic to be hydrophilic to maximize flow and minimize fouling. The membrane selectivity is primarily dependent upon the pore-size distribution. The narrower the pores size distribution, the more selective the membrane. Mechanical integrity is enhanced in such applications by slip-casting a relatively thin selective membrane onto a thicker, more durable support with large pores and high permeability, i.e., an asymmetric membrane, see Chapter 2.

Not all porous materials are ideal for ultrafiltration membranes. There are many factors that need to be evaluated before a material is deemed worthy for use in ultrafiltration applications. Some of these properties include: pore size, pore size distribution (selectivity), permeability (flux), the ability to cast the membrane material
Table 3.1. Comparison of Ceramic and Polymeric Membranes for Ultrafiltration.a,b,c

<table>
<thead>
<tr>
<th>Property</th>
<th>Ceramic (inorganic)</th>
<th>Polymeric (organic)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porosity</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Flux</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Chemical resistivity</td>
<td>good</td>
<td>poor</td>
</tr>
<tr>
<td>Thermal resistivity</td>
<td>high</td>
<td>low</td>
</tr>
<tr>
<td>Autoclavable</td>
<td>yes</td>
<td>no</td>
</tr>
<tr>
<td>Lifetime</td>
<td>long</td>
<td>short</td>
</tr>
<tr>
<td>Cost</td>
<td>high</td>
<td>moderate</td>
</tr>
</tbody>
</table>

---


onto a porous support, molecular weight cut-off, fouling characteristics (roughness, surface charge, wettability), chemical inertness and resistance, and temperature stability.

The thermolysis of carboxylate-alumoxanes yield alumina that exhibit narrow pore size distributions with pore sizes in the ultrafiltration range, see Chapter 1. The pore size and porosity are dependent on the choice of carboxylate periphery and the sintering temperature. As discussed in Chapter 2, the carboxylate-alumoxanes can be cast onto α-alumina supports without cracking or defects. The goals of the following experiments are to evaluate the properties of the asymmetric filters produced by the carboxylate-
alumoxane method, and compare them to commercially available filters. The carboxylate-alumoxane derived filters are compared to the ceramic Whatman Anodisc™ (20 nm) and the polymeric Corning Nucleopore™ (15 nm) commercial filters.

**Results and Discussion**

Carboxylate-alumoxanes, [Al(O)ₙ(OH)₂(O₂CR)₂]ₙ, are prepared from the reaction of carboxylic acids (HO₂CR) with boehmite or pseudoboehmite, [Al(OH)]ₙ. The membranes that were tested were either symmetric or asymmetric, depending on the test performed. Asymmetric membranes that were tested composed of an A-alumoxane membrane supported on a commercially available α-alumina (Refractron) support. A detailed discussion the formation of asymmetric membranes with carboxylate-alumoxanes is described in Chapter 2.

**Scanning Electron Microscopy.** When forming membranes on the surface of a support it is very important to obtain uniformity throughout the thickness of the membrane. SEM images reveal that the membranes formed from A-alumoxane are highly uniform in thickness across the whole membrane (Chapter 2). As may be seen from Figure 3.1 there are no cracks or continuous void spaces within the alumina membrane prepared from A-alumoxane. The image in Figure 3.1b is formed by slowly cutting a sample of the membrane and support with a diamond saw, hence the smooth appearance in comparison to the image shown in Figure 3.1a.

It is possible to perform multiple dip coats on the support of the membrane material. Each time the membrane is dip coated and fired it increases the thickness of the membrane, see Figure 3.2. The first dip coat of the carboxylate-alumoxane appears to form a membrane with a thickness between 2 and 3 μm (Figure 3.2a). A second dip coat and subsequent firing to 1000 °C yields a membrane that is now between 4 and 6 μm in thickness (Figure
3.2b). It is important to note that no distinct boundary layer is present between the dip coats while this has been observed for some sol-gel systems.\textsuperscript{8,9} Thus, a structurally homogeneous membrane may be prepared using mixtures of different doped

![SEM Image](image)

**Figure 3.1.** SEM images of cross-sections from two different A-alumoxane derived alumina membranes slip cast on a commercial alumina support showing the uniformity of the membrane. The differences in the images are due to the method of preparation, see text.
Figure 3.2. SEM images of cross-sections from A-alumoxane derived alumina membranes supported on a commercial support after (a) one dip coat and subsequent heating to 1000 °C and (b) a second dip coat and subsequent heating to 1000 °C.

and non-doped carboxylate-alumoxanes, to prepare a multi-layer catalytic active membrane, see Chapter 4.

Although most of the filters made from carboxylate-alumoxanes were defect free, there were some exceptions. During the determination of molecular weight cut-off
(MWCO) measurements (vide infra), one filter did not perform to expectations. It was determined that this filter had pinhole defects in the membrane surface (Figure 3.3), which must pass completely through the membrane. In addition, the surface of this coating was generally not very smooth, which may have been due to a rough or dirty support. Finding only one membrane out of 10 that did not coat completely provides a rough fabrication yield of 10%, which may be improved with further research. This is excellent, considering that the sol-gel process requires the ceramic supports to be dip coated many times before a satisfactory coating is obtained.10

Figure 3.3. SEM images of the surface of an A-alumoxane derived alumina membrane supported on a commercial support showing pinhole defects.

**Nitrogen Adsorption Pore Size Distributions.** The pore size distributions reported in Chapter 1 are from the adsorption branch of the isotherm are because it gives a better representation of the pore distribution of the whole sample. However, pore size distributions from the adsorption branch are always much broader than those from the desorption branch.11 This is due to the desorption branch overemphasizing the narrow
regions of the pore structure. An example of the difference between pore size
distributions calculated from both branches of the isotherm is shown in Figure 3.4. The
retention properties of a membrane is dependent on the neck region of a pore, therefore
the pore size distributions reported in Chapter 1 might overemphasize the actual pore
diameters. This should be considered when comparing experimental retention properties
with the nitrogen adsorption pore size distributions.

![Figure 3.4. BJH pore size distributions of A-alumoxane heated to 1000 °C from both the adsorption and desorption branches of the isotherm.](image)

**Flux and Permeability.** The flow of liquid through a membrane is a very important performance characteristic of a membrane, and it is often denoted as the flux. Darcy's law (Eq. 3.1) describes the flux of water across a porous membrane, where $\Delta P =$ pressure drop across the membrane, $\mu =$ viscosity of pure water, and $R_m =$ resistance of
the membrane. This equation is only valid when the water is very clean and no material is being deposited on the surface or in the pores.

\[ J = \frac{\Delta P}{\mu R_m} \]  

(3.1)

Darcy's law may be expanded by assuming the membrane is composed of many cylindrical pores and applying Poiseuille's law. Thus, Eq. 3.2 may be obtained, where \( \varepsilon \) = surface porosity, \( r \) = average pore radius, \( l \) = thickness of membrane, and \( \tau \) = tortuosity.

\[ J = \frac{\varepsilon r^2 \Delta P}{8\mu \tau l} \]  

(3.2)

The flux of a filter may be determined experimentally by measuring the volume of water that flows through a filter of known area over a given time period under constant pressure (Eq. 3.3).

\[ J = \frac{\text{volume water}}{(\text{membrane area})(\text{time})} \]  

(3.3)

While the flux is a beneficial parameter for comparing similar filters, a better parameter is the permeability, \( k \), (Eq. 3.4) because the thickness of the filter is not a determining factor.

\[ k = \frac{\varepsilon r^2}{8\tau} \]  

(3.4)

By applying Eq. 3.4 to Eq. 3.2 it is possible to obtain a relationship that relates the flux of a membrane to the permeability (Eq. 3.5).
\[ J = \frac{k\Delta P}{\mu l} \]  

(3.5)

The permeability can be calculated by determining the flux experimentally (Eq. 3.3) and using equation 3.5, since the pressure drop across the filter, thickness of the filter, and the viscosity of water are known.

The permeability of the commercial \( \alpha \)-alumina (Refractron) supports varied for each particular support. A total of 11 supports were measured and the mean permeability was found to be 32 \( \pm 3.22 \) \( \text{nm}^2 \). The supports were coated with A-alumoxane as discussed in Chapter 2 and were fired to 1000 \( ^\circ \)C for 3 hours. The permeabilities of the coated filters were once again measured. A mean permeability of 20.01 \( \pm 2.01 \) \( \text{nm}^2 \) was determined for the coated filters. This result is surprising similar to the \( \alpha \)-alumina supports, especially considering the nitrogen adsorption results showing that the supports had a larger pore size and larger pore size distribution than the A-alumoxane membrane layer, see Chapter 2.

**Molecular Weight Cut-Off.** The rejection characteristics of an ultrafiltration membrane are of great importance when determining the effectiveness and selectivity of a filter. The rejection characteristics are usually expressed as a molecular weight cut-off (MWCO). The MWCO may vary between 100 % (complete retention of a molecular species) and 0 % (no retention). It is generally accepted that the MWCO of a filter should have a rejection coefficient (\( \%R \)) of at least 90 % (Eq. 3.6), where \( c_f \) is the solute concentration in the filtrate, and \( c_t \) is the solute concentration in the test solution.\(^{12,13,14,15,16,17}\)

\[ \%R = 100 \left( 1 - \frac{c_f}{c_t} \right) \]  

(3.6)
Different solutes may be used to determine the MWCO of a membrane. These solutes are usually polyethylene glycol (PEG) or dextran because they are readily available in a variety of molecular weights and they are inexpensive. Dextran was chosen as the solute for these tests because they are slightly branched and are more rigid than the linear PEG, so deformation (with respect to molecular diameter) due to pressure should be minimized. Additional reason for the choice of dextran is that they have been shown not to foul alumina membranes. It should be noted however, that the absence of a perfectly spherical model compounds may cause the MWCO curves not to be ideally sharp. The molecular weight characteristics of the dextran used in this study and the solute diameters are shown in Table 3.2.

**Table 3.2.** Molecular weight and solute \( d_s \) diameters of dextran in aqueous solution used to calculate the MWCO.

<table>
<thead>
<tr>
<th>Dextran</th>
<th>Average molecular weight ( \text{g.mol}^{-1} )</th>
<th>( d_s ) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>T-10</td>
<td>10,500</td>
<td>1.8 – 3</td>
</tr>
<tr>
<td>T-40</td>
<td>37,500</td>
<td>4 – 6</td>
</tr>
<tr>
<td>T-70</td>
<td>67,800</td>
<td>6 – 9</td>
</tr>
<tr>
<td>T-500</td>
<td>413,000</td>
<td>&gt;15</td>
</tr>
</tbody>
</table>

It is possible to correlate the MWCO with the average pore size for retention coefficients greater than 80 % (Eq. 3.7). By measuring the %R against the solute of a known molecular weight (and hence the solute radius, \( r_{\text{solute}} \)), the average pore radius, \( r_{\text{pore}} \), may be calculated.
\[ \%R = 100 \left( \frac{r_{\text{solute}}}{r_{\text{pore}}} \right) \]  

(3.7)

For dextran, the average radius of gyration of a real chain, \( a_r \), and a geometric chain, \( a_g \), was chosen (see Eq. 3.8 and 3.9, respectively). This is a common method for determining the average radius of dextran for filtration purposes, where \( a_r \) and \( a_g \) are expressed in Angstroms and \( M \) equals the molecular weight of the dextran.\(^{13}\)

\[ a_r = (0.096)M^{0.59} \]  

(3.8)

\[ a_g = (0.128)M^{0.5} \]  

(3.9)

The MWCO of the supports were measured and concentration of the permeate was the same as the filtrate for all molecular weights. This result indicated that the supports allowed all of the dextran to pass through the filter. This means that the MWCO of the supports is above 500 000 g.mol\(^{-1}\). This corresponds to a nominal pore size diameter above 25 nm. In contrast, the molecular weight cut-off for the A-alumoxane derived filters significantly altered. The coated filters fired to 1000 °C for 3 hours had a MWCO in the 30,000 – 40,000 g.mol\(^{-1}\) range. This corresponds to average pore diameters between 7.0 and 8.4 nm. As discussed above, one sample did not show a retention coefficient greater than 90% for any of the dextran used in this experiment. The MWCO graph was very broad, indicating that the largest dextran passed through the filter. This was later determined to be due to pinholes and a poor coating on the support, see Figure 3.3.

As expected from the data presented in Chapter 1, the MWCO was found to depend on the sintering temperature used. An A-alumoxane coated filter fired to 1000 °C with a MWCO of 30,000 g.mol\(^{-1}\) (average pore diameter of ≈ 7 nm) was dip coated again with a 1% A-alumoxane solution and fired to 600 °C. The MWCO dropped to 11, 000
g.mol\(^{-1}\), indicating a pore diameter of \(\approx 4\) nm. The smaller pore size at lower temperatures correlates with the trend noticed by SEM and the BJH nitrogen adsorption pore size distribution discussed in Chapter 1. It should be noted however, that due to the second coating, the flux dropped significantly due to increased membrane thickness (Figure 3.2).

The MWCO is not an absolute number for size rejection. The MWCO is very dependent on the solute identity (i.e., dextran) being separated from the liquid, pressure, geometry of test cell, concentration, and fouling phenomena.\(^{19}\) It is known that globular proteins are rejected easier than branched polysaccharides or flexible polymers. For example, a membrane that rejects insulin \((M_w = 5,700)\) allows passage of a dextran with a \(M_w\) of 10,000 g.mol\(^{-1}\).\(^{16}\) Therefore, the carboxylate-alumoxane derived membranes may be useful at separating species with a MWCO well below 11,000 g.mol\(^{-1}\).

**Surface Properties.** The surface charge of a membrane can have a significant effect on the separation characteristics of a filter.\(^{20}\) The flux through the membrane changes significantly with fouling, i.e. the absorption of solute on the surface of the membrane. Fouling is usually caused by ions absorbing onto the surface from the filtrate.\(^{20}\) This depends to a large extent on the charge density on the surface and its pores. By measuring the electrophoretic mobility as a function of the pH, the zeta potential of the carboxylate-alumoxane derived alumina particles that composes the membrane was determined. The iso-electric point, or point of zero charge, of symmetric membranes was determined to exist at pH = 8.5.\(^{21}\) At higher pH, the zeta-potential was negative, while at lower pH it was positive, due to the amphoteric nature of alumina. Amphoteric materials are useful for filters because the surface charge of the filter can be changed depending on the pH of the stream, making it possible to enhance or prevent solute interaction with the membrane. This approach is commonly used in ultrafiltration systems such as the electrocoating of paint and in oil and water separations.\(^{20}\)
The wettability of a membrane is another important characteristic for evaluation. Hydrophilic membranes tend to foul less than hydrophobic membranes, especially when organic filtrates are involved. Hydrophilic membranes also tend to have higher flow rates (flux) for water filtration. A surface is considered hydrophilic if the contact angle of the wetting liquid is less than 90°. The lower the angle, the more hydrophilic the surface. The carboxylate-alumoxane derived alumina membranes had contact angles of approximately 10°.

Investigations by atomic force microscopy (AFM) can lead to interesting data on membrane surface features. AFM images of symmetric membranes derived from A-, MEA-, and a 1:1 physical mixture of A- and MEA-alumoxane are shown in Figure 3.5. These images show the surface pore opening between the alumina particles. It can be noticed that the pore openings are smallest for A-alumoxane, larger for MEA-alumoxane, and the physically mixed sample has surface pores somewhere between these. This correlates well with BJH pore distribution. The particles forming the membrane surface are between 25 and 50 nm in diameter. This corresponds well with SEM images shown in Chapter 2.

It is also possible to perform line section analysis on AFM images. The cross section of an alumina membrane derived from A-alumoxane and from MEA-alumoxane is shown in Figure 3.6. The line analysis for A-alumoxane yields surface pores between 13 and 20 nm in size. The corresponding MEA-alumoxane analysis show pore diameters between 19 and 25 nm in size. This trend follows the data from SEM and BJH experiments that reveal that A-alumoxane has smaller pores than MEA-alumoxane, however, these pores are much larger than indicated by nitrogen adsorption and MWCO experiments, see above. The overestimation of pore size by AFM is due to the pore entrance geometry. When pores are made by spherical or near spherical particles, the interstitial pore space is much larger than the pore neck (see Figure 3.7). AFM measures
Figure 3.5. AFM image of a symmetric alumina membrane derived from (a) A-alumoxane, (b) MEA-alumoxane, and (c) a 1:1 physical mixture of A- and MEA-alumoxane fired to 1000 °C for 3 hours. Adapted from D. A. Bailey, C. D. Jones, A. R. Barron, and M. R. Wiesner, *J. Membr. Sci.*, 2000, in press.
the interstitial pore space, while nitrogen adsorption and the MWCO are determined by the pore neck.

The roughness of a membrane is an important factor pertaining to fouling of a membrane. If a sample has a high degree of roughness, fouling tends to occur more readily, possibly due to filtrate particles getting more readily absorbed and trapped between the features of the membrane. Also, if a sample is very smooth, it may be used as an intermediate layer for a reverse osmosis or nanofiltration membrane.\textsuperscript{26} Chemical vapor deposition techniques also require very smooth surfaces.\textsuperscript{27,28} For the CVD of palladium onto an alumina support, it has been shown that the smoother the surface, the better the resulting palladium membrane.\textsuperscript{27} The average roughness over a 1 $\mu$m scan length is quite low for alumina derived from A-alumoxane (4 nm) and MEA-alumoxane (6 nm). Sol-gel derived membranes report roughness values up to 40 nm over the same
Figure 3.6. AFM image and associated cross-section analysis alumina symmetric membranes derived from (a) A-alumoxane and (b) MEA-alumoxane fired to 1000 °C for 3 hours. Adapted from D. A. Bailey, C. D. Jones, A. R. Barron, and M. R. Wiesner, *J. Membr. Sci.*, 2000, in press.

Figure 3.7. The overestimation of pore size by AFM for pores between spheres.
scan length.26 These sol-gel derived membranes were then used as supports for silica nanofiltration membranes, therefore it may be possible to use carboxylate-alumoxane derived alumina membranes as support layers for nanofiltration or reverse osmosis.

Comparison to Commercially Available Filters. Laboratory scale filters with pore diameters reported in the same range of carboxylate-alumoxane derived filters were obtained and tested. These were the Whatman Anodisc™ filter (alumina), and the Corning Nucleopore™ filter (polycarbonate), with reported pore diameters of 20 nm 15 nm, respectively.29,30 Sol-gel derived filters are not available for laboratory scale filtration, and therefore only a literature comparison will be discussed.

As shown in Table 3.3, the carboxylate-alumoxane derived alumina membranes have a much higher surface area and porosity than the Anodisc™ and the Nucleopore™ membranes. This is because carboxylate-alumoxane derived membranes are composed of small particles and the spaces between them are pores. The Anodisc™ filter is formed from the anodic oxidation of aluminum metal, resulting in a filter made of amorphous alumina (Figure 3.8a). The pores grow so that their diameter is proportional to the applied voltage, while current governs film thickness.20 Fine-tuning of the electrochemical parameters allows for controlled growth of a membrane film with decreased pore size. The bulk porous layer contains pores approximately 100 nm, while the membrane contains pores approximately 20 nm in diameter. The Nucleopore™ filter has even less surface area and porosity than the Anodisc™ filter. This is because the filter is made from dense polycarbonate that has been exposed to high energy particle radiation applied perpendicular to the film. As the particles travel through the film, they damage the polymer matrix. By immersing the damaged polycarbonate into an acid bath, the polymeric material is etched away where the particles have damaged the matrix.23 This results in a narrow pore size distribution, however the porosity is very low (Figure 3.8b).
Table 3.3. Comparison of commercially available ultrafiltration filters.

<table>
<thead>
<tr>
<th></th>
<th>Carboxylate-alumoxane</th>
<th>Whatman Anodisc™ (20 nm)a</th>
<th>Corning Nucleopore™ (15 nm)b</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Surface area (m²·g⁻¹)</strong></td>
<td>100 – 225</td>
<td>N/A</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Porosity (%)</strong></td>
<td>54 – 69</td>
<td>25 – 30</td>
<td>&lt;15</td>
</tr>
<tr>
<td><strong>Pore size (nm)</strong></td>
<td>8 – 20</td>
<td>20</td>
<td>15</td>
</tr>
<tr>
<td><strong>Permeability (nm²)</strong></td>
<td>20</td>
<td>3</td>
<td>0.05</td>
</tr>
<tr>
<td><strong>MWCO (10³ Da)</strong></td>
<td>15 – 45</td>
<td>20b (0%)</td>
<td>20b (44%)</td>
</tr>
<tr>
<td><strong>AFM est. pore size (nm)</strong></td>
<td>16 – 23</td>
<td>30</td>
<td>27</td>
</tr>
<tr>
<td><strong>Contact angle (°)</strong></td>
<td>10</td>
<td>10</td>
<td>30</td>
</tr>
<tr>
<td><strong>Roughness (nm)c</strong></td>
<td>4 – 6</td>
<td>6.5</td>
<td>2.8</td>
</tr>
<tr>
<td><strong>Maximum operating</strong></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>temperature (°C)</td>
<td>&gt; 600</td>
<td>&lt; 400</td>
<td>140</td>
</tr>
</tbody>
</table>

a Nominal pore size reported by manufacturer


c 1 μm scan length

The carboxylate-alumoxane derived filters have smaller pore sizes than both of the other filters tested. While the Anodisc™ and Nucleopore™ filters are believed to have a uniform pore size due to their manufacturing technique, the carboxylate-alumoxane derived membranes have an equally narrow pore size distribution, especially for a particle based membrane. This is due to the uniform particle size distribution of the starting precursor. For example, for a membrane derived from A-alumoxane, the largest
Figure 3.8. Diagram illustrating the cross-section of an Anodisc™ asymmetric filter (a) and the top section of the Nucleopore™ symmetric filter (b). Shaded areas indicate solid material.

Pore diameter shown by nitrogen adsorption is under 20 nm for a membrane that has been fired to 1000 °C. Membranes fired to 600 °C show a maximum pore diameter around 8 nm. These results indicate that membranes derived from carboxylate-alumoxanes can have smaller pores than either the Anodisc™ or Nucleopore™ membranes. It is important to emphasize that not only are the pores smaller, but they are formed and can be operated at temperatures higher than either the Anodisc™ (max. temp. 400 °C) or the Nucleopore™ (max. temp. 140 °C) filters, making the resulting membrane stable to higher temperatures.29,30

Another advantage that the carboxylate-alumoxane derived alumina membranes have over the Anodisc™ and Nucleopore™ membranes is their high permeability. The
Nucleopore™ filter has a much lower porosity (and hence pore density) leading to a very low permeability (0.05 nm²). The Anodisc™ has a higher porosity (and hence pore density) and a larger pore size than the Nucleopore™ filter which combined leads to a permeability two orders of magnitudes larger (3 nm²). The carboxylate-alumoxane derived alumina membranes have a permeability an order of magnitude larger than the Anodisc™ (20 nm²). This is due to the much higher porosity. The increase in permeability is quite amazing, especially considering that the carboxylate-alumoxane derived alumina membranes have pore sizes that are smaller than both the filters tested. Other organic membranes that have been tested also show very low permeabilities (cellulose ester 100,000 Da, cellulose ester 200,000 Da, and polyamide 100,000 Da have permeabilities of 0.12, 0.05, and 0.03 nm², respectively).\(^{31}\)

Fouling characteristics measured showed that all filters are very similar. The contact angles for the carboxylate-alumoxane derived alumina membranes and the Anodisc™ filters are around 10°. The Nucleopore™ filter was 30°. These angles are very low and indicate that all the filters are hydrophilic, which reduces fouling.\(^{22}\) The roughness as determined by 1 μm scans by AFM are also very similar with the Nucleopore™ filter being the smoothest with a roughness of 2.8 nm, followed by the carboxylate-alumoxane derived alumina membranes between 4 and 6 nm, and the Anodisc™ being the roughest at 6.5 nm. These results show that all the filters tested are quite smooth, which also reduces fouling.

Alumina sol-gel derived membranes are presently the most accepted route to making alumina ultrafiltration filters. Although not available at the laboratory scale, comparisons can be made on data reported in the literature. Lennears, Keizer, and Burgraff first developed the technique of using sol-gel processes to make alumina ultrafiltration membranes, which lead to an explosion of research in ceramic filters.\(^{32,33,34,35}\) These filters, along with all the other sol-gel derived membranes discussed below were made by the controlled hydrolysis of aluminum alkoxides to form
alumina of the boehmite structure, based on the technique by Yoldas.\textsuperscript{36} There has been little development in the field of alumina ultrafiltration membranes by the sol-gel process since all alumina ultrafiltration membranes described in the literature are based on this technique.\textsuperscript{8,10,37,38,39,40} The preparation techniques may vary the drying or sintering conditions which results to small changes in porosity or pore size. These membranes have such similar characteristics that the original methodology will be discussed here,\textsuperscript{32,33,34,35} and any improvements on this method will be discussed separately later.

The sol-gel method consists of the hydrolysis of aluminum sec-butoxide at 80 – 90 °C. Nitric acid is added to the mixture to peptize the sol particles formed. Aging is allowed to occur to allow for the formation of a stable sol, which may take up to 48 hours at reflux temperatures.\textsuperscript{32,39} A porous support is then brought into contact with the sol to form a layer of boehmite on the surface.\textsuperscript{32,33,34,35} Subsequent firing of these membranes above 400 °C yields γ-alumina membranes. Usually the support needs to be slip cast between 5 and 20 times to ensure a defect free coating.\textsuperscript{10,41} The pores were investigated by nitrogen adsorption. The pore sizes at temperatures below 900 °C all had modal diameters below 9 nm. At 1000 °C the average pore diameter increases to 78 nm. The pore sizes are comparable to carboxylate-alumoxane derived alumina membranes below 900 °C, however at 1000 °C, all carboxylate-alumoxane derived membranes have a much lower average pore size around 13 nm, see Chapter 1. The reason that their alumina membrane has a much higher pore size at 1000 °C is most likely due to sintering occurring at 1000 °C in the sol-gel derived membranes.

Leeners \textit{et al.} have reported that sol-gel membranes fired to 400 °C and 800 °C were prepared with an average pore diameter of 2.7 and 4.0 nm, respectively, by nitrogen absorption.\textsuperscript{35} However, these pore sizes were calculated based on a slit shaped model, so in actuality the cylindrical pore size is more likely to be about twice as large. The MWCO (based on %R of 90) for these membranes fired to 400 and 800 °C was determined to be 2,000 and 20,000 g.mol\textsuperscript{-1}, respectively. It is interesting to note that the
membrane fired to 800 °C is slightly smaller than the A-alumoxane derived membrane which has a MWCO between 30,000 and 40,000 g.mol⁻¹. It should be noted however that the A-alumoxane derived membrane was fired to 1000 °C, and therefore it has a better chemical and thermal stability.⁴² The sol-gel derived membranes were not tested at 1000 °C because at this temperature they were found to have very large pores (> 78 nm). The A-alumoxane derived membrane fired to 600 °C showed a MWCO of 11,000 g.mol⁻¹ which falls between the 400 °C and 800 °C sol-gel derived filters. Another group testing membranes made by the same sol-gel method reports a MWCO of 44,000 g.mol⁻¹ for membranes fired to 900 °C,⁴⁹ which is similar to the A-alumoxane derived membranes fired to 1000 °C.

Lindqvist and Lindén reported using the sol-gel process to fabricate alumina membranes that have pore size distributions with a maximum pore diameter of 23 nm at 800 °C, and 30 nm at 1000 °C.⁴⁸ The dwell time during sintering at these temperatures was only 1 hour, which may be the reason why the expected large pore growth, due to sintering at 1000 °C, had not occurred.

The doping of γ-alumina membranes with lanthanum allows for the retardation of sintering at high temperatures.⁴⁷,⁴³ The addition of 3 % La (based on cation weight) by mixing La(NO₃)₃ to the alumina sol, or by impregnating the calcined membrane followed by heat treatment stabilized pore growth to 25 nm at 1200 °C.⁴⁰,⁴³ In contrast, the untreated membranes (pure alumina) exhibited pore diameters at 120 nm at the same temperature. The stabilization is proposed to be due to the formation of lanthanum oxide of the membrane surface retarding the surface diffusion⁴⁰ and onset of a La-Al Perovskite-like phase, which has better thermal stability.⁴⁷ Previous work in the Barron group has demonstrated that it is possible to dope carboxylate-alumoxanes with a variety of metal cations via a transmetalation reaction.⁴⁴,⁴⁵ If desirable, the thermal stability of the carboxylate-alumoxanes derived membranes may be further improved by the addition of metal dopants to the carboxylate-alumoxanes, and hence the derived alumina.
An important application for ceramic membranes is virus removal from water. Researchers in Japan recently tested many commercially available filters for virus retention (coliphage T4 with a diameter of 80 nm). Included in these filters were the Anodisc™ (20 nm) and the Nucleopore™ (15 nm) and two alumina membranes formed by the sol-gel technique (Cefilt™, manufactured by Nihon Gaishi with MWCO of 50, 000 and 20, 000 g.mol⁻¹). The Anodisc™ membrane did not completely retain the virus, while the Nucleopore™ and both Cefilt filters did. The Anodisc™ filters must have had some pores which were large enough to allow passage of the virus. The Cefilt™ filters have MWCOs similar to the carboxylate-alumoxane derived alumina filters and thus shows that these filters may be good candidates for virus removal.

Porous alumina membranes have also shown to be useful in gas separations. Pore diameters of 10 – 20 nm have been used to enrich H₂ and He from gas streams of N₂, CO, CO₂, C₂H₆, and C₃H₈ with separation factors of 4.1, 3.5, 2.7, 2.6, and 5.0, respectively. Based on pore size alone, it is believed that carboxylate-alumoxane derived filters may also be useful in these areas.

Conclusions

A new process for the formation of alumina ultrafiltration membranes has been investigated. The new method is an alternative method to the sol-gel technique that had been the only method of forming alumina ultrafiltration membranes. After testing and comparing the carboxylate-alumoxane derived membranes to commercially available filters it is determined that their performance is superior to commercial ultrafiltration membranes. The carboxylate-alumoxanes derived membranes have low molecular weight cut-off values and high permeability. Contact angles show that the membrane is hydrophilic and AFM shows that the surface is quite smooth, which should reduce fouling. Carboxylate-alumoxane derived alumina membranes have similar pore characteristics to sol-gel derived membranes, however the carboxylate-alumoxane
method is a much simpler and the methodology allows for chemical control of pore size. It is possible to form defect free filters with only one slip cast which will decrease the cost and time associated with the fabrication of ceramic filters. Carboxylate-alumoxane derived alumina membranes have pore size distributions similar to the sol-gel derived membranes. Carboxylate-alumoxane derived alumina membranes are more thermally stable because they can be heated to 1000 °C, while with the sol-gel process, the alumina must be doped with metals to prevent pore growth at this temperature.

**Experimental**

Characterization and carboxylate-alumoxane synthesis are as described in pervious Chapters unless otherwise indicated. Filters derived from the thermolysis of carboxylate-alumoxanes supported on Refractron™ α-alumina supports were prepared as described in Chapter 2, except filters that were coated again (as described below). Commercial filters were obtained from Whatman™ (Anodisc™) and Corning™ (Nucleopore™) and were used as received. AFM images of samples were obtained using a Nanoscope IIIa Scanning Probe Microscope (Digital Instruments, Santa Barbara, CA) in tapping mode. FESP tips were used with a pyramidal shape and end radius of 5 – 10 nm (Digital Instruments). Samples were attached to 15 mm magnetic specimen disks with carbon tape. Roughness and cross-section analysis were determined by the accompanying Nanoscope IIIa software. Contact angles were measured using a Goniometer. Surface charge was determined by measuring electrophoretic mobility with a Zeta Meter 3.0 (Zeta-Meter, Inc).

**Formation of Filters with a Second Membrane Coating.** A previously coated filter (composed of alumina derived from A-alumoxane and a Refractron™ α-alumina support fired to 1000 °C, see Chapter 2) was slip cast again with a 1 wt% aqueous
solution of A-alumoxane. The filter was dried for 2 hours at room temperature in open atmosphere, then heated to 600 °C over four hours and held at 600 °C for 3 hours.

**Permeability measurements.** Pure water flux was measured on both the carboxylate-alumoxane derived filters and commercial samples (Anodisc™ and Nucleopore™). Samples were glued using silicone adhesive to plastic rings to adapt their size to the filtration cell. The effective filtration area was 1.61 x 10⁻³ m² in all cases. The experiment was conducted using a dead end filtration cell (Amicon, model 8200). A zero air tank was connected to the cell for pressure, and a regulator was used to set the pressure to a constant value (10 psi). Permeate was collected at atmospheric pressure, so that the pressure at the end of the regulator is equal to the transmembrane pressure. Permeate volume was measured over time to calculate flux.

**Molecular weight cut-off determinations.**12 The test solution was prepared with the following concentrations of dextran fractions (Sigma Chemical Co.): 0.25 wt % T-10 (average molecular weight 10,500), 0.10 wt % T-40 (average MW 37,500), 0.10 wt % T-70 (average MW 69,800) and 0.20 wt % T-500 (average MW 413,000). Sodium azide (99%, Aldrich) was added at a concentration of 0.05 wt % to prevent bacterial growth and (NaCl) 0.05 M. Ultrapure water was used in all the experiments (10 MΩ quality).

Samples were prepared identical to those for the permeability measurements and placed in a stirred ultrafiltration cell (Amicon, Model 8200), see Figure 3.9. The cell was modified to allow for recirculation of the feed. A hole was drilled in the top of the cell to insert a 1/8" stainless steel tube, used as inlet for the feed. The existing fitting was used as exit of flow. The feed was pumped at a rate of 100 - 110 mL / min. A valve and pressure gage at the flow exit of the cell allowed for transmembrane pressure control. The pressure in the regulator was set at 7 ± 0.5 psi. The permeate samples were collected after
allowing the system to run for 30 minutes. The velocity of the flow across the membrane was kept below 0.15 ml/min to avoid deformation effects of the macromolecules with a peristaltic pump at the permeate line. A sample of the feed was taken at the end of each filtration.

![Diagram of experimental setup]

**Figure 3.9.** MWCO experiment setup in accordance to the American Society for Testing and Materials. ASTM, Publication E 1343-90.

Feed and permeate samples were analyzed by gel permeation chromatography (GPC). A HPLC system (Waters 717plus Autosampler, Waters 600E System Controller) was used with a GPC column (TosoHaas G4000PWXL). Calibration curves (molecular weight vs. elution time) were obtained running each dextran fraction separately. The peak was assumed to correspond to the average molecular weight given by the manufacturer. The elute was collected every milliliter with a fraction collector (Waters). The concentration of solute in each fraction was determined measuring organic carbon concentration, using a Total Organic Carbon Analyzer (Shimatzu, TOC 5050A). Three HPLC runs were performed with each sample and each fraction was analyzed three times by the TOC analyzer.
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Chapter 4

Investigations of Carboxylate-Alumoxanes as Precursors to Catalytically Active Membranes

Introduction

Catalytic membranes have received a great deal of attention since the advent of inorganic membranes. Indeed, the concept of combining catalytic reactions and separation functions into one unit is quite attractive due to the improved efficiency of such reactions.\(^1\) The use of membranes in catalytic reactors varies according to reactor type, where the membrane can either be catalytic or non-catalytic. In catalytic membranes, the material from which the membrane is composed of can itself be active or, the membrane can be impregnated with an active catalyst by various methods. A non-catalytic membrane is used only as a separation barrier and the actual catalysis is performed on catalyst pellets packed within the membrane reactor system, while with catalytic membranes, the catalysis is performed by the membrane.\(^2\) Catalytic membrane reactors are classified according to the type of membrane and the location of the catalyst.\(^3\) Two common types of reactors for membrane catalysis are the inert membrane reactor with catalyst on the feed side (IMRCF) and the catalytic membrane reactor (CMR). An example of these reactors, and the traditional fixed bed reactor (FBR) that does not contain a membrane is shown in Figure 4.1.\(^1\)

Traditional heterogeneous catalytic reactions between volatile and non-volatile reactants are usually performed in a FBR (Figure 1.4a). A FBR contains catalytically active materials supported on pellets that are packed into tubes. The gas and liquid flows down the tube over the particles where the catalytic reaction occurs. However, mass transport limitations is a common problem of FBRs.\(^1,4\) In an IMRCF (Figure 1.4b), the catalytic pellets are packed inside an inert membrane. In a CMR (Figure 1.4c), the
Figure 1.4. Schematic of diagrams of (a) fixed bed reactor (FBR), (b) inert membrane reactor with catalyst on the feed side (IMRCF) and (c) catalytic membrane reactor (CMR). Adapted from K. L. Young, R. Aravind, R. J. Zawada, J. Szegner, G. Cao, and A. Varma, *Chem. Eng. Sci.*, 1994, **49**, 4823.
catalyst is supported within the membrane layer, or the membrane itself is composed of a catalytic material.\textsuperscript{1,3}

The use of membrane based catalytic reactors have several advantages over FBRs. Reversible reactions, such as Eq. 4.1, are usually limited by the concentration of the reactants or the products.

\[ A \rightleftharpoons B + C \] (4.1)

If a membrane such as the IMRCF is permeselective to one of the products, the equilibrium for a reaction will be shifted to the product side, thereby increasing the efficiency of the catalyst.\textsuperscript{3} The use of IMRCFs has been demonstrated for the removal of hydrogen in dehydrogenation catalytic reactions with rate increases as high as 15%,\textsuperscript{2,5,6,7,8}

The catalytic membranes used in CMRs can be used to separate and minimize excess reactants in the process stream, see Figure 2.\textsuperscript{3} The idea is to flow reactants A and B on opposite sides of the membrane. If A and B react irreversibly (Eq. 4.2), A and B are consumed by the catalyst inside the membrane.

\[ A + v_B B \rightarrow v_C C + v_D D \] (4.2)

The fluxes of each reactant can be adjusted to match the stoichiometric requirements of the reactions.\textsuperscript{3} By performing the catalysis in this manner, possible side reactions are minimized and one reactant can be continuously recirculated until complete conversion is obtained. The catalytic membrane may also be used in multiphase reactions such as in Eq. 4.3. An example of this reaction using a catalytic membrane is shown in Figure 4.3.

\[ A_{(g)} + B_{(l)} \longrightarrow P_{(l)} \quad (4.3) \]

The liquid and gas reactants are separated on opposite sides of the membrane. Due to capillary action, the liquid penetrates the catalytic membrane forming a gas-liquid interface where both are in contact with the catalyst.\(^3\) This system has the advantage that if A is only slightly soluble in B, it does not have to diffuse through the liquid film to get to the catalyst. This has lead to catalysis performed in CMRs to have rate of reaction increases up to 20 times that in FBRs.\(^1,3\)
Figure 4.3. Membrane system for rate enhancement of a multiphase catalytic reaction.

It is possible to add catalytically active materials to ceramic membranes by either modifying inert membranes by impregnation, precipitation-deposition, ion-exchange, or grafting techniques or by in-situ modifications such as sol-gel co-precipitation. The modification of inert membranes (i.e., post fabrication modification) does not always yield the desired active phase loading and location of the catalyst in the membrane. In addition, the post-fabrication modification technique also decreases the permeability of the membrane, probably due to clogging of pores. It is therefore desirable to find alternative methods for the fabrication of catalytically active membranes.
Previous work in the Barron research group has shown that carboxylate-alumoxanes can be doped with either a metal acetylacetonate complex, M(acac)$_n$, or a salt results in a transmetallation reaction and the formation of a doped-alumoxane, see Figure 4.4.$^{12,13,14}$ Upon thermolysis these doped-alumoxanes result in homogeneously doped-alumina. If the alumoxane is reacted with a large stoichiometric amount of the metal compound or salt, then phase pure ternary aluminum oxides are formed, e.g., Y-doped alumoxanes yield Y$_3$Al$_5$O$_{12}$ (YAG) upon thermolysis.$^{13}$ The formation of single phased materials is similar to that of traditional sol-gel methodologies, however, the alumoxane precursors are indefinitely stable, in solid and solution. In addition, these precursors show no propensity towards segregation or polymerization, and are readily processed in aqueous or hydrocarbon medium. The stability of the doped-alumoxanes and uniformity of the subsequent oxide is a consequence of the atomic level mixing produced by a unique substitution reaction. A transition metal or lanthanide ion is exchanged for an aluminum ion within the alumoxane nano-clusters and Al$^{3+}$ is elimination as Al(acac)$_3$ or [Al(H$_2$O)$_6$]$^{3+}$.

![Reaction Diagram]

**Figure 4.4.** Schematic representation of the reaction of carboxylate-alumoxane with M(acac)$_3$. 
The doped alumina formed from the thermolysis of doped carboxylate-alumoxanes have previously shown to be catalytically active.\textsuperscript{14} Manganese-doped alumina (Mn-Al\textsubscript{2}O\textsubscript{3}) formed via the doping of carboxylate-alumoxanes with Mn(acac)\textsubscript{3} at room temperature provides enhanced catalytic performance for the low temperature catalytic oxidation of dichloromethane as compared to over traditional approaches such as MnO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} prepared by the incipient wetness method, and commercial Pt/Al\textsubscript{2}O\textsubscript{3}, see Figure 4.5.

![Graph showing conversion of CH\textsubscript{2}Cl\textsubscript{2} as a function of temperature for different catalysts](image)

**Figure 4.5.** Percentage conversion/decomposition of dichloromethane (CH\textsubscript{2}Cl\textsubscript{2}) as a function of catalyst temperature for a series of oxidation catalysts: (■) Mn-doped Al\textsubscript{2}O\textsubscript{3}, formed from the sintering of Mn-doped hexanato-alumoxane; (●) MnO\textsubscript{2}/Al\textsubscript{2}O\textsubscript{3} formed by the incipient wetness method; and (△) commercial Pt-Al\textsubscript{2}O\textsubscript{3}. R. L. Cook, C. C. Wong, C. J. Harlan, A. Kareiva, and A. R. Barron, *Mater. Res. Soc. Symp. Proc.*, 1997, 454, 169.

The results of doped-carboxylate-alumoxanes as precursors to mixed metal and doped aluminum oxides as alumina based catalysts and catalyst supports led us to investigate the possibility of using carboxylate-alumoxanes as precursors to heterogeneous catalysts. We proposed that by reacting a catalytically active metal with
chemically functionalized carboxylate-alumoxanes, it should be possible to covalently bond these metals to an inorganic support with great dispersion. Thermolysis of the surface-modified carboxylate-alumoxane should result in the removal of the organic periphery, leaving behind a well dispersed catalyst on the resulting alumina. The initial studies of this method involve metathesis of higher olefins.

Olefin metathesis is an interchange of carbon atoms between a pair of double bonds. These reactions can be grouped into three categories: exchange, ring-opening metathesis polymerization (ROMP), and ring-closing metathesis.\textsuperscript{15} We are currently interested in investigating the exchange reaction for higher olefins, i.e., Equation 4.4.

\[
\begin{align*}
R_1\text{CH} &\equiv \text{CHR}_2 \\
+ &
R_3\text{CH} &\equiv \text{CHR}_4 \\
\rightarrow &
R_1\text{CH} &\equiv \text{CHR}_2 \\
&
R_3\text{CH} &\equiv \text{CHR}_4
\end{align*}
\] (4.4)

There are many different transition metals that show activity for metathesis reaction, however only three show high activities: molybdenum, tungsten, and rhenium.\textsuperscript{15,16} There has been many studies on MoO\textsubscript{3} supported catalysts therefore this system was chosen for the initial studies. Heterogeneous MoO\textsubscript{3} catalysts are widely used in industrial petrochemical processes. We are interested in metathesis of higher olefins for the Shell Higher Olefin Process (SHOP), see Figure 4.6.\textsuperscript{17,18} The SHOP process converts ethene to detergent-range alkenes. Unfortunately, not all of the olefins made from oligomerization of ethene are within the valuable C\textsubscript{6}-C\textsubscript{18} range. The olefins above and below than this range have their double bonds fully isomerized, and metathesis is performed to enhance the yield of detergent-range olefins.

Traditional methods for the synthesis of MoO\textsubscript{3} supported catalysts for metathesis can be grouped into three categories: (a) Impregnation of the support,\textsuperscript{19,20} (b) treatment of the support with Mo(CO)\textsubscript{6},\textsuperscript{21,22} and (c) treatment of the support with organomolybdenum compounds [e.g. (\pi-C\textsubscript{3}H\textsubscript{5})\textsubscript{4}Mo].\textsuperscript{23,24} Supports are generally metal
Figure 4.6. Flow diagram of the Shell Higher Olefin Process (SHOP).

oxides such as alumina, silica, or titania. After the catalyst is attached to the support, heat
treatment and oxidation or reduction is often necessary to bring the catalyst into an active
state.\textsuperscript{25} Catalysis is initiated and then propagated by the formation of metal carbene
complexes. It is usually important to pay special attention to how the catalyst systems are prepared due to many factors that affect metathesis activity. These factors include the proportions of components, pre-treatment procedures, order in which the components of the system are mixed, the period of incubation, and the nature and concentration of the active species.

This chapter reports a novel technique to form heterogeneous catalysts using surface-modified carboxylate-alumoxanes as precursors. As discussed in Chapter 1, the alumina nanoparticles formed from the thermolysis of carboxylate-alumoxanes exhibit pore diameters in the ultrafiltration range and have narrow pore size distributions, which is a characteristic of highly selective membranes. The carboxylate-alumoxanes are readily cast onto ceramic supports to form asymmetric filters (Chapter 2). These filters are uniform, smooth, and exhibit low molecular weight cut-off values and high permeability (Chapter 3). In addition, carboxylate-alumoxanes may be doped with metals via a transmetallation reaction to form catalytically active materials. Given these results, it was proposed that doped carboxylate-alumoxanes should be good precursors for the fabrication of catalytically active membranes.

**Results and Discussion**

Carboxylate-alumoxanes, \([\text{Al(O)}_x\text{(OH)}_y\text{(O}_2\text{CR)}_z\text{]}_n\), are prepared from the reaction of carboxylic acids (\(\text{HO}_2\text{CR}\)) with boehmite or pseudoboehmite, \([\text{Al(O)}\text{OH}])_n\). The doping of the carboxylate-alumoxanes was accomplished by a transmetallation reaction with the appropriate metal acetylacetonate, see Experimental. The doped carboxylate-alumoxanes were cast as a membrane onto an \(\alpha\)-alumina support, as per Method 6, Chapter 2, see Experimental. The following discussion is separated into two parts: first the formation of surface-modified carboxylate-alumoxanes as precursors to heterogeneous catalysts and membranes, and secondly, the use of doped carboxylate-alumoxanes as precursors to catalytic membranes.
Precursors for Heterogeneous Catalysts. Boehmite was refluxed in a water solution containing an appropriate amount of gluconic acid, HO$_2$C[CH(OH)]$_5$CH$_2$OH, to form gluconate-alumoxane, see Experimental. The gluconate-alumoxane is reacted with either 8 wt% or 20 wt% MoO$_3$ in an aqueous solution for 24 hours. The reaction is then filtered to collect the molybdate substituted alumoxane nanoparticles. Because the gluconate-alumoxane has hydroxyl sites available on the organic ligand, the molybdenum becomes covalently bonded to the inorganic support. The catalyst precursor is then fired to 500 °C to form alumina with MoO$_3$ uniformly dispersed on the surface. As can be seen in Figure 4.7, the 8 wt% Mo-Al$_2$O$_3$ catalyst shows molybdenum uniformly dispersed with no agglomeration of MoO$_3$. However, as the wt% of MoO$_3$ is increased to 20 wt%, agglomeration of MoO$_3$ occurs, see Figure 4.8.

![Image](image_url)

Figure 4.7. X-ray elemental maps of Mo (a) and Al (b) of 8 wt% Mo-Al$_2$O$_3$ derived from the thermolysis of Mo-surface modified gluconate-alumoxane.
Figure 4.8. X-ray elemental maps of Mo (a) and Al (b) of 20 % Mo-Al$_2$O$_3$ derived from the thermolysis of Mo-surface modified gluconate-alumoxane.

The XPS of the molybdenum-surface modified gluconate-alumoxanes, molybdenum oxide, and a catalyst fabricated by the incipient wetness technique are shown in Table 4.1. Molybdenum has the well-known doublet peak stemming from emissions from the 3d levels. Mo$^{\text{VI}}$, Mo$^{\text{V}}$, Mo$^{\text{IV}}$, and Mo$^{\text{II}}$ have reported 3d$_{5/2}$ binding energies of 232.8, 231.6, 228.8, and 227.8 $\pm$ 1 eV.$^{15,16,23,30,31,32}$ The difference between the Mo 3d binding energies of Mo$^{\text{VI}}$ and Mo$^{\text{IV}}$ have been reported to be in the range 0.7 – 3.3 eV for molybdenum oxide supported catalysts.$^{23}$ While this large range is makes it extremely difficult to definitively assign characterization, some trends can be noticed for the catalysts produced. MoO$_3$ contains one species (Mo$^{\text{VI}}$) as indicated by XPS and is shown for comparison in Table 4.1. The 8 wt% Mo-Al$_2$O$_3$ impregnated by the incipient wetness technique after heat treatment contains two Mo$^{\text{VI}}$ in two different environments. The 8 and 20 wt% Mo-surface modified gluconate-alumoxane exhibit very similar XPS spectra, with two different Mo$^{\text{VI}}$ environments present. After thermolysis at 500 °C, three different molybdenum environments are present within the alumina: Mo$^{\text{VI}}$ (Mo 3d$_{5/2}$ = 232 ±.25 eV), and two new species, most likely Mo$^{\text{IV}}$ and Mo$^{\text{II}}$ (Mo 3d$_{5/2}$ = 229.1 ±.1
Table 4.1. XPS data from the formation and thermolysis molybdenum metathesis catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Heat treatment</th>
<th>Mo 3d&lt;sub&gt;5/2&lt;/sub&gt;</th>
<th>Mo 3d&lt;sub&gt;3/2&lt;/sub&gt;</th>
<th>Abundance (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MoO&lt;sub&gt;3&lt;/sub&gt;</td>
<td>none</td>
<td>232.5</td>
<td>235.5</td>
<td>100</td>
</tr>
<tr>
<td>8wt% MoO&lt;sub&gt;3&lt;/sub&gt;-Al&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; by the incipient wetness technique</td>
<td>500</td>
<td>232.82</td>
<td>235.95</td>
<td>44.8</td>
</tr>
<tr>
<td>8%wt Mo-surface modified gluconate-alumoxane</td>
<td>none</td>
<td>231.35</td>
<td>234.48</td>
<td>27.7</td>
</tr>
<tr>
<td>8%wt Mo-surface modified gluconate-alumoxane</td>
<td>500</td>
<td>227.64</td>
<td>230.77</td>
<td>19.0</td>
</tr>
<tr>
<td>20%wt Mo-surface modified gluconate-alumoxane</td>
<td>none</td>
<td>232.12</td>
<td>235.25</td>
<td>58.5</td>
</tr>
<tr>
<td>20%wt Mo-surface modified gluconate-alumoxane</td>
<td>500</td>
<td>227.86</td>
<td>230.99</td>
<td>26.5</td>
</tr>
<tr>
<td></td>
<td></td>
<td>229.13</td>
<td>232.26</td>
<td>28.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td>232.48</td>
<td>235.58</td>
<td>45.1</td>
</tr>
</tbody>
</table>
eV, and 227.7 ± 2 eV, respectively). While the active site of catalysis is believed to occur
in less than 1 % of the total molybdenum atoms present, studies are currently being
conducted to determine the exact nature of these molybdenum sites.

The catalyst is then added to fully isomerized C\textsubscript{16} olefin under an argon
atmosphere, and the amount of C\textsubscript{16} conversion is monitored by gas chromatography
(GC), see Experimental. The conversion of fully isomerized C\textsubscript{16} olefins by our 8 wt%
Mo-Al\textsubscript{2}O\textsubscript{3} and our 20 wt% Mo-Al\textsubscript{2}O\textsubscript{3} catalysts are compared to an Al\textsubscript{2}O\textsubscript{3}
impregnated with 8 wt% MoO\textsubscript{3} and a commercial catalyst, see Figure 4.9. As may be expected, the
highly optimized commercial catalyst has the best activity of all the catalysts
investigated. The 8 wt% Mo-Al\textsubscript{2}O\textsubscript{3} shows an activity about two-thirds that of the
commercial catalyst. A traditional method of impregnation of alumina and the 20 wt%
Mo-Al\textsubscript{2}O\textsubscript{3} catalyst derived from the surface modified carboxylate-alumoxane shows no
activity for C\textsubscript{16} olefin metathesis under these conditions. It has been shown that a high
molybdenum concentration decreases the activity, probably due to inactive bulk MoO\textsubscript{3}.\textsuperscript{33}
This is most likely why the 20 wt% Mo-Al\textsubscript{2}O\textsubscript{3} shows no activity as agglomeration of
MoO\textsubscript{3} is observed by EDX analysis (Figure 4.8). It is unknown why the impregnated
alumina shows no activity, however inactive bulk MoO\textsubscript{3} may also be an explanation
because this traditional method does not ensure fully dispersed MoO\textsubscript{3}.

While the 8wt% Mo-Al\textsubscript{2}O\textsubscript{3} catalyst showed promising activity, there have been
repeatability problems from batch to batch of the surface modified carboxylate-
alumoxanes. Studies are currently being investigated to improve the consistency of the
reactions.

The surface modified carboxylate-alumoxane was made into a 1 wt% aqueous
solution and attempts were made to dip coat an α-alumina support. Unfortunately, all
Figure 4.9. The % conversion of fully isomerized C₁₆ olefin by the commercial catalyst (■), the 8wt% Mo-Al₂O₃ catalyst (▲), the 20wt% Mo-Al₂O₃ catalyst (●), and the Al₂O₃ impregnated with 8wt% MoO₃ (○).

Attempts resulted in badly cracked and poorly attached membranes. To try and determine why the membranes did not form nice membranes, such as with other carboxylate-alumoxanes studied, an attempt was made to cast gluconate-alumoxanes onto the α-alumina support. It was determined that the gluconate-alumoxane dries to a powder instead of nicely packed particles, or agglomerates as other carboxylate-alumoxanes studied, see Chapter 1. It is believed that the gluconate-alumoxane is responsible for the inability to form a catalytic membrane with this surface modified carboxylate-alumoxane. Investigations are currently underway to make other surface modified carboxylate-alumoxane derived catalytic membranes by changing the organic periphery on the carboxylate-alumoxane.
Doped carboxylate-alumoxanes as precursors for catalytic membranes.

Doped carboxylate-alumoxanes were synthesized by adding the appropriate metal acetylacetonate to MEEA-alumoxane, see Experimental.\textsuperscript{12,28,34} Titanium and erbium were chosen as dopants because these metals demonstrate that both transition metals and lanthanides can be used. Indeed, any metals that have been used as dopants in carboxylate-alumoxanes could have been used since the doped nanoparticles exhibit similar properties to the non-doped nanoparticles.\textsuperscript{12,13} Aqueous solutions (1 \% wt) of the doped carboxylate-alumoxanes were prepared and dip coated onto \(\alpha\)-alumina supports (Refractron Technologies Corp.), see Experimental. After drying at room temperature, the asymmetric filters were fired to 1000 °C.

Titanium and erbium doped alumina membranes cast by this method showed similar properties, i.e. asymmetric filters with a doped alumina membrane layer. SE and associated X-ray elemental map for the Er doped membrane top and cross-section are shown in Figure 4.10 and 4.11, respectively. As observed in these images, the Er is well dispersed, due to the intimate mixing of the dopant into the carboxylate-alumoxane precursors.\textsuperscript{12,13} In addition, the X-ray elemental map of the cross-section (Figure 4.11b) shows that the Er is concentrated in the membrane layer. This is also demonstrated in the Ti doped membrane, see Figure 4.12. Although the support shows traces of Ti, this is not due to the doped carboxylate-alumoxane. It was determined by EDX that the \(\alpha\)-alumina support also contains some Ti, which is a common sintering additive for alumina ceramics.\textsuperscript{35}

In general, the first dip coat of the doped carboxylate-alumoxane formed membranes that were similar to the membranes formed in Chapter 2. However, some pinholes were present in the membranes, see Figure 4.10a. This problem was corrected by first coating the \(\alpha\)-alumina support with a layer of A-alumoxane, the same as the filters tested in Chapter 3, then coating the asymmetric filter once again with the doped
Figure 4.10. SE image (a) and associated Er (b) X-ray elemental maps of the top of an α-alumina support coated with Er-doped MEEA-alumoxane and fired to 1000 °C.

Figure 4.11. SE image (a) and associated Er (b) X-ray elemental maps of the cross-section of an α-alumina support coated with Er-doped MEEA-alumoxane and fired to 1000 °C.

carboxylate-alumoxane. A SEM image of the top of a Ti doped membrane is shown in Figure 4.13, demonstrating the lack of defects and uniformity of the coating. The better coating is probably due to the smoother surface that the alumina derived from A-alumoxane provides over the support.\textsuperscript{36,37,38}
Figure 4.12. SE image (a) and associated Ti (b) X-ray elemental maps of the cross-section of an \( \alpha \)-alumina support coated with Ti-doped MEEA-alumoxane and fired to 1000 °C.

Figure 4.13. SEM image of the top of an \( \alpha \)-alumina support coated first with alumina derived from the thermolysis of A-alumoxane, then coated with Ti-doped MEEA-alumoxane and fired to 1000 °C.

The formation of catalytically active membranes in situ by using doped carboxylate-alumoxanes or metal surface modified carboxylate-alumoxanes results in several advantages over post fabrication methods. During impregnation or precipitation...
techniques, a common problem is non-uniformity or placement of the catalyst within the membrane.\textsuperscript{1,10} The use of doped carboxylate-alumoxanes allows for the fabrication of membranes in which the catalytic metal is intimately mixed with the alumina nanoparticles composing the membrane. The intimate mixing before fabrication of the membrane also allows for the production of membranes in which the catalyst stays in the membrane layer and does not become dispersed throughout the support or intermediate layers, as is common with post fabrication techniques.\textsuperscript{1,10} Using doped or surface modified carboxylate-alumoxanes also shortens the process times necessary to form catalytically active membranes. With post fabrication methods, the membrane has already been fired to a high temperature (> 600 °C) and then the membrane is impregnated with a catalyst and fired again to burn out residual organics or salts or to activate the metal catalyst. These steps can be combined into one step with the use of doped or surface modified carboxylate-alumoxanes. Also, the formation of ceramic membranes in general is quite expensive, and a mistake in the impregnation step during post fabrication techniques could ruin the filter. By using proposed carboxylate-alumoxane methods, it is possible to tailor and test the catalyst concentration prior to casting the membrane on the support.

The use of doped or surface modified carboxylate-alumoxanes also allows for the formation of non-uniform, or layered, catalytic membranes, see Figure 4.14. It has been reported that the closer the catalyst is located to the feed side of the membrane, the better the performance of the reactor.\textsuperscript{1,10} It has been demonstrated above that by first coating the support with an alumina membrane derived from carboxylate-alumoxanes, then coating the membrane with doped carboxylate-alumoxanes, it is possible to form layered catalytic membranes (Figure 4.13). It should also be possible to form membranes with different active catalysts supported in separate levels (Figure 4.14c).
Figure 4.14. Schematic of possible layered catalytic membranes that may be fabricated using doped or surface modified carboxylate-alumoxanes.

Conclusions

A surface modified carboxylate-alumoxane derived catalyst (8 %wt Mo-Al₂O₃) for the metathesis of C₁₆ olefins showed high activity when compared to a catalyst made by the impregnation method. When compared to the highly optimized commercial catalyst, these results appear promising. Studies are currently being investigated into the control of batch consistency and the ability to cast the surface modified carboxylate-alumoxanes into membranes. The use of metal-doped carboxylate-alumoxanes as precursors to catalytic membranes has been demonstrated by the fabrication of titanium and erbium doped alumina membranes. Using doped carboxylate-alumoxanes has
advantages over traditional post-fabrication modification methods including uniform
distribution of the catalyst only within the membrane, less energy intensive, and the
ability to produce layered catalytic membranes.

**Experimental**

Characterization was performed by methods reported in previous chapters unless
otherwise indicated. Carboxylate-alumoxanes were prepared as described in Chapter 1.
Filters derived from the thermolysis of carboxylate-alumoxanes supported on a-alumina
supports (Refractron Technology Corporation) were prepared as described in Chapter 2
or Chapter 3. Electron probe microanalysis (EPMA) was performed on a Cameca SX50
Electron Microprobe using techniques and imaging modes including: energy dispersive
X-ray spectroscopy (EDS), secondary electron emission (topography, morphology), back
scattered electron emission (atomic number contrast), X-ray emission (quantitative
analysis and element distribution mapping), and cathodoluminescence (trace element
distribution). In addition, wavelength dispersive X-ray distribution maps (i.e., elemental
maps) were used to determine the compositional homogeneity of the catalysts. The
following microprobe calibration standards were used: Mo metal (Mo), corundum Al₂O₃
(Al), quartz SiO₂ (O), ilmenite FeTiO₃ (Ti), and erbium orthophosphate ErPO₄ (Er). X-
ray photon spectroscopy (XPS) measurements were obtained on a PHI 5700 ESCA
system with a 7 mm Al monochromatic X-ray source at 45° take-off angles with a base
pressure of 10⁻¹⁰ Torr. Powdered samples were mounted by pressing them into indium
foil. Gas chromatography (GC) was performed on a HP 6890 using a DB-5 column. The
samples were diluted with dichloromethane.

**Synthesis of Gluconate-Alumoxane.** A 50 wt% aqueous solution of gluconic
acid (421 g) was added to 1200 mL of water and stirred. Catapal® B boehmite (64 g) was
then slowly added and refluxed for 24 hrs. The brown solution was then cooled to room
temperature and the solvent was removed under reduced pressure to form a brown gel. The tan-colored gluconate-alumoxane was then precipitated by the addition of ethanol and collected by filtration.

**Synthesis of MoO₃ Supported on Gluconate-Alumoxane.** Gluconate-alumoxane (30.0 g) was dissolved in 500 mL of water and refluxed. MoO₃ (3.21 g and 20.04 g for 8% and 20% respectively) was added and allowed to reflux for 24 hours. The solution was then cooled and the solvent was removed under reduced pressure to leave a dark brown solid. The solid was then refluxed for 1.5 hours in ethanol resulting in a light brown powder. The MoO₃ supported on gluconate-alumoxane was collected by filtration and activated as described below.

**Synthesis of Impregnated Alumina Catalyst.** Ammonium molybdate (Aldrich) (8 wt%) was dissolved in water and added to an extruded alumina. The water was removed under reduced pressure. The catalyst was then dried at 100 °C and activated as described below.

**Activation of MoO₃-Al₂O₃ catalysts.** All catalysts were activated by heating to 500 °C in air for four hours, then under nitrogen for 12 hours.

**Metathesis of Fully Isomerized C₁₆ olefins.** The MoO₃-Al₂O₃ catalyst (1.0 g) was added to 20 mL of fully isomerized C₁₆ olefins in a flask under argon atmosphere. 2500 ppm tetrabutyltin was added as a promoter. The reaction was heated to 120 °C and aliquots were taken at numerous time intervals and analyzed by gas chromatography to determine the amount of C₁₆ conversion.
Synthesis of Titanium Doped MEEA-alumoxane. To a solution of MEEA-alumoxane (10 g) in 200 mL CHCl₃, a solution of Ti(acac)₃ (20 g) in 200 mL of CHCl₃ was added and refluxed overnight. The volatiles were removed under vacuum and the yellow solid was washed with Et₂O and filtered to yield the Ti-doped MEEA-alumoxane.

Synthesis of Erbium Doped MEEA-alumoxane. To a solution of MEEA-alumoxane (12 g) in 300 mL H₂O, a solution of Er(acac)₃ (6.07 g) in 200 mL of H₂O was added and refluxed overnight. The volatiles were removed under vacuum and the pink solid was washed with Et₂O and filtered to yield the Er-doped MEEA-alumoxane.

Formation of Metal Doped Alumina Membranes. An α-alumina support was brought into contact with a 1 %wt aqueous solution of the appropriate doped-carboxylate-alumoxane solution so that only the top surface is touching the solution for approximately 2 – 5 seconds. The support is then shaken to remove any excess solution, and dried at room temperature. The coated support is then fired to 1000 °C to yield the doped alumina asymmetric filter.

Formation of Layered Catalytic Membranes. An α-alumina support was brought into contact with a 1 %wt aqueous solution of A-alumoxane so that only the top surface is touching the solution for approximately 2 – 5 seconds. The support is then shaken to remove any excess solution, and dried at room temperature. The coated support is then fired 1000 °C. The asymmetric filter is then brought into contact with a 1 %wt aqueous solution of Ti doped-carboxylate-alumoxane so that only the top surface is touching the solution for approximately 2 – 5 seconds. The coated asymmetric filter is then shaken to remove any excess solution, and dried at room temperature. The filter is then fired to 1000 °C to yield the layered metal-doped alumina asymmetric filter.
References


21 G. W. Wagner and B. E. Hanson, *Organometallics*, 1987, 6, 2494.


Conclusions

The carboxylate-alumoxanes are a novel, environmentally benign precursor for developing alumina bodies and films with controlled porosity. Four different organic peripheries were investigated (A-, MA-, MEA-, and MEEA-H) and the resulting morphology and porosity characteristics were determined. The methodology of the carboxylate-alumoxane system allows for chemical control over the precursors to alumina ceramics, which in turn determines the properties of the alumina formed during thermolysis. Alumina derived from A- and MEA-alumoxane have a particulate morphology, while alumina derived from MA- and MEEA-alumoxane are composed of aggregates of smaller particles. The properties of the alumina at higher temperatures are dependent on the type of morphology and on the length of the carboxylate periphery. Also, average pore sizes may be altered through either physical or chemical mixtures of the carboxylate substituents. Physical mixing of two (or more) carboxylate-alumoxanes has the advantage of simplicity in preparation and processing.

Carboxylate-alumoxanes are ideal precursors for the formation of asymmetric ultrafiltration membranes. Several different supports and methods were investigated for the formation of asymmetric alumina membranes, and it was determined that a smooth support surface, combined with small pores makes the ideal support for these membranes. The use of dilute aqueous solutions (< 2 wt%) of the carboxylate-alumoxanes allows for the formation of thin membranes (= 2 μm thick) with only one dip-coat, which did not appear to contain any defects that would be detrimental during ultrafiltration processes. This is a great improvement over the traditional sol-gel method because usually multiple dip-coatings are required to form defect free coatings.

Compared to sol-gel method, carboxylate-alumoxanes are an inexpensive, stable, and much less time and energy intensive precursor to use for the fabrication of alumina ultrafiltration membranes. After testing and comparing the carboxylate-alumoxane
derived membranes to commercially available filters it is determined that their performance is superior to commercial ultrafiltration membranes.

The carboxylate-alumoxanes derived membranes have low molecular weight cut-off values and high permeability. Contact angles show that the membrane is hydrophilic and AFM analysis revealed that the surface is quite smooth, which should reduce fouling. Carboxylate-alumoxane derived alumina membranes have similar pore characteristics to sol-gel derived membranes, however the carboxylate-alumoxane method is a much simpler and the methodology allows for chemical control of pore size. It is possible to form defect free filters with only one slip cast which will decrease the cost and time associated with the fabrication of ceramic filters. Carboxylate-alumoxane derived alumina membranes are also more thermally stable because they can be heated to 1000 °C, while with the sol-gel process, the alumina must be doped with metals to prevent pore growth at this temperature.

The use of metal-doped carboxylate-alumoxanes as precursors to catalytic membranes has been demonstrated by the fabrication of titanium and erbium doped alumina membranes. Using doped carboxylate-alumoxanes has advantages over traditional post-fabrication modification methods including uniform distribution of the catalyst only within the membrane, less energy intensive, and the ability to produce layered catalytic membranes.
Appendix A
Publications


