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Use of Epoxides in the Sol−Gel Synthesis of Porous Iron(III) Oxide Monoliths from Fe(III) Salts

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Iron oxide-based porous solids were prepared by a sol−gel process using Fe(III) salts in various solvents. It was observed that the addition of propylene oxide to Fe(III) solutions resulted in the formation of transparent red-brown monolithic gels. The resulting gels were converted to either xerogels by atmospheric drying or aerogels by supercritical extraction with CO_2(l). Some of the dried materials were characterized by nitrogen adsorption and desorption analysis and transmission electron microscopy (TEM). The results of those analyses indicate that the materials have high surface areas (∼300−400 m^2/g), pore sizes with mesoporic dimensions (2−23 nm), and a microstructure made up of 5−10 nm diameter clusters of iron(III) oxide. The dependence of both gel formation and its rate was studied by varying the epoxide/Fe(III) ratio, the Fe(III) precursor salt, amount of water (H_2O/Fe(III)) present, and the solvent employed. All of these variables were shown to affect the rate of gel formation and provide a convenient control of this parameter. Finally, an investigation of the mechanism of Fe_2O_3 gel formation was performed. Both pH and nuclear magnetic resonance (NMR) studies suggest that the added epoxide acts as an irreversible proton scavenger that induces the Fe(III) species to undergo hydrolysis and condensation to form an inorganic iron oxide framework. This method can be extended to prepare other transition- and main-group metal oxide materials.

Introduction

The many phases of the iron(III) oxides have significant relevance in the areas of academic and industrial research. The fields of chemistry, medicine, soil science, geology, and corrosion science have previous and ongoing interests in the iron oxides.[1] Iron oxides have found use in industry as inorganic pigments, ceramics, and magnetic storage media.[2−5] Academic pursuits have utilized iron(III) oxides and iron(III) oxo-bridged monomers and oligomers as catalysts,[6−11] electrochemical sensors,[12−16] and model compounds for biologically important protein systems.[17,18] In all of these areas there is a need for straightforward and dependable synthetic approaches to the iron(III) oxides.[1]

Traditionally, iron(III) oxides have been prepared by hydrolysis and precipitation from aqueous solutions of Fe(III) salts.[19] Either heating or addition of base has been shown to induce the formation of iron(III) oxide gels from such solutions.[20−22] The hydrolysis of Fe(III) ion at low pH is well understood and can be summarized by eqs 1−2.[23,24]

$$[Fe(OH_2)_6]^{3+} + H_2O \xrightarrow{K = 10^{-3.5}} [Fe(OH)(OH_2)_5]^{2+} + H_3O^+ \quad (1)$$

$$2[Fe(OH)(H_2O)_5]^{2+} \rightleftharpoons [(H_2O)_5FeOFe(H_2O)_5]^{4+} + H_2O \quad (2)$$

Although less understood, the dimer in **(2)** can undoubtedly undergo further hydrolysis and condensation to form oligomers as the pH of the system is raised. As a rule, the hydrolysis and condensation of Fe(III) species is so rapid that gelatinous precipitates are the exclusive products of such synthesis.[25] The formation of mono-

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lithic wet gels by these synthetic approaches has only been observed after several steps of washing, peptization, and prolonged dialysis.[14,26,27] More recently, there have been several reports of sol−gel synthetic approaches to the iron(III) oxides. In general, these sol−gel approaches consist of the addition of organic polydentate ligands to a solution of an Fe(III) salt followed by heating of the solution.[28−30] Refluxing results in thick sols that are then calcined to give iron(III) oxide powders. There are no reports of the synthesis of monolithic iron(III) oxide gels by this method.

We are interested in the application of sol−gel derived metal oxides as components for nanostructured energetic composite materials. It is well-known that mechanical, acoustic, electronic, and optical properties can be significantly and favorably altered in nanostructured composite materials.[31] Energetic nanocomposites are a class of materials that have both a fuel and oxidizer component intimately mixed and where at least one of the component phases has particle sizes with nanometer dimensions.[32] A sol−gel derived pyrotechnic is an example of an energetic nanocomposite, in which metal oxide nanoparticles react with nanometer-sized oxophilic metals (Al or Mg) and or other fuels in very exothermic reactions.[33] The fuel(s) reside within the pores of the solid matrix while the oxidizer is the skeletal matrix. The sol−gel formulations, reported here, allow for intimate mixing of oxidizer and fuel components at the nanoscale level and have the potential for water processing.[34] This methodology could be used to make pyrotechnic materials with potentially superior performance than existing formulations, while incorporating all the safety and low-toxicity considerations of water or other environmentally acceptable processing solvent-based systems.[35]

Historically, the sol−gel method has employed the use of metal alkoxide precursors that readily undergo catalyzed hydrolysis and condensation to form a sol of metal oxide particles with nanoscale dimensions (1−100 nm). This synthetic route has proven to be an efficient, easy, and successful approach to the production of predominantly SiO_2, Al_2O_3, and ZrO_2-based porous materials.[25] Much less sol−gel work has been published on other transition and main group metal oxides. This is largely because many of their metal alkoxides are expensive, and still others are sensitive to moisture, heat, and light making their use and long-term storage difficult. In addition, some metal alkoxides are not commercially available or are difficult to obtain, thus precluding detailed studies on the preparation, characterization, and potential applications of their resulting porous metal oxides.

We have previously used propylene oxide as a gelation promoter in the sol−gel synthesis of lanthanide and lanthanide−silicate gels using hydrated lanthanide nitrate salts.[36] Itoh et al. have reported the use of propylene oxide in the sol−gel preparation of silicate−aluminate gels using hydrated aluminum chloride as the aluminum oxide source.[37] Here we report the first use of propylene oxide as a gelation agent for the sol−gel synthesis of a monolithic porous iron(III) oxide from simple Fe(III) salts. We believe this to be an important new synthetic route to high surface area, low density, monolithic porous iron oxide materials. In addition, this method is applicable in a variety of solvents with several different epoxides and makes use of several stable Fe(III) salts, which allow the process to be inexpensive and more facile than previous methods to produce porous iron(III) oxide monoliths. In a larger sense, we recognize that this synthetic method can be easily extended to the preparation of many other main group and transition metal oxide porous solids from simple metal ion salts instead of metal alkoxide precursors.

Experimental Section

Preparation of Fe_2O_3 Gels from Fe(III) Salts. Ferric nitrate nonahydrate, $Fe(NO_3)_3{\cdot}9H_2O$, ferric chloride hexahydrate, $FeCl_3{\cdot}6H_2O$, and $FeCl_3$ salts were obtained from Aldrich Chemical Co. and used as received. The attempted synthesis of Fe_2O_3 gels was performed in the following solvents, all of which were reagent grade or better: ethanol (200 proof; Aaper), 1-propanol (J.T. Baker), *tert*-butyl alcohol (J.T. Baker), acetonitrile (EM Science), water (distilled), ethyl acetate (Mallinckrodt), 2-ethoxyethanol (Chemical Samples Co.), *N*,*N*-dimethylformamide (Fluka), and the methanol, tetrahydrofuran (THF), acetone, ethylene glycol, propylene glycol, formamide, 1,4-dioxane, benzyl alcohol, nitrobenzene, hexanes, and dimethyl sulfoxide (DMSO) were all from Aldrich Chemical Co. The propylene oxide was also obtained from Aldrich Chemical Co. All syntheses were performed under ambient conditions. In a typical experiment, 0.65 g of $Fe(NO_3)_3{\cdot}9H_2O$ (1.6 mmol) was dissolved in 3.5 mL of 200 proof ethanol to give a clear red-orange solution that remained unchanged upon storage, under room conditions, for several months. If, instead, a 1.0 g portion of propylene oxide (17 mmol; propylene oxide/Fe = 11) was added to the solution, there was rapid (<1 min)

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color change as the solution became an intense dark red-brown color. (**Caution:** the color change is accompanied by significant heat generation, which in some cases led to rapid boil over of the synthesis solution. The authors recommend the cautious addition of the epoxide to the Fe(III) solution in a well-ventilated lab space.) With time, the solution transformed into a rigid red-brown gel. Gel formation usually occurred within several minutes. Unless otherwise stated, all synthesis experiments used 3.5 mL of solvent, [Fe(III)] = 0.35 M, and an epoxide/Fe ratio of 11. In some experiments, the epoxide was added in smaller portions (sum total was still 1.0 g) over a period of several days. In those cases the Fe(III) solutions were covered during the time between addition of propylene oxide aliquots.

Some experiments were performed to help elucidate the role of H_2O in Fe_2O_3 gel formation in nonaqueous solvents. In those experiments the Fe(III) precursor salt used was anhydrous $FeCl_3$. In a typical experiment 0.26 g (1.6 mmol) of $FeCl_3$ was dissolved in 3 mL of 200 proof ethanol. To this solution a known amount of distilled water was added, and the resulting solution stirred for ~15 s. Then a 1.0 g quantity of propylene oxide (17 mmol) was added to the solution; it was then covered and allowed to gel under ambient conditions. We also examined the effect that the order of addition, of the water and propylene oxide, had on gel formation. This was done by first adding the propylene oxide to a stirred Fe(III) solution, waiting ~5 min, and then adding the aliquot of water (6 equiv relative to Fe(III)).

A series of synthesis experiments were performed where a dissolved salt was present in the Fe(III) solution before epoxide addition. The salts used in these experiments were NaCl (J.T. Baker), NaBr (J.T. Baker), $Na(CH_3COO)$ (J.T. Baker), Na_2SO_4 (Aldrich), and NH_4NO_3 (Alfa Aesar). In a typical experiment 3 equiv (relative to Fe(III)) of a particular salt was dissolved in a 3.5 mL aqueous solution that contained [Fe(III)] = 0.35 M (1.6 mmol). To that solution was added a 1.0 g aliquot of propylene oxide (17 mmol). The solution was then covered and allowed to gel.

Processing of Fe_2O_3 Gels. Aerogel samples were processed in a Polaron supercritical point drier. The solvent liquid in the wet gel pores was exchanged for $CO_2(l)$ for 3−4 days, after which the temperature of the vessel was ramped up to ~45 °C, while maintaining a pressure of ~100 bar. The vessel was then depressurized at a rate of about 7 bar/h. For aerogel processing we preferred to use polyethylene vials to hold the gels during the extraction process. This was done because much less monolith cracking was observed than when Fe_2O_3 gels were processed in glass vials. Xerogel samples were processed by drying in a fume hood at room temperature for 14−30 days. Under these conditions high vapor pressure solvents, like ethanol, were evaporated, and the wet gels were converted to xerogels.

Study of pH of Aqueous Fe(III) Solution during Gelation. A 0.43 M aqueous solution of Fe(III) was made by dissolving 2.30 g of $FeCl_3{\cdot}6H_2O$ (8.5 mmol) in 20 mL of distilled H_2O. The solution was stirred with a magnetic stir bar on a stirring plate. A glass pH electrode interfaced with a Hanna Instruments model 9020 pH meter was immersed into the solution, and the resulting pH was measured. Then a 4.5 g (77 mmol) aliquot of propylene oxide was added to the stirring solution, and the pH was recorded at regular intervals for the next 60 min. An identical experiment was performed using 3.60 g of $Fe(NO_3)_3{\cdot}9H_2O$ (8.7 mmol).

Physical Characterization of Fe_2O_3 Aerogels and Xerogels. Surface area determination and pore volume and size analysis were performed by BET (Brunauer−Emmett−Teller) and BJH (Barrett−Joyner−Halenda) methods using an ASAP 2000 surface area analyzer (Micromeritics Instrument Corp.).[38] Samples of approximately 0.1−0.2 g were heated to 200 °C under vacuum (10^{-5} Torr) for at least 24 h to remove all adsorbed species. Nitrogen adsorption data were taken at five relative pressures from 0.05 to 0.20 at 77 K, to calculate the surface area by BET theory. Bulk densities of both xerogels and aerogels were determined by measuring the dimensions and mass of each monolithic sample.

Table 1. Summary of Synthetic Conditions for the Synthesis of Fe_2O_3 Gels ([Fe(III)] = 0.35 M; Propylene Oxide/Fe = 11)

precursor salt	solvent	H_2O/Fe	gel formation	t_{gel} (min)
$Fe(NO_3)_3{\cdot}9H_2O$	water	58	no	
$Fe(NO_3)_3{\cdot}9H_2O$	ethanol	9	yes	3
$Fe(NO_3)_3{\cdot}9H_2O$	1-propanol	9	yes	3.5
$FeCl_3{\cdot}6H_2O$	water	55	yes	3
$FeCl_3{\cdot}6H_2O$	methanol	6	yes	23
$FeCl_3{\cdot}6H_2O$	ethanol	6	yes	25
$FeCl_3{\cdot}6H_2O$	ethanol	9	yes	5.5
$FeCl_3{\cdot}6H_2O$	1-propanol	6	yes	60
$FeCl_3{\cdot}6H_2O$	1-propanol	9	yes	6
$FeCl_3$	water	49	yes	2
$FeCl_3$	ethanol	0	no	
$FeCl_3$	ethanol	1	no	
$FeCl_3$	ethanol	2	no	
$FeCl_3$	ethanol	3	no	
$FeCl_3$	ethanol	4	no	
$FeCl_3$	ethanol	5	no	
$FeCl_3$	ethanol	6	yes	180
$FeCl_3$	ethanol	9	yes	5

High-resolution transmission electron microscopy (HRTEM) of dry Fe_2O_3 gels was performed on a Philips CM300FEG operating at 300 keV using zero loss energy filtering with a Gatan energy imaging filter (GIF) to remove inelastic scattering. The images where taken under BF (bright field) conditions and slightly defocused to increase contrast. The images were also recorded on a 2K × 2K CCD camera attached to the GIF.

Both ^1H and $^{13}C\{^1H\}$ NMR experiments were performed on a Bruker DRX-500 spectrometer using a HCX 5 mm probe. Bloch decay experiments (^1H) were performed at 500.13 MHz with excitation pulses of 6 μs and relaxation delays of 30 s. ^{13}C excitation pulses were 14 μs, and ^1H decoupling was accomplished by WALTZ-16 decoupling with ^1H 90 pulse lengths of 80 ms and with a relaxation delay of 300 s. Solution NMR spectra were taken on the syneresis fluid from aged wet Fe_2O_3 gels made from the $FeCl_3{\cdot}6H_2O$ precursor salt in D_2O (Aldrich) and C_2D_5OD (Aldrich) and from the $Fe(NO_3)_3{\cdot}9H_2O$ precursor in C_2D_5OD. Spectra were also taken of the synthesis solution of the attempted preparation of an Fe_2O_3 gel using $Fe(NO_3)_3{\cdot}9H_2O$ in D_2O. This final sample contained large amounts of the paramagnetic Fe^{3+} ion. Both types of NMR spectra contained broad and shifted peaks due to the Fe^{3+} ion. To correct this, disodium ethylenediaminotetraacetic acid (Na_2-EDTA) was added to the samples to complex dissolved Fe^{3+}. This treatment resulted in spectra with sharp and unshifted peaks.

Results and Discussion

Gel Formation Studies. As described in the Experimental Section, red-brown Fe_2O_3 gels were prepared through the simple addition of an epoxide to a solution of an Fe(III) salt. Soon after addition of the epoxide the solution changed color from red-orange to dark red-brown. This color change was accompanied by an exothermic reaction that was followed by formation of a monolithic, dark red-brown, transparent gel. The whole sequence of events (from epoxide addition to gelation) occurred relatively rapidly (from as short as 1 min to as long as several hours, depending on synthetic conditions). A summary of the various synthetic conditions used to prepare Fe_2O_3 gels is shown in Table 1.

It is instructive to note how we defined and determined the gelation point and the Fe_2O_3 stoichiometry, reported in this study. All of the attempted syntheses

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were performed in glass scintillation vials so we could easily observe the flow of the reaction mixtures until the onset of gelation. We have qualitatively defined the gel point to be that at which the solution ceased to discernibly flow under the influence of gravity. In regard to the reported stoichiometry, it is very probable that the iron(III) oxide gel obtained upon drying contains significant amounts of both water and or hydroxyl groups; therefore, it is likely an iron oxyhydroxide. We are currently attempting to determine the stoichiometric amounts of H_2O and hydroxyl groups in the material, results of which will be presented at a later date. Therefore, for simplicity, we have omitted recognizing these constituents with our abbreviated stoichiometry, Fe_2O_3.

According to Table 1, several synthetic combinations resulted in the formation of strong red-brown monolithic gels. There are some interesting trends in Table 1 that warrant further discussion. Iron(III) oxide gels can be made using all three Fe(III) inorganic precursor salts attempted ($Fe(NO_3)_3{\cdot}9H_2O$, $FeCl_3{\cdot}6H_2O$, and $FeCl_3$). These salts are relatively inexpensive, easy to obtain, and can be stored under room atmosphere. In addition, Fe_2O_3 gels can be prepared in both aqueous and nonaqueous solvents. However, note that Fe_2O_3 gels can be formed in water with the $FeCl_3{\cdot}6H_2O$ and $FeCl_3$ salts but not with the $Fe(NO_3)_3{\cdot}9H_2O$ precursor.

Careful inspection of Table 1 also indicates that some water is present in all of the successful gel syntheses (present as waters of hydration from the precursor salt, as the solvent, or as an added reagent). This was not unexpected, as it is likely the olation and oxolation of aquo and aquo−hydroxy Fe(III) species (see **(1)**−**(2)**) that are responsible for gel formation.[21] The absence of water in the synthesis precludes the formation of the initial hexaaquo Fe(III) complex shown in **(1)**, and thus no polycondensed species can form. This hypothesis is supported by the fact that attempted synthesis of Fe_2O_3 gel from $FeCl_3$ in anhydrous ethanol resulted in an indefinitely stable clear yellow-orange solution.

In a series of experiments, summarized in Table 1, portions of $FeCl_3$ were dissolved in ethanol, and to those solutions varying amounts of water were added. Identical amounts of propylene oxide were added to each solution, and they were monitored for gel formation. Gel formation was observed in all of the vials where the mole ratio of H_2O/Fe was six or greater. However, the solutions where $H_2O/Fe \leq 5$ were stable indefinitely. Some hydrolysis and condensation of Fe(III) had undoubtedly occurred in these solutions, as they were dark red in color, but not enough had taken place as to induce gel formation.[19] These experiments indicate that there is a threshold amount of H_2O needed for successful gel formation by this method. It is worthwhile to note that the threshold amount of water needed is significantly larger than the 3 equiv predicted when stoichiometry is considered (i.e., $2Fe^{3+} + 3H_2O \rightarrow Fe_2O_3 + 6H^+$). As with other sol−gel preparation methods, the sequence of addition of reagents is crucial, and the materials reported here are no exception. All successful syntheses required the presence of water in the Fe^{3+} solution *before* the addition of propylene oxide. If water was added after the epoxide was mixed with the anhydrous Fe^{3+} solution, the resulting product was a brown gelatinous precipitate instead of a rigid gel.

According to Table 1, the rate of gel formation appears to be faster for gels formed in alcoholic solvents (specifically ethanol and 1-propanol) using the $Fe(NO_3)_3{\cdot}9H_2O$ precursor as opposed to the $FeCl_3{\cdot}6H_2O$ salt. Addition of an extra 3 equiv of H_2O to the syntheses with the chloride salt accelerates the gel formation process significantly, as is shown in Table 1. Notwithstanding, the gel times for the gels made with the chloride salt are still longer than those observed for gels made with the nitrate salt. Therefore, both the identity of the counterion and the amount of water present affect the rate of gelation.

Another synthetic parameter that was extensively investigated was the ratio of propylene oxide to Fe(III). Several experiments were run where that ratio was varied from 3 to 25. The rate of gel formation was observed to increase with this ratio. The dependence appears to be asymptotic as there is relatively little difference (approximately a factor of 2) in the gelation time for syntheses where the ratios were 11 and 23, respectively. However, the difference between the gel times for the two syntheses where the ratios were 7 and 6, respectively, is a factor of 1800. These experiments also indicate that there is a critical propylene oxide/Fe(III) ratio below which no gel formation was observed, even after several months. That minimum value is 6 for the synthetic conditions described in Table 1 ([Fe] $= 0.35$ M; $H_2O/Fe = 9$; solvent = ethanol). However, it was not necessary that all 6 equiv of propylene oxide be delivered at one time.

Transparent deep dark red gels were also formed using a delayed-addition synthetic method. For example, 4 equiv of propylene oxide (relative to Fe(III)) was added to solution containing dissolved Fe(III). On standing for 6 days there was no gel formation in this solution. Subsequent addition of an extra 4 equiv of propylene oxide resulted in the formation of a red-brown gel within 45 min. According to our previous experiments, 4 equiv of propylene oxide is not sufficient to induce the gelation of the solution. Therefore, neither aliquot of propylene oxide was large enough to cause gelation, but the sum total of the two was.

Effect of the Solvent on Fe_2O_3 Syntheses. Solvents are used in sol−gel synthesis as a media for the hydrolysis and condensation of precursors and also to control the concentrations of reactants, which influence the gelation kinetics. Through careful choice of the solvent and its unique properties (i.e., surface tension, dielectric constant, and dipole moment) parameters such as the rate of gel formation, gel structure, and drying behavior can be changed.[39] Therefore, to more thoroughly understand the effect of solvent in the formation of Fe_2O_3 gels by the epoxide addition method, we attempted to make monolithic Fe_2O_3 gels in a series of solvents. The results of this study are summarized in Table 2. It is apparent that monolithic Fe_2O_3 gels can be readily prepared in several different solvents. However, successful syntheses were not achieved in all of the solvents utilized.

In general, polar protic solvents were the most suitable solvents for formation of monolithic red-brown

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Table 2. Summary of Synthetic Conditions for the Synthesis of Fe_2O_3 Gels from $FeCl_3 \cdot 6H_2O$ Precursor ([Fe(III)] = 0.35 M; Propylene Oxide/Fe = 11) (ppt = Precipitate Gel)

solvent	H_2O/Fe	gel formation	t_{gel}
water	55	yes	3 min
methanol	6	yes	23 min
ethanol	6	yes	25 min
1-propanol	6	yes	60 min
tert-butanol	6	no	ppt
acetone	6	no	
THF	6	no	ppt
acetonitrile	6	yes	6 h
ethyl acetate	6	no	ppt
DMF	6	yes	1.5 h
ethylene glycol	6	yes	<12 h
propylene glycol	6	yes	<12 h
formamide	6	yes	45 min
1,4-dioxane	6	no	ppt
ethoxyethanol	6	no	
benzyl alcohol	6	yes	∼40 days
DMSO	6	yes	4 h
nitrobenzene	6	no	

Fe_2O_3 gels. We believe that the hydrogen-bonding characteristics of these solvents promotes the growth of clusters of iron(III) oxide material that undoubtedly contain surface hydroxyl groups into rigid gels. Alternatively, polar aprotic solvents were fair solvents for the synthesis of Fe_2O_3 monoliths. Attempts to synthesize Fe_2O_3 gels in some polar aprotic solvents resulted in the formation of gelatinous precipitates or no gel formation at all (e.g., acetone). In these cases, it is likely that either the Fe_2O_3 clusters grew too large too fast and thus precipitated out of solution or the solvent was not able to support clusters of a sufficient size for gel formation. Syntheses in nonpolar solvents were unsuccessful because sufficient amounts of the Fe(III) salt precursor could not be dissolved in them.

Some of the Fe_2O_3 gels shown in Table 1 were dried under atmospheric or supercritical conditions with CO_2(l) to produce xerogel and aerogel monoliths, respectively. Figure 1 contains photos of monolithic Fe_2O_3 xerogel and aerogel samples. These photos indicate that monolithic Fe_2O_3 aerogels and xerogels can be formed using this straightforward preparation method. Typical densities of the dried Fe_2O_3 aerogels are 0.07−0.2 g/cm^3, and those for xerogels are 0.85−1.00 g/cm^3. Previously, monolithic gels of Fe_2O_3 had only been achieved after several steps of washing, peptization, and dialysis.[12,14,27]

Microscopy of Fe_2O_3 Gels. We utilized high-resolution transmission electron microscopy (HRTEM) to examine the morphology of Fe_2O_3 aerogels. Figure 2 contains two micrographs of an Fe_2O_3 aerogel. Figure 2a is a low-magnification micrograph that reveals the expanded treelike structure of the aerogel. Qualitatively, the material appears to be a collection of clusters that contain cavities of mesoporous (20−50 nm) dimensions. The micrograph in Figure 2b is of higher magnification than that in Figure 2a and provides a fine representation of the size, shape, and connectivity of the clusters that make up the aerogel. It appears that these particles are relatively uniform spheres with most having diameters in the 5−10 nm range. The particles appear to be connected to one another to form clusters. These results indicate that Fe_2O_3 made by the epoxide-addition method is made up of nanometer-sized clusters. The observed Fe_2O_3 aerogel microstructure is consistent with the generic sol−gel mechanism for gel formation. According to that mechanism, the initial monomer (hydrated Fe(III) species in this case) polymerizes to form small oligomers. These oligomers then undergo further growth until they begin to link together to form a sol. These particles eventually link together to form larger clusters, which then connect to one another to produce an extended network throughout the medium that then rapidly thickens to form a gel.

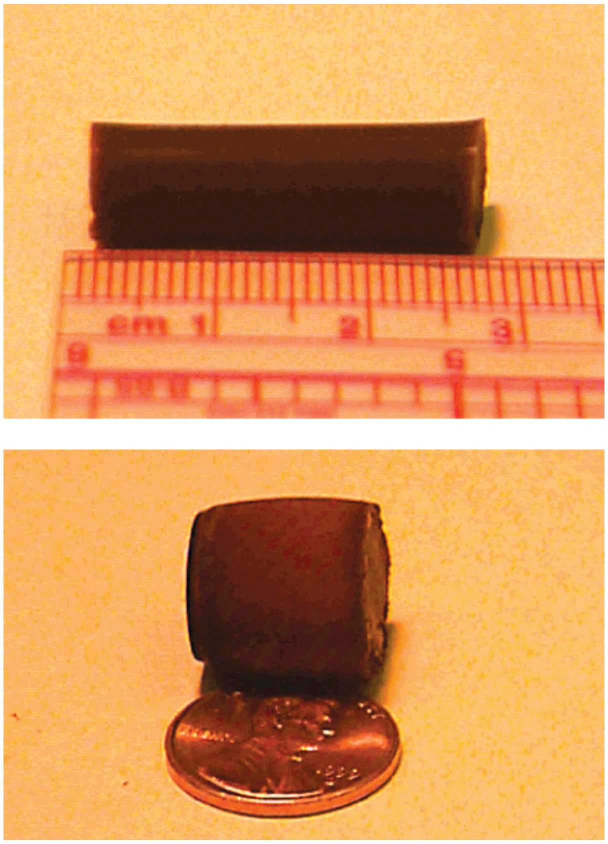


Figure 1. (a, top) Photographs of Fe_2O_3 xerogel and (b, bottom) aerogel monoliths.

Surface Area, Pore Size, and Pore Volume Analysis. Table 3 summarizes the surface areas, pore volumes, and average pore sizes for two aerogels and a xerogel. In general, all of the materials listed in Table 3 have high surface areas and pore diameters whose dimensions are in the micro to lower mesoporic (2−20 nm) region. Note that the xerogel solid has a comparable total surface area to the aerogel material made under identical conditions. However, the pore volume and average pore diameter of the xerogel sample are significantly smaller than that of the aerogel sample (0.22 mL/g and 2.6 nm compared to 1.25 mL/g and 12 nm, respectively). In addition, the absorption−desorption isotherm of the xerogel solid is a type I isotherm, indicative of a microporous solid, while the isotherm for the aerogel sample is a type IV isotherm, indicative of a mesoporous solid. The differences in the results for these two samples are most likely due to the different processing conditions each was subjected to. Simply put, the evaporation of the ethanol from the xerogel sample exerted substantial capillary forces on the gel's pore structure, which resulted in shrinkage of the pores, relative to the aerogel sample. The surface areas reported in Table 2 for the Fe_2O_3 gels (300−400 m^2/g) are significantly higher than those reported for other

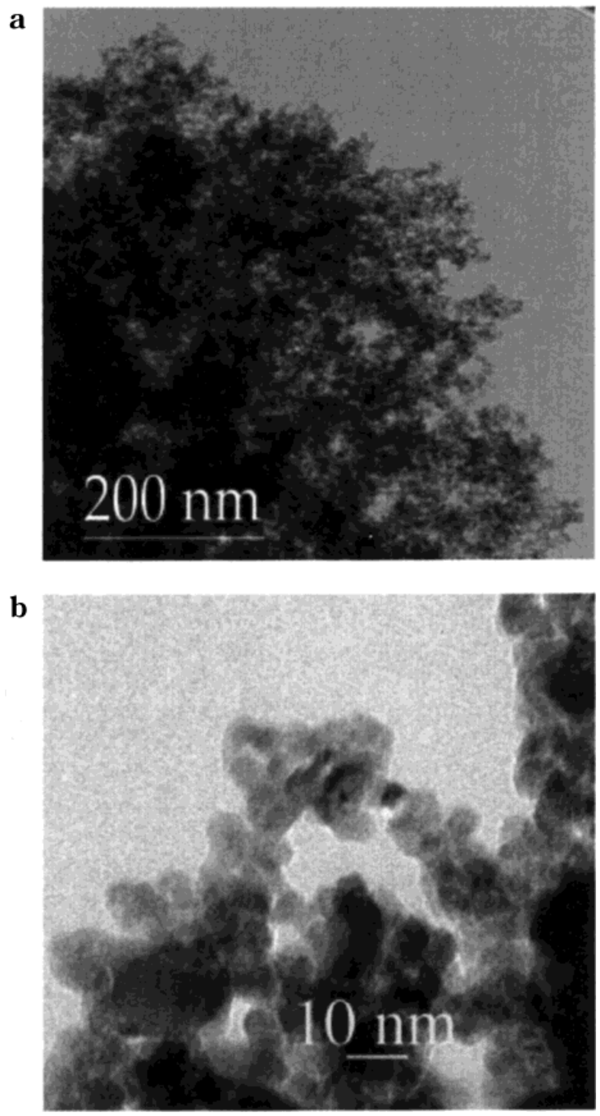


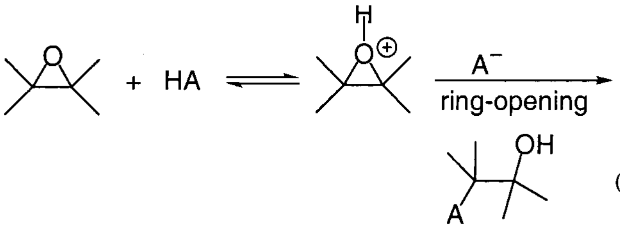
Figure 2. High-resolution transmission electron micrographs (HRTEM) of an Fe_2O_3 aerogel at different magnifications.

Table 3. Summary of N_2 Adsorption/Desorption Results for Dry Fe_2O_3 Gels Prepared in Ethanol

gel type	precursor salt	surf. area (BET) (m^2/g)	pore vol (mL/g)	av pore diam (nm)
xerogel	$Fe(NO_3)_3{\cdot}9H_2O$	300	0.22	2.6
aerogel	$Fe(NO_3)_3{\cdot}9H_2O$	340	1.25	12
aerogel	$FeCl_3{\cdot}6H_2O$	390	3.75	23

sol–gel preparations of Fe_2O_3 solids (10–80 m^2/g).[8,29] These results, along with the low-density measurements, indicate that the dry Fe_2O_3 gels made by this method are unique and new materials that should be evaluated in applications utilizing Fe_2O_3.[2–16]

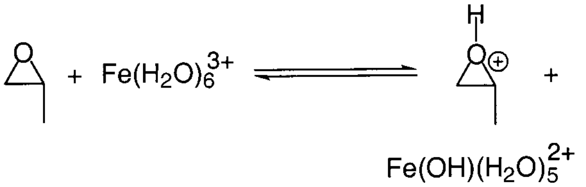
Role of Propylene Oxide in Gel Formation. To more completely understand the processes that cause gelation by this method, we investigated the role that propylene oxide assumes in it. Traditionally, propylene oxide has found extensive use in organic syntheses as an acid scavenger.[40] It acts as an acid scavenger through protonation of the epoxide oxygen and subsequent ring opening by the nucleophilic anionic conjugate base.[41] This process is shown in **(**3**)**.



(3)

It is our contention that the epoxide also acts as a proton scavenger in the method described here.

If the propylene oxide in this system is acting as an acid scavenger, then it likely consumes protons from the hydrated Fe(III) species as is shown in the equilibrium in **(**4**)**.



(4)

It is well-known that the aqua ion $[Fe(H_2O)_6]^{3+}$ is a strong acid, and epoxides are easily protonated by strong acids.[23] Therefore, it is likely that the equilibrium in **(**4**)** has a significant amount of the protonated epoxide species shown on the right. The Fe(III) complex on the right side of **(**4**)** can undergo further hydrolysis and condensation to form more condensed Fe(III) oxide species. The protons generated in these reactions are consumed by protonation of the epoxide. The protonated epoxide can then be irreversibly ring-opened by a suitable nucleophile. The net effect of this is the elimination of protons from solution.

On an elementary level the epoxide can be regarded as a base, and the main synthetic pathway to iron(III) oxide and oxyhydroxide solids is through the addition of base to aqueous Fe(III) solutions.[19–22] The addition of bases like OH^-, CO_3^{2-}, and NH_3 has been a popular route to prepare Fe(III) gels. With all of these approaches, Fe(III) solids or gels are precipitated from solution. This is due to the rapid reaction rate of the base with the Fe(III) species.[25] This rapid rate of reaction gives rise to regions of nonuniform Fe_2O_3 particle production within the solution as well as large Fe_2O_3 clusters that cannot be stabilized by the solvent, and thus precipitation occurs instantly. However, in the present situation the epoxide is not a strong enough base to induce immediate precipitation. Instead, the epoxide mixes with the Fe(III) species to give a homogeneous solution before a significant increase in pH occurs. With time, the epoxide begins to consume protons, and the pH increases slowly and uniformly throughout the solution. It is likely that the relatively slow and homogeneous pH increase of the solution allows the uniform formation of dimers and then oligomers, which link together through olation and oxolation to give a sol of iron(III) oxide particles that subsequently cross-link to give a monolithic gel. To help support the mechanistic hypotheses discussed above, several experiments were performed.

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(40) Dobinson, B.; Hofmann, W.; Stark, B. P. *The Determination of Epoxides*; Pergamon Press: Oxford, 1969.

(41) Stenmark, G. A. *Anal. Chem.* **1957**, *29*, 1367.

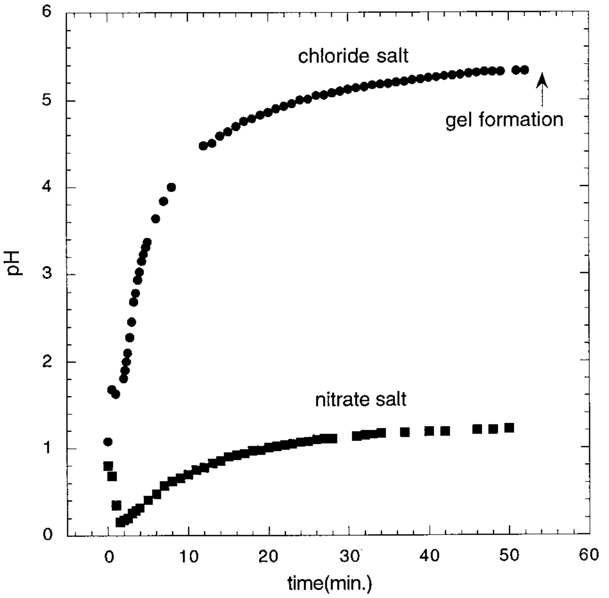


Figure 3. pH vs time since epoxide addition for the synthesis of Fe_2O_3 in water with the $FeCl_3{\cdot}6H_2O$ and $Fe(NO_3)_3{\cdot}9H_2O$ salts.

From the data presented in Table 1 we noted that no gel formation was observed when $Fe(NO_3)_3{\cdot}9H_2O$ was used as the Fe(III) salt in aqueous solution. However, when $FeCl_3{\cdot}6H_2O$ was used, under the same conditions, gel formation was observed. The reasons for these observations can be rationalized by examining Figure 3. Figure 3 is a plot of the solution pH vs reaction time for two different aqueous solutions of Fe(III) that have had propylene oxide added to them. The two experiments are identical except for the fact that one used $Fe(NO_3)_3{\cdot}9H_2O$ and the other $FeCl_3{\cdot}6H_2O$ as the precursor. According to Figure 3, the pH of both solutions increased with time after addition of propylene oxide. For the experiment using the $Fe(NO_3)_3{\cdot}9H_2O$ precursor the pH initially drops from 0.8 to 0.2 and then gradually rises to ~1.2 where it then remains unchanged. These measurements help explain why no gel formation was observed in this particular experiment. At this pH most of the Fe(III) species are aquo and aquo−hydroxy complexes that are present as monomers, dimers, and small oligomers.[19,25] This was not the case in the same experiment with the $FeCl_3{\cdot}6H_2O$ precursor.

After propylene oxide addition, the pH of the Fe(III) solution made with $FeCl_3{\cdot}6H_2O$ increased rapidly from ~1 to ~5 within 20 min. The pH continued to rise after that, but at a much slower rate, until gel formation was observed at a final pH value of ~5.2. At these pH values the Fe(III) species in solution are large cationic oligomers of Fe(III) hydroxy and oxo−hydroxy species that are formed through the processes of olation an oxolation.[25] As the pH rises, these clusters eventually condense to make a gel. The data in Figure 3 provide insight into explaining the differing results from the two experiments; however, a more fundamental question to be addressed now is, why was there a large pH difference? This can be understood by consideration of the nucleophilic character of the counterions present in each salt.

When $Fe(NO_3)_3{\cdot}9H_2O$ is used as the precursor, the potential nucleophiles present are nitrate ion and water.

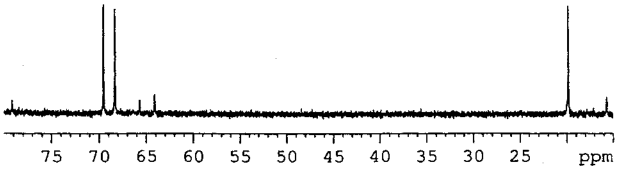
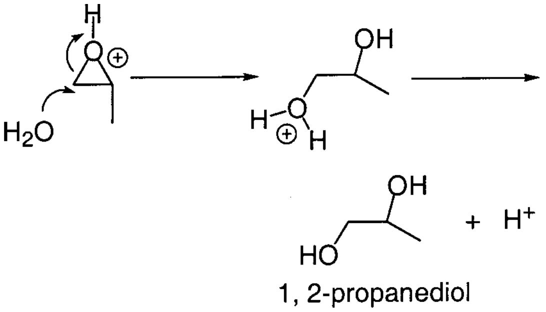


Figure 4. ^{13}C NMR of the EDTA-treated synthesis liquid from attempt to make Fe_2O_3 gel in D_2O using $Fe(NO_3)_3{\cdot}9H_2O$ as a precursor salt.

Under some conditions, water is considered a better nucleophile than the nitrate ion, and therefore, the protonated species in (4) could be preferentially ring-opened by water.[42] This leads to the proposed scenario shown in (5).

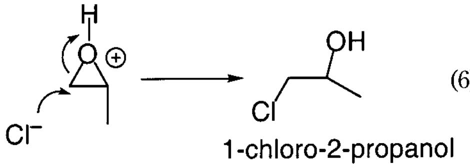


(5)

Here the water attacks a ring carbon and then goes through a deprotonation step to give 1,2-propanediol and regenerate a proton. Since a proton is regenerated, the process is catalytic in protons, and thus, the pH of the solution should not rise appreciably. The observation that the pH of the $Fe(NO_3)_3{\cdot}9H_2O$ salt solution, in Figure 3, only rises a small amount supports this proposed mechanistic step.

To further clarify our proposed mechanism, we employed nuclear magnetic resonance spectroscopy (NMR). Figure 4 contains the ^{13}C NMR spectrum of the liquid from the attempted synthesis of Fe_2O_3 from $Fe(NO_3)_3{\cdot}9H_2O$ in D_2O. The dominant product (~80%) in this spectrum (peaks at ~20, 68, and 69 ppm) was identified as 1,2-propanediol. As previously stated, this product is made by the ring-opening nucleophilic attack by the water and does not result in the net consumption of protons which would cause the pH to rise. The slight rise in pH indicated in Figure 3 is from the production of a small amount of 1- and 2-nitrooxy-2-propanol. These compounds are the products of ring-opening nucleophilic attack by the nitrate ion.

When $FeCl_3{\cdot}6H_2O$ is utilized as a precursor, the potential nucleophiles are chloride ion and water. Chloride ion is generally considered a better nucleophile than water, and therefore, the protonated epoxide is probably preferentially ring-opened by the chloride ion (6), and the resulting species is 1-chloro-2-propanol.



(6)

Note that in (6) no proton is regenerated, as is in (5), and therefore, overall protons are consumed which

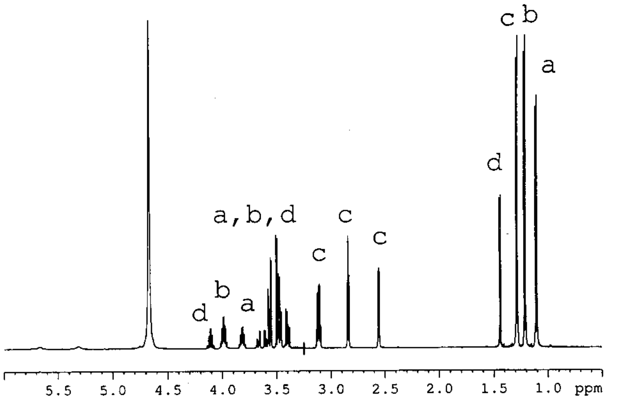


Figure 5. ^1H NMR spectrum of the synthesis liquid expelled from an Fe_2O_3 gel, made with $FeCl_3·6H_2O$ salt in D_2O. The peak assignment is: (a) 1,2-propanediol, (b) 1-chloro-2-propanol, (c) propylene oxide, and (d) 2-chloro-1-propanol. The large peak at ~4.7 ppm is from H_2O.

raises the pH and leads to Fe_2O_3 gel formation. The observation that the pH of the $FeCl_3·6H_2O$ salt solution rises a great deal before gel formation (Figure 3) supports this proposed mechanistic step.

We performed ^1H NMR on the pore liquid expelled during syneresis of an Fe_2O_3 gel made using $FeCl_3·6H_2O$ in D_2O, and that spectrum is shown in Figure 5. Careful analyses and assignment of the spectrum indicated the presence of four different distinct products. These products have been identified and quantified as unreacted propylene oxide (38%), 1-chloro-2-propanol (30%), 2-chloro-1-propanol (8%), and finally 1,2-propanediol (25%). The chlorinated alcohols are isomers of the product described by **(**6**)**, and the diol is the product of the reaction shown in **(**5**)**. The presence of significant levels of 1,2-propane diol in the NMR spectrum indicates that the water is reasonably competitive with the chloride ion for ring opening of the epoxide. This helps explain why an excess of propylene oxide (≥ 6) is required to induce gelation. It may also help explain why at least 6 equiv of H_2O is needed for gel formation. (The stoichiometric amount of water needed is only three (see Table 1).) These NMR results suggest that a substantial fraction of both propylene oxide and water are consumed in the side reaction to produce 1,2-propanediol. Nonetheless, enough chloropropanol was made to increase the pH to a level where the gel formed. It is worth noting that Itoh et al. detected chloropropanol using gas chromatography/mass spectrometry when they used propylene oxide to prepare Al_2O_3 gels using $AlCl_3$ in solution.[37]

According to Table 1, Fe_2O_3 gels are readily prepared, from the $Fe(NO_3)_3·9H_2O$ precursor, in nonaqueous media (e.g., ethanol). It is probable that under these conditions (minimal water content and a solvent with poor nucleophilic properties) the nitrate ion is a suitable nucleophile that favors the formation of the nitrate–ester of the alcohol and the net consumption of protons (see **(**3**)**). Both ^1H and ^{13}C NMR results, not shown here, indicate that the 1- and 2-nitrooxy-2-propanol are the preferred products when Fe_2O_3 gel is made with $Fe(NO_3)_3·9H_2O$ in CD_3CD_2OD. This causes the net consumption of protons, which drives the equilibrium in **(**5**)** to the right, and thus, polymeric condensed Fe_2O_3 species form.

If the previous explanation of Fe_2O_3 gel formation in water is valid, then one would predict that the addition of Cl^- anions to the aqueous synthesis using $Fe(NO_3)_3·9H_2O$ should induce Fe_2O_3 gel formation. This has been proven to be true as Fe_2O_3 gel formation was observed using $Fe(NO_3)_3·9H_2O$ in water when a suitable amount (3 equiv relative to Fe) of chloride ion (introduced as NaCl) was added to the Fe(III) solution, before epoxide addition. To demonstrate that this observation was not dependent on the chloride anion exclusively, several salts containing different anions (some good nucleophiles, other poor ones) were added to aqueous phase syntheses of Fe_2O_3 gels from $Fe(NO_3)_3·9H_2O$. The results of these experiments are as follows. Gel formation occurred with the addition of salts containing good nucleophilic anions such as Cl^-, Br^-, and $CH_3CO_2^-$.[42] However, the addition of salts containing poor nucleophiles such as SO_4^{2-} and NO_3^- anions did not result in gel formation. This approach maybe useful to prepare Fe_2O_3 gels under conditions (i.e., solvent, precursor salt) where gelation is not initially observed.

The mechanistic studies reported here suggest that propylene oxide acts as a proton scavenger to induce Fe_2O_3 gel formation. Through its unique chemistry the epoxide acts as an irreversible proton sink that induces the pH of the solution to rise slowly and homogeneously which favors the formation of monolithic Fe_2O_3 gels. Larger than expected (on a stoichiometric basis) amounts of both propylene oxide and water are needed for gel formation because of alternative side reactions (most notably the formation of 1,2-propanediol). It is important to realize that the epoxide acts as a gelation agent that is consumed in the process of gel formation and not as a catalyst. We would also like to emphasize that the optimal conditions will likely change as the solvent, counterion, and epoxide do.

In summary, the use of propylene oxide as a gelation agent for the sol–gel synthesis of porous monolithic Fe_2O_3 solids from solutions of Fe(III) salts was extensively investigated. Several different Fe(III) salts, solvents, H_2O/Fe(III) ratios, and epoxide/Fe(III) ratios were utilized to prepare gels with varying gelation times. We have found this method to be straightforward, safe, and versatile for the rapid preparation of monolithic Fe_2O_3 aerogels and xerogels. In addition, detailed experiments suggest that the epoxide acts as an irreversible proton sink to induce Fe_2O_3 gel formation. The epoxide-addition method is applicable for the synthesis of other porous metal oxides. We have prepared dried aerogel monoliths of porous Cr_2O_3, Al_2O_3, In_2O_3, Ga_2O_3, SnO_2, ZrO_2, HfO_2, Nb_2O_5, and WO_3 under a variety of different conditions using simple salts of the respective ions and epoxides. This synthetic approach provides an economical, simple, and versatile route to these materials, some of which have a variety of potential applications. We have also discovered that many other commercially available epoxides can also be utilized in the preparation of porous metal oxide monoliths, results of which will be reported later.

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(42) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry, Part A: Structure and Mechanisms*, 3rd ed.; Plenum Press: New York, 1993.

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