SYNTHESIS OF ORDERED NANOENERGETIC COMPOSITES

A Thesis
presented to
the faculty of Graduate School
University of Missouri-Columbia

In partial fulfillment
of the Requirements for the Degree
Master of Science

By
MEHENDALE BHUSHAN J
Dr Gangopadhyay Shubhra, Thesis Supervisor
May 2005
ACKNOWLEDGEMENTS

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Energetic materials can be defined as the substances or mixtures that react chemically to release energy required for their intended application. "Pyrotechnics", "explosives" and "propellants" are subclasses of energetic materials and thermite is a subgroup of pyrotechnic. Conventionally thermite materials are synthesized either by physical mixing of solid oxidizers and fuels on a macro scale (also known as energetic composite) or creating a monomolecular energetic material, in which each molecule contains an oxidizing and a fuel component. For the energetic composites, the total energy that can be released after combustion can be much greater than that of monomolecular materials. However, for the composites the burn rate is relatively slow when compared to that of monomolecular materials. It is known that the energy release and the burn rate can be significantly different in nanostructured materials (1 to 100 nm) called as nanoenergetics. A new approach to synthesize nanoenergetic materials is developed using the sol-gel chemistry. This synthesis method offers a better control over the composition of the energetic material at the nanometer scale, which is generally difficult to achieve by conventional techniques. In the present sol-gel approach to synthesize energetic composite, fuel nanoparticles are added just before the gelation of oxidizer. This may adversely affect the interfacial area for the energetic reaction which may result in the lower energy release and burn rates. To address this issue the main focus of this thesis is to create uniform pores and their distribution using templating agent during sol-gel synthesis of oxidizer and subsequent impregnation of fuel. This will result in homogeneous nanoporous oxidizer network with high interfacial area for energetic reaction and will thus improve the energy release and burn rates.
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ABSTRACT

Energetic materials can be defined as the substances or mixtures that react chemically to release energy required for their intended application. "Pyrotechnics", "explosives" and "propellants" are subclasses of energetic materials and thermite is a subgroup of pyrotechnic. Conventionally thermite materials are synthesized either by physical mixing of solid oxidizers and fuels on a macro scale (also known as energetic composite) or creating a monomolecular energetic material, in which each molecule contains an oxidizing and a fuel component. For the energetic composites, the total energy that can be released after combustion can be much greater than that of monomolecular materials. However, for the composites the burn rate is relatively slow when compared to that of monomolecular materials. It is known that the energy release and the burn rate can be significantly different in nanostructured materials (1 to 100 nm) called as nanoenergetics. A new approach to synthesize nanoenergetic materials is developed using the sol-gel chemistry. This synthesis method offers a better control over the composition of the energetic material at the nanometer scale, which is generally difficult to achieve by conventional techniques. In the present sol-gel approach to synthesize energetic composite, fuel nanoparticles are added just before the gelation of oxidizer. This may adversely affect the interfacial area for the energetic reaction which may result in the lower energy release and burn rates. To address this issue the main focus of this thesis is to create uniform pores and their distribution using templating agent during sol-gel synthesis of oxidizer and subsequent impregnation of fuel. This will result in homogeneous nanoporous oxidizer network with high interfacial area for energetic reaction and will thus improve the energy release and burn rates.
CHAPTER 1: INTRODUCTION

Energetic materials are defined as the substances or mixtures that react chemically and release energy required for their intended application. Thermite is a subgroup of pyrotechnics which involves mixing of solid or liquid fuel with oxidizer which, when ignited, undergo chemical reaction and produce energy in form of heat. The molecule rich in oxygen called the oxidizer molecule reacts with the oxygen deficient molecule usually called as the fuel to undergo the reduction-oxidation reaction known which can be represented by

\[ M + AO \rightarrow MO + A + \Delta H \]  

(1.1)

In this reaction the oxidizer molecules are reduced and the fuel molecules are oxidized. This reaction is highly exothermic reaction which produces energy in terms of heat of reaction. The energy release depends on the composition of energetic material. Composition containing homogenous distribution of oxidizer and fuel will result in higher interfacial area for the energetic reaction thus resulting in greater energy release and burn rates. The energy release can be advantageously used in several applications like munitions, thermal switches, source of energy (energy storage devices), smart bombs, micro thrusters, microaerospace and satellite platforms and precision cutting, and in biomedical applications for localized destruction of pathological tissues etc [1,2]

Conventionally thermites are synthesized either by physically mixing oxidizer and fuel on a macro scale or by incorporating oxidizing and the fuel as monomolecule [3]. The composites made by physical mixing of the oxidizer and fuel molecules may result in high energy release but slow burn rate due to the random distribution of the oxidizer and
fuel molecules. However the monomolecular energetics show low energy release but high burn rates. Thus there has always been a compromise between energy release and burn rate. It is known that the energy release and burn rate can be significantly and favorably altered in nanostructured materials (1 to 100 nm) called nanoenergetics [4].

Nanoenergetics are composite materials made by mixing oxidizer and fuel at a molecular level. A new approach to synthesize nanoenergetic materials was developed using the chemical sol-gel chemistry. It involves the reactions of chemicals in solution to produce nanometer-sized particles called “sol”. The sols can then be linked to form “gel” with the remaining solution residing within the pores. The sol-gel approach to energetic materials provides better control over the composition of the solid at the nanometer scale which is difficult to achieve by conventional techniques [5].

Traditionally, the sol-gel method has employed the use of metal alkoxide or salts as precursors that readily undergo hydrolysis and condensation reactions to form sols of the metal oxide nanoparticles in the solution. The sols further undergo polymerization and cross link to form an oxidizer network. During this step however, solution phase is trapped inside oxidizer gel. When solution phase is removed, nanoporous oxidizer material is produced. Metal alkoxide are generally expensive, sensitive to moisture, heat and light making long term storage difficult [6], therefore, metal salt precursors can be preferred in synthesizing oxidizer.

In the present sol gel synthesis method, fuel nanoparticles are added just before gelation of oxidizer. In this approach it is likely that the interfacial area for energetic reaction can be lower due to inhomogeneous distribution of fuel and oxidizer. This will result in low energy release and burn rate. To address this issue, the focus of this thesis is
to synthesize ordered nanoporous oxidizer by employing an organic template during sol-gel synthesis followed by impregnating the pores with fuel nanoparticles. This method will have an advantage of homogeneous distribution of the oxidizer and the fuel nanoparticles thus increasing the interfacial area which will lead to higher energy release and burn rate. In this study we measured only the burn rates of ordered nanoenergetic composites synthesized here. The remaining part of the thesis is divided into chapters as follows.

**Chapter 2** is an overview of the basics of the conventional sol-gel process applied in synthesis of the nanoporous oxidizer network. In depth explanation of synthesis of the nanoporous iron oxide network using iron nitrate as a precursor is explained.

**Chapter 3** describes the concept of organic templating via surfactant and block-copolymer. It explains formation of micelle in the organic compounds and how it can be utilized in formation of the templates over which the inorganic oxidizer network can be formed. The organic/inorganic interaction is explained in short. Template removal leaves behind the ordered inorganic imprints with uniform pores that the organic material leaves behind. Use of various ionic and non ionic surfactants have been explained in the formation of ordered nanoporous iron oxide.

**Chapter 4** is an attempt to throw light on the challenges in removing the organic template from the organic/inorganic interactions. Template removal methods such as annealing, supercritical extraction and chemical treatment are described.

**Chapter 5** introduces reader to various ways of impregnation of the fuel into the nanoporous oxidizer network to synthesize ordered nanoenergetic composites.
Chapter 6 provides results on the burn rate measurements. We used on chip diagnostic method to measure the burn rates.

This is followed by thesis conclusion and future recommendations.
2.1: Background

The sol-gel process involves the evolution of inorganic networks through the formation of a colloidal suspension (sol) and gelation of the sol to form a network in a continuous liquid phase (gel) [7,8]. Basically three reactions generally describe the sol-gel process: hydrolysis, alcohol condensation, and water condensation as can be seen from the following [9].

\[
\begin{align*}
M-O-R + H_2O & \rightarrow M-OH + R-OH \quad \text{(Hydrolysis)} \\
(\text{Metal alkoxide}) & \quad (\text{Water}) & \quad (\text{Metal Hydroxide}) & \quad (\text{Alcohol}) \\
M-O-R + HO-M & \rightarrow M-O-M + R-OH \quad \text{(Alcohol Condensation)} \\
(2.2) & \quad (\text{Metal-Oxide-Metal}) & \quad (\text{Metal-Oxide-Metal}) & \quad (\text{Alcohol}) \\
M-OH + HO-M & \rightarrow M-O-M + H_2O \quad \text{(Water Condensation)} \\
(2.3) & \quad (\text{Metal Hydroxide}) & \quad (\text{Alcohol}) & \quad (\text{Water})
\end{align*}
\]

Where \(M=\text{Metal, } R=\text{Alkyl group.}\)

The condensation reaction results in the formation of the sol (M-O-M). This sol further interlinks together to form a cross linking and the process is called polymerization. This results in the formation of the gel from the sol. The most important step in this route is the formation of an inorganic polymer by hydrolysis reactions, during which the molecular precursor is transformed into a highly cross linked solid [10]. The gel so formed can be dried in air to form xerogels or treated with supercritical fluids to remove liquids in the pores. The gels formed by this method are called aerogels. Xerogels are more dense material than aerogels which is exhibited in figure below.
Recently, metal salt precursor iron nitrate ($\text{Fe}_2\text{O}_3, 9\text{H}_2\text{O}$) was used to synthesize iron oxide gel via the sol-gel chemistry. The procedure involved dissolving the iron nitrate in ethanol ($\text{C}_2\text{H}_5\text{OH}$) and then adding the propylene oxide ($\text{C}_3\text{H}_6\text{O}$) which acts as a protonation agent and brings about the gelation. This work suggests that gels exist mainly in three phases depending on the concentrations of the above three chemicals used. These phases are shown in a ternary following phase diagram.

*Fig1. Xero gel vs Aerogel*

Overview of the sol-gel process
This chapter covers synthesis of iron oxide gel corresponding to the concentrations of black and brown phases (as shown in figure above) using iron nitrate as a precursor.

2.2: Experimental

2.2.1: Gel synthesis Iron (III) nitrate nonahydrate (Fe(NO$_3$)$_3$ 9H$_2$O) (5gms) (Sigma Aldrich and used as obtained) was added in 42.5ml of ethyl alcohol (200 proof) (Apper and used as obtained). sonicated for ten minutes. This ensures complete dissolution of the iron nitrate. To this solution, 25.9ml of propylene oxide was added slowly under constant
stirring. The color of the solution changed to almost black within a minute and the gelation occurred in about 17 hours forming the black gels.

Different concentrations of Iron nitrate, ethanol and propylene oxide were used to make gels in both black phase and brown phase. The gelation time varied with the change in the concentrations. Several different concentrations of the iron nitrate, ethanol and propylene oxide were used to make gels. These gels prepared using above experimental conditions were annealed in air at 400°C for 3 hrs to remove impurities.

2.2.2: Microstructural Characterization The microstructure of the gels were analyzed by TEM (Transmission electron microscopy) using JEOL 1200 EX. To prepare samples for TEM, a pinch of gel sample was placed in a resin and cured and sectioned using microtoming.

2.3: Results and Discussion

Traditionally iron(III) oxides have been prepared by hydrolysis and precipitation from the aqueous solutions of iron(III) salts. Addition of base solution like ethanol has shown to induce the formation of the iron(III) oxide gels from such solutions.[11, 12]. The hydrolysis of iron(III) ion at low pH (0.1 to 0.3) has been reported in various papers and can be summarized as below [13]

\[
\begin{align*}
\text{Fe(NO}_3\text{)_3,9H}_2\text{O} & \quad \text{C}_2\text{H}_5\text{OH} \quad \rightarrow \quad [\text{Fe(OH)}_6\text{]}^{3+} + 3 (\text{NO}_3\text{)}^3+ + 3\text{H}_2\text{O} \quad \text{-------- (2.4)} \\
[\text{Fe(OH)}_6\text{]}^{3+} + \text{H}_2\text{O} & \quad \rightleftharpoons [\text{Fe(OH)(OH)}_2\text{]}^{3+} + \text{H}_3\text{O}^+ \quad \text{-------- (2.5)}
\end{align*}
\]
\[
\text{[Fe(OH)(OH}_2\text{)}_2\text{]}^{2+} + \text{H}_2\text{O} \rightleftharpoons [\text{Fe(OH)}_2(\text{OH}_2\text{)}_4]^{+} + \text{H}_3\text{O}^+ \hspace{1cm} \text{(2.6)}
\]

\[
\text{FeOOH} + \text{FeOOH} \rightarrow \text{Fe}_2\text{O}_3 + \text{H}_2\text{O} \hspace{1cm} \text{(2.7)}
\]

As could be seen from the equation 2.4, the Fe(III) salt viz Iron nitrate undergoes the hydrolysis reaction to form the \([\text{Fe(OH)}_2(\text{OH}_2\text{)}_6]^{3+}\) complex with the liberation of the water molecules and the \((\text{NO}_3)^{3-}\) species. \([\text{Fe(OH)}_2(\text{OH}_2\text{)}_6]^{3+}\) so formed are in a highly unstable state and undergoes reversible reaction with water to form the dimmers as given in equation 2.6. This further undergoes hydrolysis to form \(\alpha\)-FeOOH (ferrihydrite). Two molecules of the FeOOH react to form \(\alpha\)-Fe\(_2\)O\(_3\) with a liberation of a water molecule (eq 2.7).

The above reactions (2.5 and 2.6) are reversible reactions. It is known that at the pH of around 0.2 (which is typically the pH of the solution of iron nitrate in ethanol), Fe(III) species exists as monomers, dimers, and small oligomers. Addition of propylene oxide causes protonation of the epoxide oxygen and subsequent ring opening by the nucleophilic anionic conjugate base as can be seen from the reaction below.

\[
\text{Epoxide} + \text{HA} \rightleftharpoons \text{Epoxide}^+ \hspace{1cm} \text{ring-opening} \hspace{1cm} \text{OH}^- \rightarrow \text{Epoxide}^+ \hspace{1cm} \text{OH}^-
\]

A=Acid, H=Hydrogen atom

Fig 3: Representation of the protonation of epoxide by ring opening [13,14]

Propylene oxide is consuming the protons liberated from the hydrated Fe(III) species as could be seen from the following reaction.
Thus addition of propylene oxide initiates the reaction in one direction preventing back conversion of the oxo-complexes of Fe(III) ion. Every time a proton (H⁺) is liberated in the reaction it is consumed by the propylene oxide thus opening the ring which is irreversible reaction, finally leading to the formation of FeOOH molecules which then undergo final hydrolysis to form \( \alpha-\text{Fe}_2\text{O}_3 \) [eq 2.7, 13]. Since all the protons in the solution liberated are now consumed there is a decrease in the number of H⁺ ions in the solution. This results in the increase in the pH value.

Addition of propylene oxide causes drastic change in the pH of the solution. The change in pH with respect to the time since the addition of propylene oxide was monitored which is shown in figure below.

\[
\text{Epoxide} \quad \text{Oligomer}
\]

**Fig 4. Use of Propylene oxide as acid scavenger. [13, 14]**

**Fig 5. Graph showing increase in the pH value on addition of Propylene oxide**
The optimized concentrations of Iron nitrate nonahydrate, ethanol and propylene oxide were obtained after several trials (table 1). The optimization was based on the minimum amount of propylene oxide and ethanol required and less gelling time required. This is as shown by the point highlighted on the ternary phase diagram below.

![Ternary phase diagram](image)

**Fig 6: Black phase point on ternary phase diagram [10a]**

Table 1: Different phases, concentrations of various chemicals and gelation time

<table>
<thead>
<tr>
<th>Gel Number</th>
<th>Phase</th>
<th>Iron Nitrate (gm)</th>
<th>Ethanol (ml)</th>
<th>Propylene oxide (ml)</th>
<th>Gelling time</th>
</tr>
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<tr>
<td>1</td>
<td>Black</td>
<td>5</td>
<td>42.5</td>
<td>25.9</td>
<td>16 hrs</td>
</tr>
<tr>
<td>2</td>
<td>Black</td>
<td>5</td>
<td>75</td>
<td>51</td>
<td>22hrs</td>
</tr>
<tr>
<td>3</td>
<td>Black</td>
<td>6</td>
<td>51</td>
<td>31.08</td>
<td>12 hrs</td>
</tr>
<tr>
<td>4</td>
<td>Brown</td>
<td>2.5</td>
<td>8.636</td>
<td>2.495</td>
<td>3 hrs</td>
</tr>
<tr>
<td>5</td>
<td>Brown</td>
<td>2.0</td>
<td>3.358</td>
<td>0.8</td>
<td>1 hr 20 min</td>
</tr>
<tr>
<td>6</td>
<td>Brown</td>
<td>4.0</td>
<td>13.82</td>
<td>5</td>
<td>3 hr 15 min</td>
</tr>
</tbody>
</table>
The as synthesized black phase and brown phase gels are shown below.

![Image of black phase gel](image1)

![Image of brown phase gel](image2)

Fig 7: Black phase Gel prepared in our lab  Fig 8: Brown phase Gel prepared in our lab

These gels were annealed at 400°C for 3 hours. The TEM image of the black phase gel is shown in figure 9. The results of the TEM shows collapse in the pore boundaries and also a random arrangement of the pores within the oxidizer. The pore size varied from about 1nm (represented by point B in the image below) to 10nm (represented by point A in the image below). Also as can be seen from the figure below the distribution of the pores is not uniform. The sample is more porous at one place while it is less porous at other. This shows that using traditional sol-gel synthesis route, the pore size is non uniform and they are randomly distributed.

![TEM image of iron oxide sample](image3)

Fig 9: TEM image of iron oxide sample made by Sol-Gel synthesis
It is known that the gels made in black phase are more porous as compared to brown phase gels [13]. Therefore in the next part of the studies we focused our attention to synthesize black phase gels.
CHAPTER 3: SYNTHESIS OF ORDERED NANOPOROUS IRONOXIDE BY SURFACTANT TEMPLATING:

3.1: Background

Although the sol-gel method has proved to be a better way of making porous oxidizer than other conventional pyrotechnics, the major drawback of the sol-gel process is that it lacks in uniform porosity and narrow pore size distribution. This could be explained due to the fact that the polymerization of the sol into a gel is a random process and although stirring and sonication may help in dispersing the sol, it cannot be made perfectly uniform throughout the solution and leads to random distribution of pores throughout the gel and the pore size distribution cannot be controlled. This fact leads to the need for investigating into the modifications of the process to account for the uniformity in the pore formation in the oxidizer network and to be able to tailor the pore size to the particle size of the fuel. This will ensure proper mixing of the fuel particles with the oxidizer and increase in the area of contact or surface area available for the Redox reaction. One way to achieve this is via the self assembly of the organic compounds to form templates and introducing the inorganic oxidizer network around the templates to form the organic/inorganic interactions. The removal of organic templates from the sample leaves behind the imprints of the inorganic oxidizer network with the voids in place of the organic compounds.
3.2: Concept of surfactant Templating

Templating is defined, in a general sense, as a process in which an organic species functions as a central structure about which the inorganic oxide moieties organize into a crystalline lattice [15-18]. A template is a structure (usually organic in nature) around which a material (often inorganic) nucleates and grows in a “skin-tight” fashion, so that upon the removal of the templating structure, its geometric and electronic characteristics are replicated in the (inorganic) material [19, 20].

Templating is usually achieved by using the surfactants. Surface active agents commonly known as surfactants are bifunctional molecules that contain a solvent-loving (lyophilic) head group and a solvent-hating (lyophobic) tail within same molecule (i.e., they are amphiphiles). As a result of their amphiphilic nature, surfactants can associate into supramolecular arrays [21]. The head groups can be cationic, anionic or nonionic and the tail groups primarily consisting of hydrocarbons can consist of one, two or three saturated or nonsaturated chains [22]. When such molecules are dissolved in the solvent, due to the amphiphilic nature of the molecule, they rearrange themselves to form circular structures called micelle with a lyophilic head towards the solvent and the lyophobic tails away from the solvent. This arrangement minimizes the unfavourable interactions of the tails with the solvent but introduces a competing unfavourable interaction, the repulsion of the charged head groups. The balance between these competing factors determines the relative stability of the micelles. For organic/inorganic interactions the stability of the micelle is an important factor as the ordering of the inorganic species depend on how stable the micelles are [23]. Depending on the concentration of the surfactant in the
solvent various arrangements of the micelles are possible. At a very low concentration (typically about 0.1 to 3% by wt) of the surfactant, the molecule exists as an individual species in the solution. At a slightly higher concentration called as critical micellar concentration (CMC) (typically around 5-10% by wt) the surfactant molecules come together to form circular aggregates called micelle. As the concentration of the surfactant is further increased the micelles come together to form cylindrical structures. Further increase in the concentration of the surfactant leads to the formation of hexagonal structural arrangement as could be seen from fig 10a below. Further increase in the concentration leads to the cubic bicutaneous structures fig 10b. if the concentration is further increased lamellar structures are formed as one seen in fig 10c. further increase in the micellar concentration might lead to the inverse micell formation, usually not a desirable arrangement for templating [24].

Fig 10. Three structure types of Surfactant a) Hexagonal  b) Cubic Bicutaneous  c) Lamellar [22]
3.3: Self-assembly of inorganic species by surfactant templating

It is known that some organic species, when dissolved in solution can template small inorganic groups via electrostatic, van der Waals, and hydrogen-bonding interactions to form nanostructured materials with tailorable pore shapes and sizes with the pore size depending mainly on the chain length of the hydrophobic tail of the organic surfactant used [25]. Prior to the addition of the inorganic precursor, the surfactant molecules are in a dynamic equilibrium of different forms of micelles and single molecules. Upon the addition of the inorganic species, an inorganic-organic mesophase is formed. The polymerization of the inorganic precursor leads to a continuous change of the charge density at the surfactant-inorganic interface, thus, the system responds by steadily re-arranging the mesophase morphology. As a consequence, each surfactant can act as a template for the formation of several different mesostructures, depending on the reaction conditions [26]. The type of bonding between the organic species and the inorganic molecules depends on the type of the organic compounds. For instance the anionic or cationic surfactant can have an ionic and electrostatic bonding with the inorganic molecules, while the nonionic surfactants can have hydrogen bonding with the inorganic molecules [27].
As could be seen from fig 11 above the organic species are represented by the head group and the tail group while the inorganic molecules are represented by the green center and brown dots (right top corner labeled a). When these organic molecules are dissolved in the solvent with the concentration of the organic molecules exceeding the CMC, these molecules form the micelles as could be seen from second block labeled b. These micelles have a closed packing density as the organic concentration increases in the mixture. The result is the self assembly of inorganic molecules (as it polymerizes) over the micelles of the organic species as seen in the third block labeled c. This arrangement is uniform all through the solution. After the inorganic precursor

*Fig 11: Assembly of inorganic species over the templated organic structures [24]*
polymerizes around the templated organic species, this template is removed. Removal of
the template leaves behind the structure with the inorganic species forming uniform pores
and the distribution of the pores is uniform throughout the sample as seen from schematic
in fig above labeled d.

3.4: Surfactant templating using ionic, non-ionic surfactant and block co-polymer

We have made use of ionic surfactant Cetyl trimethyl ammonium chloride
(CTAC), a quaternary ammonium compound (Cationic) and non-ionic co-block polymers
(Brij76) as templating agents. Other co-block polymers like Ps-b-Pb, and Ps-b-PMMA)
were also used in few experiments.

It is know that the interaction of the organic–inorganic species could be either by
ionic bonding or hydrogen bonding depending on the organic surfactant used. The
Cationic surfactant interacts with the inorganic species with the (S+I-) interactions where
S represents the surfactant or the organic species and I represents the inorganic species
mainly oxides of metals. However in case of the non-ionic surfactant templating the
organic-inorganic species interaction is via the Hydrogen bonding usually represented as
(S°I°). it is known that mesoporous materials prepared in the presence of neutral
surfactants as the template usually have improved stability. [28,29]. Ctyl trimethyl
ammonium chloride (C_{19}H_{42}NCl) is a cationic surfactant with a positive charge on the
head of the micelle. When this cationic surfactant is dissolved in water which acts as a
good solvent for the surfactant, the micelles formed have a net positive charge on its head
formed due to the chlorine atoms and the tails formed due to the hydrocarbons. The over
all micelle formation could be summarized from the figure below.
When this surfactant solution is added to the solution containing iron oxide made by dissolving iron nitrate in ethanol, the positive charge on the methyl group attracts the negative charge on the oxygen atoms from iron oxide (Fe$_2$O$_3^-$). Thus the resulting assembly can be represented by the schematic as shown below.

Fig 12 Schematic representation of Micelle formation in CTAC
As could be seen from the figure the assembly of the inorganic iron oxide over the organic CTAC surfactant is by the ionic bonding between the positive charge due to methyl group and the negative charge on the oxygen atoms from iron oxide molecule. This explains why it was difficult to achieve good results when CTAC was used although similar processing parameters were used as Brij76. The ionic bonding between the organic–inorganic species is stronger as compared to that between Brij76 and iron oxide as Brij76 is a non ionic surfactant and the organic–inorganic interactions is due to the hydrogen bonding.
3.4.1: Experimental

3.4.1.1: Synthesis of ordered nanoporous iron oxide gel with CTAC as templating agent

Cetyl trimethyl ammonium chloride (C_{19}H_{42}NCl) was obtained from the Arquad as “Arquad 16/29”, 29% by weight of surfactant in water. Various ratios by weight of surfactant to the iron oxide were experimented varying from 3% to 17% by weight of surfactant. 5gms of Iron nitrate was dissolved in 42.5 ml of ethanol. This solution was added to 2ml (3% by wt of surfactant) and 11ml (17% by wt of surfactant) respectively. The resultant mixture was sonicated for 10 minutes to ensure complete dissolution of iron nitrate and good mixing of the surfactant with the solution. 25.9ml of the propylene oxide was added to this mixture with constant stirring. The solution was stirred till further stirring was not possible. The gelling time for this experiment was less than 1 minute for 17% surfactant and around 2-3 minutes for surfactant with 3%. The gelling time was recorded from the time of addition of the propylene oxide.

3.4.1.2: Synthesis of ordered nanoporous iron oxide gel with Brij76 as templating agent

Polyethylene glycol octadecyl ether (Brij76) was obtained from Sigma Aldrich and was used as obtained. In one beaker 0.357gms of Brij 76 was added in 15ml of ethanol (200 proof) and the temperature of the solution was maintained at 60 C for 15 minutes with constant stirring. We refer this solution as A. In another beaker 5gms of Iron nitrate was
dissolved in 27.5 ml of ethanol (200 proof). This solution is designated as solution B.

Solution B was placed in a sonicator bath for about 10 minutes with constant stirring to ensure complete dissolution of iron nitrate in ethanol. Solution B is then slowly added to solution A under gentle stirring. The resultant mixture was then placed in sonication bath for another 10 minutes. After sonication 25.9ml of the propylene oxide was added to this solution under constant stirring. The solution was stirred till the viscosity increased and further stirring was not possible. The gelling time for this experiment was around 1-2 minutes from the point of addition of the propylene oxide.

3.4.1.3: Characterization The gels synthesized were characterized using FTIR (Fourier Transformed Infrared Spectroscopy) using Thermo Nicolet FTIR. The gels obtained were dispersed in iso-propanol and spin coated on silicon wafer (10-20 Ωcm). The substrates were dried at 90 C for 10 minutes. The total number of scans were 1024 with resolution of 8 cm⁻¹. All the FTIR graphs were corrected for their baseline using a 20 point baseline correction using the Microcal Origin 6 software.

3.5: Results and Discussion

3.5.1: Ferrihydrite gels prepared with CTAC
The table 3 shows the various concentrations of the CTAC used and the corresponding concentrations of Iron Nitrate, Ethanol and Propylene oxide. The corresponding gelling times is also noted.

Table 2: Various concentrations of CTAC

<table>
<thead>
<tr>
<th>No</th>
<th>Phase</th>
<th>Iron Nitrate (gm)</th>
<th>Ethanol (ml)</th>
<th>Propylene oxide (ml)</th>
<th>CTAC (ml), % wt</th>
<th>Gelling time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Black</td>
<td>1</td>
<td>8.5</td>
<td>5.18</td>
<td>0.4, (3%)</td>
<td>3mins</td>
</tr>
<tr>
<td>2</td>
<td>Black</td>
<td>1</td>
<td>8.5</td>
<td>5.18</td>
<td>1.13, (8.5%)</td>
<td>1min</td>
</tr>
<tr>
<td>3</td>
<td>Black</td>
<td>1</td>
<td>8.5</td>
<td>5.18</td>
<td>2.2, (17%)</td>
<td>&gt;1min</td>
</tr>
</tbody>
</table>

The FeOOH gels were dried in air at room temperature for aging. The images of the 3% and 17% CTAC are as shown in figures 12 and 13 below.

*Fig 14: 3% CTAC*  
*Fig 15: 17% CTAC*
The gels were characterized by FTIR as shown below.

As could be seen from the fig above the presence of –CH vibrations at around 2930 cm\(^{-1}\) suggests the presence of the organic species in the sample. Also the broad stretching vibration of -OH peak around 3000-3600 cm\(^{-1}\) implies the presence of the water in the sample in the form of free and bonded water. The peak at around 1630 cm\(^{-1}\) is the bending mode of the water in the sample [30]. The absorption peaks around 800 cm\(^{-1}\) to 1500 cm\(^{-1}\) are associated with the ethanol solvent used, residual propylene oxide or side products of the ring opening of propylene oxide. The broad absorption peak around
500 cm\textsuperscript{-1} to 700 cm\textsuperscript{-1} can be associate with the Fe-O linkages. Various peaks associated with different bonds are summarized in the table 5 below.

Table 3 Peak description in FTIR

<table>
<thead>
<tr>
<th>No</th>
<th>Wave Number cm\textsuperscript{-1}</th>
<th>Bond</th>
<th>Type</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>500-700</td>
<td>Fe-O</td>
<td>Stretching</td>
</tr>
<tr>
<td>2</td>
<td>800-1500</td>
<td>Ethanol, residual propylene oxide or side products of the ring opening of propylene oxide.</td>
<td>Stretching</td>
</tr>
<tr>
<td>3</td>
<td>~1630</td>
<td>-OH</td>
<td>Bending</td>
</tr>
<tr>
<td>4</td>
<td>~2930</td>
<td>-CH</td>
<td>Stretching</td>
</tr>
<tr>
<td>5</td>
<td>3000-3600</td>
<td>-OH</td>
<td>Stretching</td>
</tr>
</tbody>
</table>

The point of significance to be considered is that the ratio of the surfactant to the amorphous $\alpha$ Fe\textsubscript{2}O\textsubscript{3} is more in 17% surfactant as compared to that of 3% surfactant ratio. This is also true for the ratio of surfactant to water. This is in conjunction with the theory that increase in the concentration of the surfactant will increase the number of micelles and thus decrease the inorganic binding per unit site. In short since the packing density of the micelles increases with the increase in the concentration of the surfactant, the inorganic wall thickness decreases. This is desirable as decrease in the inorganic wall
thickness will increase the surface area of contact between oxidizer and the metal. This could be understood from the schematic shown below.

![Schematic](image)

Fig 17: schematic showing effect of concentration of surfactant on formation of micelles

Since it was desirable that the sample be more porous 17% surfactant was considered appropriate concentration for all the future experiments that were carried out.

3.5.2: Ferrihydrite gels prepared with Brij 76

The table 4 shows various concentrations of Brij 76 and the corresponding gelling time.

<table>
<thead>
<tr>
<th>No</th>
<th>Phase</th>
<th>Iron Nitrate (gm)</th>
<th>Ethanol (ml)</th>
<th>Propylene oxide (ml)</th>
<th>Brij76 (ml), % wt</th>
<th>Gelling time</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Black</td>
<td>1</td>
<td>8.5</td>
<td>5.18</td>
<td>0.4, (3%)</td>
<td>3mins</td>
</tr>
<tr>
<td>2</td>
<td>Black</td>
<td>1</td>
<td>8.5</td>
<td>5.18</td>
<td>1.13, (8.5%)</td>
<td>1min</td>
</tr>
<tr>
<td>3</td>
<td>Black</td>
<td>1</td>
<td>8.5</td>
<td>5.18</td>
<td>2.2, (17%)</td>
<td>&gt;1min</td>
</tr>
</tbody>
</table>
The ferrihydrite gels so made were dried in air the fume hood for aging. The figure below shows the gel made with 17% by wt of Brij 76 and figure 19 shows the FTIR of the as synthesized gel.

![Image of gel made with 17% Brij 76](image180x484.png)

**Fig 18:** 17% Brij 76

![Image of FTIR spectrum](image260x628.png)

**Fig 19:** FTIR of ferrihydrite gels with 17% by wt of Brij 76 at room temperature
As expected the –CH stretching peak was observed at around 2930 cm\(^{-1}\) which clearly indicates the presence of organic species in the sample. It is to be noted that the sample has considerable amount of -OH peak around 3000-3600 cm\(^{-1}\) indicating the presence of very likely free and bonded water. As discussed before the other absorption peaks are 1630 cm\(^{-1}\) from bending mode of the water in the sample, the absorption peaks around 800 to 1500 are associated with the ethanol solvent used, residual propylene oxide or side products of the ring opening of propylene oxide. The broad absorption peak around 500 cm\(^{-1}\) to 700 cm\(^{-1}\) are those from the Fe-O linkages The peak at 2353 cm\(^{-1}\) is from the carbondioxide peak present in the chamber.

In few other experiments some co block polymers like PolyStyrene-b-PolyButedene, Polystyrene-b-PolyMethylMethaAcrylate were also used in various proportions. Further the gels were processed in various different ways like, annealing in atmosphere, annealing in nitrogen, supercritical treatment and chemical means of removing the organics followed by the annealing. Treatment of the gels was a challenge as each method of treatment has its own disadvantages which hindered the performance of the final nanoenergetic composites.
CHAPTER 4 REMOVAL OF SURFACTANT AND OTHER IMPURITIES.

4.1: Background

The ferrihydrite gels made need further processing to synthesize Fe$_2$O$_3$. The FTIR spectra of the as synthesized FeOOH gels (fig 14 and 17) indicates presence of –OH from free and bonded water and –CH groups from the organics used in the synthesis. Therefore the aim of this study is to synthesize Fe$_2$O$_3$ oxidizer gel from FeOOH gel and remove water and organic impurities.

4.1.1: Removal of Impurities by annealing

Standard practices suggest that the gels be aged at room temperature in air followed by annealing them at various temperatures to remove the liquid phase from the sample. The aging of the sample removes the excess water from the gels by evaporation and gives them mechanical strength. When the gels are annealed at temperatures above the room temperature, the water and other liquids trapped in the polymerized oxidizer undergoes a phase change from liquid to the gas phase and is removed by evaporation. However it is believed that the surface areas and the pore volumes decreases with the increasing temperatures. This can be explained as follows. As could be seen from the FTIR graphs of the samples at room temperatures, there are a lot of hydroxyl groups present in the sample most of them being surface hydroxyl groups adsorbed. At elevated temperatures these hydroxyl groups undergo condensation resulting in evaporation. This process results in bringing the microparticles closer due to the evaporation of water. [31]. Thus annealing the samples in air results in the collapse of the pores and is not a suitable method of processing the samples for making nanoporous iron oxide. Secondly since the
hydrocarbons were removed by decomposition at elevated temperatures above 300°C, the residues remained in the sample thus contaminating the sample. Also at elevated temperatures, there is a possibility of the organic species reacting with the polymerized iron oxide network thus forming by-products which are not desirable and could lead to the in competency of the samples in making nanoenergetics

4.1.2: Removal of Impurities by super critical solvent extraction

Conventionally aerogels are made by the supercritical treatment of the sample with the solvents like carbon dioxide in its supercritical state. A supercritical fluid exhibits physicochemical properties intermediate between those of a liquid and a gas. It has relatively high, liquid-like density at high pressure, which acts as a good solvent and the mass transfer is fast relative to liquid in supercritical fluids [32]. The critical point for carbon dioxide is around 31.06°C temperature and 73.8bar. At pressures and temperatures above the critical point, carbon dioxide exists in a supercritical phase and we have made use of this phase for the solvent exchange from the sample for the supercritical Carbon dioxide which can then be removed easily by depressurizing and heating. Supercritical extraction usually is done at high pressures. Supercritical solvent extraction method produces aerogels which are highly porous (usually 85-99% porous). However supercritical processing is costly as it involves equipments of high cost. Also high pressures around 7000 psi makes the process not safe.
4.1.3: Removal of Impurities by Ethanol treatment

Recent development in the synthesis of ordered structure silicates like MCM41 have made use of the chemical route in extraction of the templating agents while preserving the pore walls [33]. It is believed that the polar solvents like ethanol, Methanol, chloroform, acidic solution of dimethyl ether and so on can dissolve the organic species and still keep the pore boundaries intact. The organic species once dissolved remains in the solution and can be removed easily by filtration [34,35]. This method has an advantage over the other two methods as this method preserves the pores on annealing the sample and also since this processing is done at room temperature and pressure the process is extremely safe.

4.2: Experimental:

4.2.1: Annealing of ferrihydrite gels

The ferrihydrite gels made with 3% and 17% cetyl trimethyl ammonium chloride (CTAC) and Brij76 as a templating agents were annealed at three different temperatures at 200°C, 300°C and 400°C for 6 hrs. The gels were characterized by FTIR using the Thermo Nicollet machine. The TGA analysis was carried out using the Thermo Nicollet machine and the TEM characterization was done using the JEOL machine.

4.2.2: Supercritical solvent extraction of ferrihydrite gels

In one experiment small sample of iron oxide gel made with Brij 76 template was placed in the Supercritical machine chamber. The sample was pressurized to 7000 psi (482.65 bar) and maintained at 80°C. Carbon dioxide was admitted to the chamber at the
above mentioned temperature and pressure. The sample was held under this temperature and pressure for 24 hrs. Later the chamber was flushed with carbondioxide couple of times and then depressurized to 200 psi (13.79 bar). The gels were characterized by FTIR using the Thermo Nicollet machine. The TGA analysis was carried out using the Thermo Nicollet and the TEM characterization was done using the JEOL machine.

4.2.3: Ethanol treatment of ferrihydrite gels

In one Experiment Ethyl alcohol (200 proof) was used as a chemical solvent to dissolve Brij76 as it is known that ethanol is a good solvent for dissolving Brij76 [36]. The sample was soaked in excess ethyl alcohol for 2 days with constant stirring and the temperature was maintained at 60 C. The gels were characterized by FTIR using the Thermo Nicollet machine. The TGA analysis was carried out using the Thermo Nicollet machine and the TEM characterization was done using the JEOL machine.

4.3: Results and discussion

4.3.1: Analysis of ferrihydrite gels by annealing in air

The as synthesized ferrihydrite gels are shown in figure 12 and 13. The FTIR of the as synthesized gel using 3% CTAC surfactant is as shown in figure below.
The FTIR above shows the predominance of the broad water peak (3000 cm\(^{-1}\) to 3600 cm\(^{-1}\)) and around 1630 cm\(^{-1}\), the organic peak (2939 cm\(^{-1}\)) and 800 cm\(^{-1}\) - 1500 cm\(^{-1}\), the amorphous iron oxide peaks from 480 cm\(^{-1}\) to 520 cm\(^{-1}\). This indicates that the sample has a free and bonded water and the organics inside the pores.

**Fig 20: FTIR of Ferrihydrite gels with 3 % by wt of CTAC without annealing**

**Fig 21: FTIR of Ferrihydrite gels with 3 % by wt of CTAC after annealing at 200 °C**
However the reduction in the peaks of water and organic peaks are observed when the sample is annealed at 200°C for 6 hrs. Also separation of peaks around 480 cm\(^{-1}\) to 520 cm\(^{-1}\) suggest partial crystallization of the Fe\(_2\)O\(_3\).

![Absorbance vs. Wave Number Graph](image)

*Fig 22: FTIR of Ferrihydrite gels with 3% by wt of CTAC at 300°C*

After annealing the sample at 300°C, the surfactant (-CH vibration peak at 2939 cm\(^{-1}\) ) seems to have completely gone indicating the surfactant has been removed leaving behind the structure. However the water peak is still significantly seen in the sample which suggests further heating will be required to remove the water. Also noteworthy is the increase in separation of peaks at around 500 cm\(^{-1}\) which suggests growth of crystallization of Fe\(_2\)O\(_3\) from amorphous phase.
The FTIR for the sample annealed at 400° C for 6 hrs shows complete removal of the organics and also further reduction in the water peak. The small water peak still seen can be accounted for the bonded hydroxyl groups from the sample which has not undergone the condensation reaction.

Figure below shows the ratio of water to iron oxide in the sample at various temperatures. As could be seen the ratio varies from 1.09 without annealing to about less than 0.025 at 400° C.
Similar observations were found for sample with 17% by wt of Ctyl trimethyl ammonium chloride as a Templating agent and is summarized as below.

![Graph showing the ratio of water to iron oxide peak at various temperatures for 17% CTAC surfactant at various temperatures](image)

**Fig 25: FTIR of Ferrihydrite gels with 17% by wt of CTAC at various temperatures**

A graph similar to that for 3% showing the ratio of water to iron oxide peak at various temperatures was plotted with varying temperatures. The ratio varied from 1.35 to 0.5 between no annealing and annealing at 400° C.
Thermo gravimetric analysis was done on the 3% and 17% CTAC samples using Thermo Nicollet machine. Small amount of both samples were analyzed under nitrogen atmosphere.

**Fig 26: Ratio of water to iron oxide at various temperatures**

**Fig 27: TGA Analysis on 3% CTAC sample**
The TGA analysis on both the 3% and 17 % CTAC samples shows a steep reduction in the weight at around 800°C which could be accounted for evaporation of the free water and the liquid phase with boiling point around 800°C. However another reduction in weight is seen around 230°C ~ 240°C. This can be accounted for the liberation of the organic species from the sample that decompose at around 250°C. This observation is also in conjunction with the FTIR measurements where a –CH peak observed in a sample annealed at 200°C but does not appear in the sample with 300°C annealing.

The transmission electron microscopy was done on the samples to see the ordering of the oxidizer network. It was observed that samples with 3% and 17 % by wt of ctyl trimethyl ammonium chloride as a templating agent showed increased ordered structure respectively as could be seen visually with the TEM images.
The TEM images for 3% and 17% surfactant were in accordance with the theory that the templating agent would bring about the ordering of the oxidizer network thus minimizing the random arrangement of the pores in the oxidizer network [37]. Also the
pore size distribution was minimized as could be seen from the figures above. However it was observed that the pore size that could be obtained by using CTAC was around 2~4 nm [38]. This is due to the short chain length of the hydrocarbons in the compound (C_{19}H_{42}NCl) that determines the diameter of the micelle and thus the pore size.

This observation directed my research to concentrate on using the Polyethylene glycol octadecyl ether, (C_{58}H_{118}O_{2}) also known as Brij 76. The large number of hydrocarbons in the compound meaning long chain of tails suggested that the pore size be at least 8~10nm. The following figures below shows the FTIR graphs at no annealing, 200, 300 and 400 C respectively with

![FTIR Graph](image)

*Fig 31: FTIR of 17% Brij76 sample, no annealing*
Fig 32: FTIR of 17% Brij76 sample after annealing at 200 °C

Fig 33: FTIR of 17% Brij76 sample after annealing at 300 °C
Fig 34: FTIR of 17% Brij76 sample after annealing at 400 °C.

Fig 35: FTIR of 17% Brij76 sample at various temperatures.
The graph of the ratio of water to iron oxide peak was plotted for various temperatures and is as shown below.

![Graph showing the ratio of water to iron oxide peaks at various temperatures](image)

*Fig 36: Ratio of water to iron oxide at various temperatures*

It was observed that the –CH vibration peak was seen in the sample annealed at 300 °C which was not the case with the surfactant CTAC. The reason for this is the long chain hydrocarbons in Brij76 as compared to that in the CTAC. This was verified and confirmed with the TGA analysis performed on a small sample made with Brij76 as templating agent. The TGA graph shows a reduction in wt of the sample at around 80 °C which could be accounted for the evaporation of the water and other liquids. However there is no considerable change in wt until around 350 °C when the hydrocarbons begin to decompose. This is in conjunction with the FTIR which shows the presence of the –CH peak in a 300 °C annealed sample while the peak is absent in the 400 °C annealed sample.
The TEM image of the sample made with Brij76 as a templating agent is as shown in the figure. The sample shows homogenous pore distribution with an average pore size of about 8-10nm.

Fig 37: TGA Analysis on 17% Brij76 sample

Fig 38: TEM image of iron oxide sample with 17% Brij76 as Templating agent made by Sol-Gel synthesis
Annealing in air at various temperatures have proved to remove the free water and the surfactant from the sample as was expected. The sample now has a minimum distribution of the pore size and the pores are uniformly distributed throughout the sample. However annealing the samples in air had few major drawback. Since the samples were annealed in the air the evaporation of the liquids leads to the shrinkage of the sample material. This makes the material dense and this could adversely affect the burn rates. Another problem could be due to the presence of the hydrocarbons present in the sample. These hydrocarbons decompose at high temperatures and may contaminate the sample. This could also lead to low burn rates.

4.3.2: Analysis of ferrihydrite gels by supercritical solvent extraction

The figure below shows the FTIR comparison of the as synthesized sample and the one treated with supercritical carbondioxide without annealing. The sample treated with supercritical carbondioxide treatment showed significant reduction in the –OH peak from 3000 cm\(^{-1}\) to 3600 cm\(^{-1}\) as expected. However there was no significant change in the –CH peak at 2939 cm\(^{-1}\). This signifies that the supercritical treatment was not efficient in removing the organic species although it efficiently removed the liquid phase from the sample.
This sample was further annealed at $400^\circ$C for 3 hours with the ramp rate of $1 ^\circ$C per minute and characterized for its structural details by the transmission electron microscopy.

**Fig 39:** FTIR of Ferrihydrite gels with 17% by wt of Brij76 treated with supercritical Carbon dioxide at 7000 psi and $80 ^\circ$C

**Fig 40:** TEM image of iron oxide sample with 17% Brij76 as Templating agent made by Sol-Gel synthesis and treated with supercritical carbon dioxide.
The supercritical carbondioxide treatment on the iron oxide samples made with brij 76 although proved successful in removing the water from the sample was not really useful for removing the organic templates. The organic species were still required to be removed by annealing the sample to elevated temperatures. This still leads to the decomposition of the organic compounds leaving behind the carbon that might contaminate the samples and hinder its performance. Besides, the expensive equipment set up required for the supercritical treatment and the working conditions like extremely high pressures is not acceptable in the industry. Also this increases the cost of production and a cause for finding an alternative to the process.

4.3.3: Analysis of ferrihydrite gels by ethanol treatment

The figure below shows a FTIR comparison of the as synthesized sample and the one treated with ethanol solvent.

Fig 41. FTIR of Iron oxide gel trated with Ethanol for two days at 60 C
The FTIR shows decrease in the –OH and the –CH peaks at (3000 – 3600 ) and 2939 respectively when treated with ethanol as compared to that of the as made sample as could be seen from the figure above. The bar graphs were plotted for the ratio of surfactant to iron oxide and water to iron oxide respectively. It is observed that soaking the sample in ethanol reduces the ratio of surfactant of iron oxide by 89% while that the ratio of water to iron oxide is reduced by 78%.

Fig 42: % Reduction of Surfactant with ethanol treatment
This method of removing the organic templates and the water species from the as made gels is highly efficient as is carried out at as low temperatures as 60°C. Also the Transmission Electron Microscopy done on these samples after annealing them at 200°C for 6 hours with the ramp rate of 1°C shows that the gels have highly ordered structures. The pore walls are intact and do not collapse as is the case in annealing the samples directly.

![Graph showing -78% reduction in water/iron oxide peak](image)

**Fig 43. % Reduction of water with ethanol treatment**

![TEM image of iron oxide sample with 17% Brij76 as Templating agent made by Sol-Gel synthesis and treated with Ethanol.](image)

**Fig 44: TEM image of iron oxide sample with 17% Brij76 as Templating agent made by Sol-Gel synthesis and treated with Ethanol.**
CHAPTER 5 FUEL NANOPARTICLE IMPREGNATION IN ORDERED NANOPOROUS IRON OXIDE

5.1: Background

Since the invention of the black powder, energetic materials have been made by mixing the oxidizer and the fuel material on the macro scale. This physical mixing however does not ensure homogeneous mixing of the oxidizer and the fuel particles leading to reduced interfacial area. This may result in incomplete redox reaction leading to reduced energy densities and lower energy release rates. However making nanoenergetics using sol-gel synthesis method enables precise control over the particle size at nanometer scale thereby increasing the interfacial area for the redox reaction. Nanoenergetics using sol-gel synthesis is made by physical mixing the fuel nanoparticles with the oxidizer gel just before the gelation of the oxidizer occurs. This prevents the coagulation of the metal atoms and ensures distribution throughout the oxidizer sample. However this mixing method still lacks uniform distribution of the metal atoms in the oxidizer network. This might result in localized oxidizer rich and oxidizer deficient areas in a sample. As could be seen from the figure below taken from the LLNL, when aluminum was added to this oxidizer just before the gelation, aluminum is not intimately mixed through out the sample and metal rich and oxidizer rich areas can be seen.
This inhibits the complete oxidation reduction reaction when initiated and also results in the loss of energy. In other words the energy content of the sample is reduced. Also since the distribution of the pores is random, now occupied by the metal, the flame propagation is not directional, thus reducing the speed of propagation, which is an important factor of consideration in making thermites or explosives. This problem can be solved by making the ordered nanoporous oxidizer network by modified sol gel synthesis using the templating agents and then impregnating the fuel atoms into the oxidizer network. This ensures homogeneous mixing of the fuel atoms with the oxidizer thus increasing the energy content and the energy release rate.

5.2: Strategies for impregnation

We have developed a novel methods of impregnating the fuel nanoparticles in the ordered nanoporous iron oxide network made by sol-gel synthesis.
5. 2.1: Single step impregnation

This method as we call it a one step impregnation process is a method of intimately mixing the fuel nanoparticles with the ordered iron oxide network during the process of the synthesis of iron oxide gel using the modified sol-gel synthesis method. The schematic representation of this method is shown in the following figure.

![Schematic representation of the one step Aluminum Impregnation method](image-url)
In this method aluminum nanoparticles are coated with a monolayer of poly(4 vinyl pyridine) polymer to make the surface lyophobic. These surface coated aluminum particles are then added to the mixture containing iron nitrate solution dissolved in ethanol and brij 76. the 4PVP coated aluminum nanoparticles remain inside the micelles of the brij76 due to the lyophobic nature to minimize the surface tension. Propylene oxide is then added to the mixture to initiate gelation to for ferrihydrite gels. The template is then remove to obtain the ordered nanoporous oxidizer with fuel particles residing in the pores.

5.2.2: Two step impregnation

Another method of aluminum impregnation was proposed which involved the making of the ironoxide gels and processing them first and then functionalizing the pores in the oxidizer network to make them liyophobic and assemble the aluminum particles with liyophobic surface as discussed before. Although experiments were not performed using this method in our lab, it is proposed that this method shall also yield good impregnation of the fuel nanoparticles. The over all process can be schematically represented as shown in the figure below.
In one beaker 0.357gms of Brij 76 was dissolved in 15ml of ethanol (200 proof) and the temperature of the solution was maintained at 60°C for 15 minutes with constant stirring. This solution is called solution D. In another beaker 5gms of Iron nitrate nonahydrate was dissolved in 27.5 ml of ethanol (200 proof). This solution is called solution E. Solution E was placed in a sonicator bath for about 10 minutes with constant stirring to ensure that all iron nitrate nonahydrate is dissolved in ethanol. Solution E is then slowly added to the functionalized pores where due to lyophobic nature, the aluminum particles will occupy the pores.

Fig 47 Schematic representation of the two step fuel impregnation method
solution D with slow stirring. The resultant mixture was then placed in sonication bath for another 10 minutes. This is called solution F.

In this method ordered nanoporous iron oxide is first synthesized using brij76 as a templating agents. The gels are further processed to remove the template to get ordered pores in the oxidizer. Then the pores in the oxidizer are functionalized by polymer coating to achieve lyophobic surface on the pores. Aluminum nanoparticles coated with 4PVP are then added to this oxidizer. Due to lyophobic nature of the aluminum surface and the pores, aluminum nanoparticles resides inside the pores of the oxidizer. The polymer coatings can then be removed to achieve ordered iron oxide nanoporous oxidizer with aluminum particles residing inside the pores.

5.3: Experimental

5.3.1: Synthesis of ordered nanoporous iron oxide gel using Brij76 as a templating agent

In one beaker 0.357gms of Brij 76 was dissolved in 15ml of ethanol (200 proof) and the temperature of the solution was maintained at 60 C for 15 minutes with constant stirring. This solution is called solution D. In another beaker 5gms of Iron nitrate nonahydrate was dissolved in 27.5 ml of ethanol (200 proof). This solution is called solution E. Solution E was placed in a sonicator bath for about 10 minutes with constant stirring to ensure that all iron nitrate nonahydrate is dissolved in ethanol. Solution E is then slowly added to solution D with slow stirring. The resultant mixture was then placed in sonication bath for another 10 minutes. This is called solution F.
5.3.2: Monolayer coating of (4vinyl pyridine) on aluminum particles

About 0.5 gms of aluminum was dispersed in excess ethanol and sonicated for 3 hrs. The solution is then centrifuged to remove the larger particles that stick on the wall due to larger weights as compared to those with the smaller particles thus experiencing greater centripetal force. The smaller particles remain in the solution because of the smaller weights and thus smaller centripetal force experienced. This remaining solution was collected and sonicated again for 3 hrs. This process was repeated for several times to ensure narrow distribution of the aluminum particle size. About 1ml of 0.001 molar solution of the poly(4vinyl pyridine) was added to this solution and the sonicated for additional 4 hrs. Finally the solution was centrifuged to recover the aluminum particles coated with the monolayer of the poly (4vinyl pyridine) and dried at 80 °C for 3 hrs.

5.3.3: Mixing of the aluminum particles with solution F

The aluminum particles coated with the poly (4vinyl pyridine) now has a liyophobic surface. These particles are slowly added to the solution F prepared as discussed above in section 5.2.1. The resultant mixture is stirred continuously. Finally 25.9 ml of the propylene oxide was added to this solution with constant stirring until all the heat from the solution is given out. The gelling time for this experiment was around 1-2 minutes after the addition of the propylene oxide. The gels were aged in air for 2 days and then annealed at 200 °C for 6 hrs.
5.4: Results and discussion

It is believed that some polymer like poly (4vinyl pyridine) which are aromatic compounds with benzene rings structures and Nitrogen atom attached on one of the carbon chains and the organic group on the other, has a tendency to bind metals like aluminum. The nitrogen atom provides the binding site for the metal atoms while the organic compounds are open ended which provides the hydrophobic surface. P4VP is extremely attractive because of the strong affinity of the pyridyl group to metals and metal oxides. Another advantage of the P4VP is that each single molecule has numerous binding sites, so even if each site has low affinity on the whole the molecule acts as a good binder as could be seen from the figure.

Fig 48 Schematic representation coating aluminum with poly (4vinyl pyridine)

Now the micelles formed due to Brij76 templating has a liophilic surface with the ferrihydrate molecules bonded by the hydrogen bonding. The core of the micelles has a liophobic nature. When the aluminum nanoparticles with a liophobic surface are added to this solution, to minimize the surface tension these particles find its way inside the core of the brij76 micelles where the repulsive force between the liophobic surface of aluminum and the lyophilic surface of the micelles is minimum.
The SEM imaging was done on the aluminum impregnated iron oxide sample as shown in figure below.

![Fig 49 SEM image of iron oxide with Al impregnation.](image)

The SEM image suggests that the distribution of the aluminum particles is fairly uniform as could be seen from the bright spots throughout the sample. The SEM image was supported by the EDS that was performed on two samples, one as synthesized iron oxide and other, iron oxide with aluminum impregnation using the above mentioned strategy.
The EDS shows a strong peak corresponding to aluminum in sample 2 which was absent in the sample 1 as could be seen from the figure below.

Fig 50 EDS of samples with and without aluminum

It is important to realize that there are a few basic differences in the two approaches of the impregnation of the aluminum atoms into the ordered iron oxide network. In the first method as the aluminum particles are impregnated during the synthesis of iron oxide gel, that is when the iron oxide is still in a liquid phase, addition of the poly(4 (vinyl pyridine)) coated aluminum will result in the swelling of the pores formed by the micelles of the Brij76. This means that the aluminum particle size could be larger than the pore diameter of the Brij76 micelle. However in the second method since
the iron oxide gel is already processed and the organic templates removed completely, the pore size remains constant and care needs to be taken that the aluminum particles to be impregnated are smaller than the actual pore size in the oxidizer network. Although apparently the one step impregnation method seems to have an advantage of adding any size aluminum particles careful study needs to be done on the maximum size of the particles that can be successfully added without breaking the micelles or forming the reverse micelles. This is true because as the size of the aluminum particles increases in comparison to the micelle diameter of Brij76, each surfactant molecule tend to separate from each other. This reduces the binding force on the surfactants and can result in breaking of the micelle. On the other hand in a two step impregnation method, care should be taken to add right proportion of the aluminum to avoid making a fuel lean mixture or a fuel rich mixture.
CHAPTER 6 BURN RATE MEASUREMENTS

6.1: Background

The important property of the thermite material is its burn rate or the self propagation of the flame on ignition. It is believed that this burn rate highly depends on the size of the reacting particles and also the homogeneity of the oxidizer and fuel in a nanoenergetic composite material. The thermite reaction in the energetic composites are usually triggered by the CO\textsubscript{2} laser and the burn rates are recorded using the high speed camera [39]. However due to the high cost of the optical setup used to measure burn rates, we have made use of the novel on-chip diagnosis method using the principle of time varying resistance (TVR) of the sputter coated thin platinum (Pt) film.

6.2: Experimental

6.2.1: Burn rate measurement setup

Glass substrates (Fisher Scientific, MA) were cleaned with Piranha solution (H\textsubscript{2}SO\textsubscript{4}:H\textsubscript{2}O\textsubscript{2} as 3:1 v/v) and rinsed with distilled water and dried in oven at 110\textdegree C for 5-10 min. An aluminum foil mask was used to create a pattern of a heater and TVR detector by sputtering platinum film of about 130 nm thickness using the Sputter Coating System by Emitech, K-575X, UK.

0.2gms of nanoporous iron oxide was mixed with 0.12gm of 80nm aluminum particles and the mixture was dispersed in propanol and sonicated for 8 hrs. This homogenous dispersion was coated with a paintbrush on a chip to spread it from a heater
to resistance detector. Three to five coats were applied in this manner and the chip was
dried in oven at 80-90 °C for 10 min to remove the solvent.

A voltage divider circuit (Figure 51) was used to measure the voltage drop across
TVR detector film. Current of 2-3 Amp was supplied to the heater and the excitation
voltage of 1.5 volts was applied to the detection film. A data acquisition (DAQ) card
(PCI-MIO-16E-1) with a sampling rate of $1.25 \times 10^6$ samples/sec from National
Instruments Inc., TX was used to acquire the voltage drop data with the help of the
LabView software (version 7.1, National Instruments Inc). On ignition, as flame
propagates, the voltage across the TVR film changes over a certain time period. By
knowing this time period and the length of energetics coating (corresponds to length of
TVR film of 0.027- 0.054 m), the burn rate was determined as distance traveled per unit
time.

Fig 51 Schematic representation of the Ignition Testing Device
6. 3: Result and discussion

6. 3.1 Burn rate measurement of composites containing aluminum nanoparticles and nanoporous iron oxide synthesized with and without surfactant at fuel to oxidizer ratio of 1.4

The aluminum nanoparticles have a passivation layer of few nanometer thickness. As the thermite reactions are vary sensitive to active aluminum content, we calculated the active content assuming the average coating of the alumina to be about 2 nm. The amount of aluminum to be added to nanoporous iron oxide was determined based on the equivalence ratio (Φ) [41] which is defined as below

\[
\Phi = \frac{(F/A)_{\text{Actual}}}{(F/A)_{\text{Stoichiometric}}}
\]

In this equation, F represents the Al fuel and A represents the oxidizer. Based on the reaction stoichiometry and active aluminum content, the equivalence ratio was calculated as 1.4. At this ratio fuel and oxidizers were mixed and coated on a chip and the burn rates were measured as per the procedure outlined in the experimental section. The burn rates of the composites containing aluminum nanoparticles and nanoporous iron oxide synthesized are inferred by the change in resistance across the platinum film as function of real time, which are shown in figures 52 and 53.
Fig 52 Burn rate of composite of Iron oxide(synthesized without surfactant)/Al nanoparticles

Fig 53 Burn rate of composite of Iron oxide(synthesized with surfactant)/Al nanoparticles
The change in resistance over a time period (fig 52,53) indicates three distinct steps. The first and the third steps (A and C) are relatively faster compared to step B. The multiple steps that we observed during resistance change of the TVR film can be due to several factors. When reaction is triggered, iron oxide reacts with aluminum and produce aluminum oxide and metallic iron. The TVR platinum film is susceptible to form an alloy with the metallic iron that is produced during the thermite reaction. This reaction is believed to be slower than the thermite reaction itself. In parallel iron oxide can also be oxidized to higher valency state to form Fe$_x$O$_y$. Such compounds however can be reduced in presence of Fe-Pt alloy. Thus from the mechanistic point of view, on initiating thermite reaction between iron oxide and aluminum on platinum film several parallel reactions can occur which are shown below.

![Reaction pathways for thermite reaction between iron oxide and aluminum on platinum film showing three parallel consecutive reactions indicated by A, B and C](image)

**Fig 54** Reaction pathways for thermite reaction between iron oxide and aluminum on platinum film showing three parallel consecutive reactions indicated by A, B and C
On analyzing the mechanistic explanation, we noticed that the overall change in the resistance will reflect not only the thermite reaction but also several other parallel reactions. As thermite reaction is initiated first, the change in the resistance that occurred during step A would be more appropriate to discern the controlling mechanism. Therefore to determine the burn rate we assumed resistance response over a time period that corresponds to step A only.

The burn rate in case of composite containing nanoporous iron oxide (synthesized using 17% surfactant) and aluminum nanoparticles was measured as 14.9 m/s which is eight fold higher than the burn rate of composite containing nanoporous iron oxide (synthesized without surfactant) and aluminum nanoparticles. Comparing these results suggests that the use of surfactant during iron oxide synthesis improves performance of nanoenergetic composites.

6.3.2: Effect of various equivalence ratios on burn rate of nanocomposite of iron oxide and aluminum

Nanoporous iron oxide prepared using 17% surfactant was mixed with aluminum nanoparticles (80nm) at various equivalence ratios and their burn rates were measured. This is to understand the sensitivity of thermite reaction with respect to the active aluminum content. The equivalence ratio was determined as described earlier and it was varied between 0.6 to 1.6. The resistance response over a time period for the composites with equivalence ratios of 0.6 and 1.2 are shown in figures 56,57 respectively. The resistance response appears to be similar to the equivalence ratio of 1.4 (fig 53,54) indicating three distinct steps. Based on the mechanistic explanation given earlier we
chose resistance response over time period corresponding to step A only to determine the burn rates. For a equivalence ratio of 0.6 the burn rate was 7.5 m/s where as for 1.2 the burn rate was 14.1 m/s.

Fig 55 *Burn rate of composite of Iron oxide/Al nanoparticles at equivalence ratio of 0.6*

Fig 56 *Burn rate of composite of Iron oxide/Al nanoparticles at equivalence ratio of 1.2*
The burn rates were also measured at other equivalence ratios of 1.4 and 1.6. The dependence of burn rate with respect to equivalence ratio is shown in the figure 58. It can be observed that the burn rate is optimum at around equivalence ratio of 1.4.

![Burn rate dependence on equivalence ratio](image)

*Fig 57 Burn rate dependence on equivalence ratio*

We compared the burn rates of composites of nanoporous iron oxide (synthesized using 17% by weight of surfactant) / aluminum nanoparticles (composite A) with those reported for composites of nanoporous iron oxide (synthesized without using surfactant) / aluminum nanoparticles (composite B) [42] and it is shown in figure 59. It can be observed that the burn rates obtained for composite A with equivalence ratios of 0.6 to 1.6 are higher than those reported for composite B [42].
The composite A has been prepared using surfactant where as the composite B has been prepared by other [42] without the use of surfactant. The use of surfactant will increase the porosity and decrease the pore size distribution leading to ordered nanoporous oxidizer. When this material is mixed with the fuel nanoparticles and ignited, it is possible that the hot spot density in the combustion wavefront will increase and this will lead to higher burn rates.

Fig 58 Burn rate comparison at various equivalence ratios.
6.3.3 : Burn rate measurements of the composites with nanoporous iron oxide (synthesized with different concentrations of surfactant) and aluminum nanoparticles

Nanoporous iron oxide prepared using surfactant concentrations in the range of 0 to 20 % by weight. These nanoporous iron oxide were mixed with aluminum nanoparticles at the equivalence ratio of 1.4 and their burn rates were measured. The following figure shows the effect of surfactant concentration that was used to prepare iron oxide on the burn rates of the composites.

Fig 59 Burn rate dependence on concentration of surfactant used for synthesis of nanoporous iron oxide
As the surfactant concentration increases from 0% to 20% the burn rate increases up to 15% and then decreases. There is a possibility that at higher surfactant concentration residual contaminants can reduce the burn rate.

The burn rates measured for various composites synthesized at various experimental conditions are summarized in Table 5.

*Table 5: Burn rates of composites of nanoporous iron oxide and aluminum nanoparticles measured by on chip method*

<table>
<thead>
<tr>
<th>S.N.</th>
<th>Process description</th>
<th>$\phi$ ratio</th>
<th>Velocity (m/sec)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Without surfactant</td>
<td>1.4</td>
<td>10.8</td>
</tr>
<tr>
<td>2</td>
<td>3% surfactant</td>
<td>1.4</td>
<td>13.8</td>
</tr>
<tr>
<td>3</td>
<td>15% surfactant</td>
<td>1.4</td>
<td>18</td>
</tr>
<tr>
<td>4</td>
<td>17% surfactant</td>
<td>1.4</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>20% surfactant</td>
<td>1.4</td>
<td>16.8</td>
</tr>
<tr>
<td>6</td>
<td>17% surfactant</td>
<td>0.6</td>
<td>7.5</td>
</tr>
<tr>
<td>7</td>
<td>17% surfactant</td>
<td>0.9</td>
<td>10.5</td>
</tr>
<tr>
<td>8</td>
<td>17% surfactant</td>
<td>1.2</td>
<td>14.1</td>
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<tr>
<td>9</td>
<td>17% surfactant</td>
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<td>15</td>
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<tr>
<td>10</td>
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<td>1.6</td>
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</tr>
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</table>
CHAPTER 7 CONCLUSION

The use of organic templating via the surfactants and the block copolymers to make ordered oxidizer network has been successfully implemented at our labs. This technique in making Nanoenergetics have proved to increase the burn rates. The use of organic templating although being used for thin films on silica to make MCM families, is not very common for making nanoenergetics. The successful use of Brij76 in templating the iron oxide using the sol-gel synthesis have paved a path into investigating use of various other polymers as a template to tailor the pore size. Other potential polymers with variable micelle sizes could be diblock polymers like Polystyrene-b-Polybutidene, Polystyrene-b-Polymethylmethacrylate and tri block polymers like Polyethyleneoxide-Polypropyleneoxide-Polyethyleneoxide and so on. The two techniques for impregnation of fuel nanoparticles during and after synthesis of the oxidizer network as discussed in chapter 5 can be better techniques than physically mixing of the fuel nanoparticles just before the gelation of the oxidizer network as is done conventionally so far. The burn rate tests performed on the ordered and unordered samples suggests that the ordered oxidizer sample is better than the conventionally sol-gel made samples by at-least a factor of 10. In general the synthesis of ordered oxidizer network in making a nanoenergetic composite using templating has a potential of commercialization and is expected to be the process adopted by the industries in near future. The simplicity of the process and safer working conditions (as it involves wet chemistry) makes the process all the more attractive as opposed to the conventional physical mixing of the powders which involves risk of explosion during the synthesis.
**Future work**

Over a period of one and half year, my research involved extensive study of the theory of templating and the organic/inorganic interactions, use of various organic compounds as a potential templating agent, developing the process for making ordered nanoenergetics using templating and processing the samples to remove the templates. Although successful in making ordered oxidizer network and removing the templates using chemical means to preserve the pores, the project is still not complete and needs further investigation and research in following directions as could be categorized below.

1) Brij 76 was used in most of the experiments as a templating agent. This is a nonionic surfactant and have proven stability as opposed to the ionic surfactant CTAC. Brij76 forms micelles under certain conditions altogether different than any other surfactant or polymer. Investigation is required in studying various parameters that affect the formation of the micelles in various surfactants and polymers and be optimized to be used with the synthesis of oxidizer using sol-gel method.

2) As mentioned earlier, out of the two methods for the impregnation of the metal atoms into oxidizer, few experiments on the one step impregnation method were performed and analyzed. However due to the time constraints further studies could not be done in either of the methods. These methods of adding the metal atoms into the oxidizer needs immediate investigation as it has a potential of intimately mixing the fuel and the oxidizer thus increasing the energy densities further.
3) The ignition testing performed on the samples were based on the sensors developed at our labs. Although the time required for change in the resistance of the sensor gives a measure of the speed of the thermite on ignition, further studies are necessary for measuring the accurate burn rates of the nanocomposites.

4) Finally other materials needs to be investigated for the use of oxidizer other than iron oxide as the energy densities and the propagation speeds are also the characteristics properties of the material itself and the atomic structures of the same.
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