Multi-scale characterization of nanostructured sodium aluminum hydride

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MULTI-SCALE CHARACTERIZATION OF NANOSTRUCTURED SODIUM ALUMINUM HYDRIDE

by

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ABSTRACT

Complex metal hydrides are the most promising candidate materials for onboard hydrogen storage. The practicality of this class of materials is counter-poised on three critical attributes: reversible hydrogen storage capacity, high hydrogen uptake/release kinetics, and favorable hydrogen uptake/release thermodynamics. While a majority of modern metallic hydrides that are being considered are those that meet the criteria of high theoretical storage capacity, the challenges lie in addressing poor kinetics, thermodynamics, and reversibility. One emerging strategy to resolve these issues is via nanostructuring or nano-confinement of complex hydrides. By down-sizing and scaffolding them to retain their nano-dimensions, these materials are expected to improve in performance and reversibility. This area of research has garnered immense interest lately and there is active research being pursued to address various aspects of nanostructured complex hydrides. The research effort documented here is focused on a detailed investigation of the effects of nano-confinement on aspects such as the long range atomic hydrogen diffusivities, localized hydrogen dynamics, microstructure, and dehydrogenation mechanism of sodium alanate. A wide variety of microporous and mesoporous materials (metal organic frameworks, porous silica and alumina) were investigated as scaffolds and the synthesis routes to achieve maximum pore-loading are discussed. Wet solution infiltration technique was adopted using tetrahydrofuran as the medium and the precursor concentrations were found to have a major role in achieving
maximum pore loading. These concentrations were optimized for each scaffold with varying pore sizes and confinement was quantitatively characterized by measuring the loss in specific surface area.

This work is also aimed at utilizing neutron and synchrotron x-ray characterization techniques to study and correlate multi-scale material properties and phenomena. Some of the most advanced instruments were utilized for this work and their data collection and analysis are reported. Quasielastic neutron scattering experiments were conducted at NIST Center for Neutron Research to characterize atomic hydrogen diffusion in bulk and nano-confined NaAlH₄. It was observed that upon confinement of NaAlH₄, a significantly higher fraction of hydrogen atoms were involved in diffusive motion on the pico-second to nano-second timescales. However, the confinement had no impact on the lattice diffusivities (jump/hopping rates) of atomic hydrogen, indicating that the improved hydrogen release rates were not due to any kinetic destabilization effects. Instead, the investigation strongly suggested thermodynamic destabilization as the major effect of nano-confinement. The local interaction of the metal sites in metal organic frameworks with the infiltrated hydride was studied using extended x-ray absorption spectroscopy technique. The experiments were conducted at Center for Advanced Microstructures and Devices at Louisiana State University. The metal sites were found to be chemically un-altered, hence ruling out any catalytic role in the dehydrogenation at room temperatures. The fractal morphology of NaAlH₄ was characterized by ultra-small angle x-ray scattering experiments performed at Argonne National Lab. The studies quantitatively estimated the extent of densification in the course of one desorption cycle. The particle sizes were found to increase two-fold during
heat treatment. Also, the nano-confinement procedure was shown to produce dense mass fractals as opposed to pristine NaAlH₄, exhibiting a surface fractal morphology. Based on this finding, a new method to identify confined material from un-confined material in nano-composites was developed and is presented. Preliminary results of modeling and correlating multi-scale phenomena using a phase-field approach are also presented as the foundation for future work.
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DEDICATION

To my parents

Mrs. Thulsi Prema and Dr. N. C. NaraseGowda
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CHAPTER 1

INTRODUCTION

1.1 Background

With a looming energy crisis and growing environmental concerns, the interest in alternative energy technologies has been a priority in every nation in the world. In the long run, there are very few contenders for replacing oil, hydrogen being the most promising of them all owing to its abundance and cleanliness. The hydrogen economy has three thrust areas – Production, Storage and Utilization (energy conversion), each with issues related to cost, performance and efficiency. Together they form a closed loop hydrogen cycle which is illustrated in Figure 1.1.

Figure 1.1: Illustration of the hydrogen cycle.
It is apparent that 90% of the universe known to man is made up of hydrogen, although almost none of it is readily available because it is bound either to oxygen (forming water) or to carbon (thus making hydrocarbons). Hence, hydrogen has to be produced or extracted, which requires additional energy. Despite the energy input needed to “extract” or produce pure hydrogen from its bound state, it is still an attractive option because of its energy content and cleanliness. On a gravimetric basis, hydrogen has three times the energy content compared to any of the petroleum based fuels [1]. When hydrogen production is achieved by harvesting renewable energy sources such as solar or wind, the energy-balance analysis of this area appears very reasonable (although the current costs of hydrogen production from renewable are high). It is important to note that the limiting challenges in economical hydrogen production are not in the availability of hydrogen sources, but in the domain of being able to harvest renewable energy economically and efficiently. Research in sustainable energy includes photo-voltaics, wind energy harvesting, hydrothermal energy, etc. On an optimistic note, this area is growing quickly.

Development of fuel cell technology and improvement in efficiency of the internal combustion engine over the years has enhanced the prospects of a hydrogen economy. The utilization of hydrogen either in a fuel cell or an internal combustion engine to produce energy is an area that has fewer problems compared to the other thrust areas (production and storage) in the hydrogen cycle. The major challenge, however, is in safe and efficient storage methods for hydrogen. Being the lightest gas, it faces the issue of a very low volumetric energy density. In more practical terms, storing enough
hydrogen in a small volume is the basic challenge that has impeded the development of hydrogen based technologies as energy alternatives.

In mobile applications, usable hydrogen can be stored either as a gas, liquid, or as a solid compound. To store enough hydrogen, gas tank systems require storage pressures in excess of 500 bars [2] and liquid tank systems need an additional refrigeration system to maintain cryogenic storage temperatures. In comparison, solid state storage methods are more practical and safe. Solid hydrogen storage can be achieved in two ways: physisorption of molecular H\textsubscript{2} in porous, high surface area materials, or by chemisorption of atomic hydrogen in lattices. H-storage by chemisorption covers the various solid hydrides. Within solids, the issues are (broadly) three-fold: reversible storage capacity, kinetics of hydrogen release/uptake and thermodynamics of hydrogen release/uptake. To the end-user, these issues translate to the driving range at full tank capacity, the time for re-fueling (uptake) or power out-put (energy release per unit time), and efficiency (energy input vs. energy output), respectively. The yardstick in developing a viable storage system is a set of criteria formulated by the US Department of Energy (DOE) which are mentioned in Table 1.1 [3].

Most modern candidate materials that fall into the classification of metal hydrides, complex metal hydrides and chemical hydrides are able to meet the storage capacity criteria. They are hindered by (i) very poor kinetics; (ii) limited thermodynamic range, or (iii) both. The practicality of this technology lies in developing material systems that strike a balance between these three attributes. This research effort is aimed at addressing these challenges by adopting "nanostructuring" as a strategy to destabilize the materials kinetically and thermodynamically. The focus of the dissertation is in developing novel
synthesis routes to achieve nano-sizing of complex hydrides and exploring state-of-the-art characterization experiments to study the resulting material changes on multiple scales.

**Table 1.1: US-DOE targets for Hydrogen Storage [3]**

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<td>1.8</td>
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<tr>
<td>• Hydrogen Density</td>
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<td><strong>Volumetric Capacity</strong></td>
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<td>3.3</td>
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</table>

### 1.2 Complex Metal Hydrides

Complex metal hydrides have traditionally been the most promising materials for solid state hydrogen storage. Many light metal complex hydrides such as NaAlH₄ and LiBH₄ have been studied as candidate hydrogen storage materials for many years [4-7].
Among the general class of complex hydrides, NaAlH₄ has been an archetypal material of investigation. The major focus of literature on complex hydrides has been in the area of addressing its kinetic and thermodynamic limitations.

In the recent years, nanostructuring of complex hydrides has emerged as a very popular strategic direction for researchers in the field of solid state hydrogen storage. Nanostructuring broadly refers to limiting the material geometries to the nanometer scale in at least two dimensions of space. These may include synthesis of thin films [8], nano-wires [9], nano-particles [10], or nano-confined material [11-15]. One of the more traditional techniques for size-reduction is high energy ball milling. It reduces the crystallite sizes but is limited to a couple hundred nanometers at most. However, size reduction by high energy ball milling, despite being moderately effective in the first cycle of desorption, does not prevent particle agglomeration during heat treatment. Since these materials are expected to perform reversibly, ball milling is ineffective in the long run because the fine nano-sized structures do not remain beyond one desorption cycle. In order to completely assess the size related advantages of these materials, it is necessary to not just reduce the particle size but also retain its nano-dimensions throughout the desorption process and over multiple cycles. This idea has attracted a lot of interest recently and has led to the concept of nano-confinement. Complex metal hydrides have been confined in a variety of nano-porous materials such as porous silica [11], carbon scaffolds [12-14], and MOFs [15].

Nano-confinement is expected to enhance hydrogen release rates, reduce temperatures of hydrogen release, and also enhance reversibility in complex hydrides. A reduced crystallite size implies that the net diffusion path-length of H-atoms in the lattice
is reduced too. This leads to a quicker release of hydrogen compared to micron-scale crystals. Size reduction to nano-scales also leads to a great increase in the surface to bulk ratio, at which conditions, the surface energies, and interface have a greater influence in the material’s dehydrogenation properties [16, 17]. It is also viewed as a thermodynamic destabilization that is caused by spatial confinement. An alteration in thermodynamics also leads to different reaction mechanisms for nano-sized materials. During heat treatment, particles densify by agglomeration, and this phenomena leads to the need for long-range mass transport for further desorption. The problem with long range transport of metallic species is that in pristine complex hydrides, upon the completion of each desorption (heating) cycle, the final phases are segregated so much that a second rehydrogenation almost never succeeds in attaining full capacity. Thus, retaining the spent products in close proximity for the next cycle of rehydrogenation is important and nano-scaffolding or nano-confinement would serve this purpose.

1.3 Outline

The main objective for this research is to comprehensively study the behavior of nanostructured sodium alanate over multiple length scales. The results presented in this dissertation are primarily of sodium alanate (NaAlH₄) with the certainty that these results and strategies may readily be applied to the general class of complex hydrides.

Chapter 2 gives the details of the nanostructuring methodologies and morphologies of the various scaffolds included in the study. The Chapter reports characterization of nano-porous scaffolds before and after sodium alanate infiltration using N₂ – BET, XRD, DSC and SEM-EDS. The synthesis procedures and data reported in this Chapter were performed / collected at the Institute for Micro-manufacturing (IfM),
Louisiana Tech University. *In-situ* XRD experiments were performed at Brookhaven National Laboratory in Upton, NY over 96 hours of beam-time in one beam-time award.

Chapter 3 is devoted to the study of lattice diffusion of atomic hydrogen in nanostructured sodium alanate. Both long-range diffusion and localized dynamics of H-atoms are quantitatively studied by Quasi-Elastic Neutron Scattering (QENS). The experiments were performed at NIST Center for Neutron Research (NCNR), Gaithersburg, MD. The data was collected on two instruments – Disk Chopper Spectrometer (DCS) and High Flux Backscattering Spectrometer (HFBS) over 312 hours of cumulative beam-time divided among three beam-time awards.

Chapter 4 discusses the local chemistry around the metal sites in Metal Organic Frameworks (MOFs) which were one of the scaffold materials used in the project. The effect of infiltration on the oxidation state and local co-ordination of the metal sites reported. The experimental technique used was X-ray Absorption Spectroscopy (XAS) and data was collected at the Center for Advanced Microstructures and Devices (CAMD) at Baton Rouge, LA.

Chapter 5 is dedicated to the investigation of morphology/microstructure of both pristine and nanostructured sodium alanate. The changes in morphology during the various process treatments such as heat, ball-milling and Ti-doping were studied using Ultra Small Angle X-ray Scattering (USAXS) technique. A novel approach to identify the confined hydrides was developed using USAXS data analysis. The data was collected at the Advanced Photon Source (APS) at Argonne National Laboratory over 192 hours of beam-time divided among two beam-time awards.
Chapter 6 is a foundation for future work. This chapter explores the fundamentals required for the development of mathematical models to correlate morphology evolution and phase transformation in terms of atomic diffusion. The chapter is aimed at establishing ground-work for theoretical multi-scale modeling. An attempt has been made to model the morphology evolution and phase transformation kinetics using the phase-field method.
CHAPTER 2

NANO-SCAFFOLDING OF SODIUM ALANATE

2.1 Introduction

Nano-scaffolding refers to the confinement of solid materials within the pores of a scaffold structure. Pristine NaAlH₄ particles have an average size of ~30 μm and after high energy ball milling for 5-15 min, their sizes get reduced to <1μm and extended hours of high energy milling can downsize to 150-200 nm at the most [10]. In order to further reduce and retain the sizes, the NaAlH₄ particles were confined within the pores of various scaffolds using wet chemistry procedures. The range of confinement sizes varied from 200 nm to less than 2 nm. The morphology of various scaffolds of different pore sizes and pore structures are characterized using metrology instruments. The stability and compatibility of the scaffolds with both the hydride and the reagents used in wet infiltration procedures are also investigated.

2.2 Methodologies

2.2.1 Wet Chemical Synthesis

Nano-confinement can be achieved either by melt infiltration or by wet solution infiltration. Melt infiltration involves heating the material to its melting temperatures in the presence of porous scaffolds which allows the melt to seep into the pores of the scaffolds. The scaffolds, however, need to be stable at the chosen melting temperatures.
Melt infiltration has been adopted successfully for various metal hydride-scaffold combinations [12, 18-20]. However, the final product is obtained only after re-hydrogenating the sample prior to any further study. Wet solution infiltration, in contrast, is performed at room temperatures using a precursor solution. All nano-samples reported in this dissertation were prepared by solution infiltration using THF as a solvent. The scaffolds used were Alumina (Whatman® Anodisc™ membranes), silica (SBA-15, Claytec, Inc.), and MOFs (Basolite F® and Basolite C®, Sigma Aldrich). Sodium Alanate (SAH or NaAlH₄) (Hydrogen storage grade) was purchased from Sigma Aldrich. From here on, Basolite F is also referred to as Fe-BTC and Basolite C is also referred to as Cu-BTC in the text. BTC [1, 3, 5 Benzene Tri-Carboxylate] is the organic linker that connects the metal sites to form the porous structure of the MOFs. Basolite C and Basolite F are comprised on unsaturated Cu²⁺ and Fe³⁺ metal sites, respectively.

2.2.1.1 Wet Solution Infiltration

The as-received NaAlH₄ was first milled for five min using tungsten carbide milling apparatus in a CertiPrep® Spex™ 8000M high energy ball mill. The milled NaAlH₄ sample (here on referred to as ‘micro-NaAlH₄’ or ‘micro-SA H’) was dissolved in tetrahydrofuran (THF) in various concentrations to prepare the precursor solutions for the scaffolds. Prior to use, the as-received scaffolds (Fe-BTC, SBA-15, Cu-BTC and Alumina) were heated to 200 °C for four hours to ensure that the volatile impurities within the pores were expelled. For SBA-15 and the MOFs, the precursor solutions were dropped on to the scaffolds in NaAlH₄/scaffold weight ratios specified in Table 2.1 to form slurries. The same NaAlH₄/scaffold ratios are used by other researchers for similar confinement studies of NaAlH₄ [15]. The technique adopted for the porous alumina
scaffolds was very similar to a technique referred to in literature as ‘template wetting’ which is used to synthesize polymer nano-tubes and nano-wires [21]. The template with vertical pore wells were treated as a substrate, placed on a dry Teflon plate, and the precursor solution was dropped using a μ-pipette. The solution, by virtue of surface energy, seeped into the pores. Each template was loaded with ~100 μL of precursor solution at once. This was repeated twice, followed by a THF wash which clears out any excess NaAlH₄ lying on the surface of the templates. Unlike the synthesis of nano-wires and nano-tubes, the goal of this study was to fill the pores rather than just wet it. Hence, a more concentrated precursor solution was used, but the concentrations were small enough to allow seepage into the pores successfully without clogging the pore openings (which happens when very high concentrations are used).

**Table 2.1:** Synthesis parameters for wet infiltration of NaAlH₄ into various scaffolds.

<table>
<thead>
<tr>
<th>Scaffold</th>
<th>Vendor specified Pore Size (nm)</th>
<th>SAH/THF (mg/ml)</th>
<th>SAH/Scaffold</th>
</tr>
</thead>
<tbody>
<tr>
<td>Porous Alumina</td>
<td>100</td>
<td>50</td>
<td>-</td>
</tr>
<tr>
<td>SBA-15</td>
<td>8-10</td>
<td>1</td>
<td>1:1</td>
</tr>
<tr>
<td>Fe-BTC (MOF)</td>
<td>&lt;2</td>
<td>1</td>
<td>1:1</td>
</tr>
<tr>
<td>Cu-BTC (MOF)</td>
<td>&lt;2</td>
<td>1</td>
<td>1:1</td>
</tr>
</tbody>
</table>

The wet slurry (for SBA-15 or MOFs) and the wet templates (for porous alumina) were vacuum-dried for 10 min and then allowed to dry inside the glove box under circulating N₂ atmosphere for a day. The procedure yields fine powdered samples (in the
case of MOFs and SBA-15) or dried templates (in the case of porous alumina) of nano-confined NaAlH₄ (referred to as "nano-NaAlH₄" here on). Vacuum is expected to play a dual role: (i) to remove THF faster under ambient temperatures and (ii) the suction pressure aids in driving the suspended NaAlH₄ into the pores of the scaffold. Figure 2.1 shows the pristine NaAlH₄ and Figure 2.2 shows the SEM images of the various scaffolds before and after infiltration with NaAlH₄. Figures 2.2 (a-b) are of the Fe-BTC MOF scaffold, Figures 2.2 (c-d) are of Cu-BTC MOF, Figures 2.2 (e-f) are of SBA-15, and Figure 2.2 (g-h) are of porous alumina before and after sodium alanate infiltration. The pores of the MOFs and SBA-15 are too small (<10 nm) for the SEM to clearly observe and identify the confinement. The forthcoming data in this dissertation from other techniques confirm nano-confinement more lucidly. However, the pores of alumina (100 nm, Figures 2.2 (g-h)) are well resolved using a SEM. The dark circular spots are of the empty pores and the lighter circular features indicate the filled pores. The infiltrated Cu-BTC (Figure 2.2(d)) sample shows a bulk NaAlH₄ particle that remains un-confined on the surface of the MOF.

Figure 2.1: SEM image of pristine NaAlH₄ (as received from Sigma Aldrich).
Figure 2.2: SEM images of various scaffolds before (left) and after (right) wet infiltration of NaAlH₄. (a-b) Fe-BTC MOF, (c-d) Cu-BTC MOF, (e-f) SBA-15, (g-h) Porous alumina.
2.2.1.2 \textit{Titanium Grafting}

Ti-grafting was performed on SBA-15 scaffolds to disperse Ti ions, scarcely, on the inner walls of the pores. A published procedure [22] was followed with slight modifications. SBA-15 (as received, colored white) was dehydrated at 300 °C for four hours. Fifty µL of titanium isopropoxide was mixed with 8 ml of ethanol and immediately added to the heat-treated SBA-15. The slurry was left to dry under flowing N$_2$ for a day. The dried sample was then calcined at 300 °C for three hours to reduce the precursor complex on the SBA surface to Ti ions. The final yield appears charred (beige/brown) in contrast to the pure SBA-15 (white).

2.2.2 Instrumentation

\textit{In-situ} XRD was used to investigate the stability of Fe-BTC with and without the infiltrated NaAlH$_4$ over the entire desorption temperature range. Experiments reported in this article were conducted at NSLS, Brookhaven National Lab on the X14A beam-line, which is equipped with a capillary heating set up. The samples were loaded in quartz capillary tubes (0.5 mm/Charles Supper Co.) and their edges sealed with adequate volume allowance for the desorbed hydrogen. At the beam-line, the capillaries were placed within another capillary (0.7 mm) with a constant purge of N$_2$ gas and aligned to the incoming beam. A tungsten coil, controlled by a thermostat, was wound around it to create an \textit{in-situ} furnace set-up. The wavelength of the incident beam at the beam-line was 0.77 Å and the corresponding 2θ range investigated was 0° to 40°. XRD data was collected for every 5.0 °C rise in temperature at a ramp rate of 2.0 °C/min. The XRD scattering of SBA-15 occur at very low angles (2θ ~ 1°) and the instrumental limitation of XRD to reach low angles impeded its data collection on SBA-15.
Differential scanning calorimetry (DSC) data was collected on a Q2000 series DSC from TA Instruments. Samples were loaded in small aluminum cans and hermetically sealed with an aluminum lid. The typical mass of samples measured was <5 mg. The data was collected by ramping temperatures at 2.0 °C/min. There were three trials done for each sample and the reported data are either the average or the best of the three trials.

The morphology of scaffolds and hydrides were investigated using a N₂-BET instrument (Quantachrome® Nova2200). Small amounts (~1.0 g) of samples were loaded into the bulb of the sample holder, degassed for three hours at 200 °C and data was collected in multi-point BET mode to extract specific surface areas and pore size distribution in addition to the sorption isotherms.

### 2.3 Results and Discussion

#### 2.3.1 EDS Characterization of Ti-grafted SBA-15

The SEM and EDS of the final product (Ti-grafted SBA-15) is shown in Figure 2.3. The elemental histogram revealed that the gravimetric ratio of Ti/Si was around 8% (1:0.08). This corresponds to a Ti-precursor to SBA-15 wt. ratio of around 1:20 chosen at the beginning. The infiltration of 4.0% (mol) Ti-doped NaAlH₄ into SBA-15 and infiltration of NaAlH₄ into Ti-grafted SBA-15 enables a distinction between bulk and surface Ti-catalysis, respectively, which is a major research topic among theoretical researchers [23]. The 4% (mol) Ti-doped NaAlH₄ was prepared by high energy ball milling of TiCl₃ with NaAlH₄. During the ball-milling process, Ti enters the NaAlH₄ lattice constituting “bulk” Ti. The samples developed here were meant to serve as specimens to validate the theoretical calculations by experiments.
The small confinement sizes of <10 nm segregate a limited number of NaAlH₄ formula units comparable to the crystallite sizes and geometries chosen for theoretical studies. However, the incompatibility of Ti-grafted SBA-15 with THF reagent, and in general, with any kind of wet infiltration technique limited further studies on these materials. Nevertheless, the synthesis procedures developed here were successful in dispersing very low amounts of Ti on the silica surface. As an alternative to wet infiltration, dry ball-milling was tried in the interest of breaking the porous SBA-15 into small (cup like) chunks which could get loaded with NaAlH₄ during the turbulence of the milling operation.

The energy dispersive spectroscopy (EDS) technique was used to estimate the Ti: NaAlH₄ molar ratio with prior knowledge of the SBA: NaAlH₄ weight ratio (chosen to be 1:1 for ball-milling). The SEM/EDS is shown in Figure 2.4. The elemental ratio of Ti/Na was around 3.6% (1: 0.036). This is in an acceptable statistical range with the 4% (mol) doped samples and re-iterates the precision with which known amounts of Ti can be deposited on the pore surface by this technique.
2.3.2 Pore Morphology of Scaffolds

Porous alumina (100 nm) exhibits a Type III isotherm (BET [24] and IUPAC [25] classification) which does not reach an adsorptive saturation, as shown in Figures 2.5 and 2.6. This isotherm type often means that the interaction of the adsorptive gas (N₂) and the adsorbent is poor, and because of this the gas molecules fail to form a mono-layer. At saturation pressures (\(P_o\)), there is an infinite amount of gas on the surface without a layered arrangement. The Type III isotherms are therefore not the perfect examples for a quantitative BET analysis. However, a qualitative trend which observes specific surface area before and after the sodium alanate infiltration confirms a reduction in SSA after infiltration showing that the pores were indeed filled. Generally, in situations where Type III isotherms are encountered, it is possible to get a different isotherm type by choosing a different adsorbate gas with a higher BET constant (C). The BET constant is a measure of adsorption energies needed to form a mono-layer. The isotherm type of porous alumina after NaAlH₄ infiltration is also shown (Figure 2.6). The specific volume of adsorptive gas on the y-scale is clearly reduced, which implies that the accessible surface area for
adsorption is reduced. This is a strong indication that the pores are occupied with NaAlH$_4$. The isotherm also shows that the sample retains its Type III behavior post infiltration reiterating the morphological stability of the scaffolds.

Figure 2.5: N$_2$ sorption isotherms of porous alumina (100nm) before NaAlH$_4$ infiltration showing Type III behavior.
SBA-15, in contrast to porous alumina, exhibits a Type IV isotherm showing saturation in adsorption/desorption at pressures closer to the saturation pressure ($P_o$). The isotherms for SBA-15 before and after infiltration are shown in Figures 2.7 and 2.8, respectively. Type IV isotherms are classical representations of pores that are in the form of capillaries, which is in agreement to the known pore structure of SBA-15 and is also seen in the SEM micrographs. The reduction in volume of $N_2$ gas adsorbed/desorbed on the y-scale confirms a loss in accessible specific surface area and the retention of the isotherm type implies that the morphology of the pore remains intact post infiltration. The quantitative aspects of the surface area and volume are discussed further in later sections.
Figure 2.7: N\textsubscript{2} sorption isotherms of porous SBA-15 (8 nm) before NaAlH\textsubscript{4} infiltration showing Type IV behavior.

Figure 2.8: N\textsubscript{2} sorption isotherms of porous SBA-15 (8 nm) after NaAlH\textsubscript{4} infiltration showing Type IV behavior.
The sorption profile of Fe-BTC is shown in Figure 2.9. The Fe-BTC MOF exhibits a Type II sorption isotherm. The adsorption never reaches a saturation owing to an indefinite multi-layer formation. However, the infinite multi-layer adsorption is preceded by a mono-layer at lower pressures and a capillary condensation phenomenon at mid-higher pressures leading to the flat portion at mid-pressures. Such an isotherm often represents materials that have a wide range of pore sizes. The MOFs are known to be inter-connected and possess more than one uniquely sized pores and in may cases have pore openings that are smaller than the pore itself. It is also suggested in literature that the pores, especially micropores (<2 nm), may get filled with N$_2$ gas molecules rather than forming layers [26]. Figure 2.10 shows the isotherm after the alanate infiltration and the reduction of y-scale confirms loss in the surface area while the retention of Type II sorption profile confirms the stability of the scaffolds.

![Figure 2.9: N$_2$ sorption isotherms of Fe-BTC MOF (<2 nm) before NaAlH$_4$ infiltration showing Type II behavior.](image)

Figure 2.10: N₂ sorption isotherms of Fe-BTC MOF (<2 nm) after NaAlH₄ infiltration showing Type II behavior.

The pore size distributions of the scaffolds were evaluated from the BET isotherms based on the density functional theory (DFT) method. In SBA-15 (Figure 2.11), the mean half-pore size was found to be ~30 Å. There is an additional distribution at ~15 Å, suggesting that a small fraction of pores are narrower. In contrast to the supplier's specification of pore sizes (8 nm), the experimental results reported here under-estimated the pore dimensions. The changes in pore size distribution show that both pores (15 Å and 30 Å) were filled with NaAlH₄. The ~30 Å pores were not completely filled, thus leaving a distribution centered at ~25 Å after infiltration. Also, some pores at the smaller size (~15 Å) remain even after infiltration.

The experiments on Fe-BTC revealed unique information on their morphology. As indicated by a Type II isotherm, the pore-size distribution (Figure 2.12) revealed multiple pore sizes ranging from ~15 Å to ~80 Å. This indicates a highly inter-connected
porous structure with secondary and even tertiary pores having different pore openings. This type of morphology has been reported for many other MOFs as well. The major fraction of the pores has half-widths less than 1.5 nm.

\[\text{Figura 2.11: Pore size distribution of SBA-15 before and after NaAlH}_3\text{ infiltration obtained from } N_2 - \text{BET experiments (DFT method).}\]
Figure 2.12: Pore size distribution of Fe-BTC MOF before and after NaAlH$_4$ infiltration obtained from N$_2$ – BET experiments (DFT method).

The pore size analysis yielding the volumetric and accessible surface area parameters was developed using the DFT method. DFT analysis is an available feature in the Autosorb software of the instrument (Quantachrome Instruments). The DFT method is based on fitting the theoretical isotherms of individual pores to the experimental data which yields the volumetric (and surface) contributions of the various pores to the adsorption. The pore structures of both Fe-BTC and SBA-15 are preserved after NaAlH$_4$ infiltration, confirming that the scaffolds are robust and stable hosts for the confined material. Table 2.2 lists the specific surface area (SSA) and the pore volume of the scaffolds before and after the infiltration procedure. All scaffolds show a reduced SSA after sodium alanate infiltration. The SSA of the SBA-15 reduced from ~730 m$^2$/g to ~125 m$^2$/g and that of Fe-BTC reduced from ~750 m$^2$/g to ~240 m$^2$/g after infiltration. The decrease in SSA was complimented by a reduction of pore volume (also evaluated
from BET isotherms) from 1.147 cc/g to 0.311 cc/g (73% loading) in SBA-15 and from 0.43 cc/g to 0.17 cc/g (60% loading) in Fe-BTC. The reduction in accessible pore volume confirms that the pores were occupied by NaAlH₄.

Table 2.2: Effect of NaAlH₄ infiltration on the specific surface area and pore volume of various scaffolds.

<table>
<thead>
<tr>
<th>Scaffold</th>
<th>Vendor Specified Pore Size (nm)</th>
<th>SSA (m²/g) {Pore volume (cc/g)} Before Infiltration</th>
<th>SSA (m²/g) {Pore volume (cc/g)} After Infiltration</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alumina</td>
<td>100</td>
<td>1539 {-}</td>
<td>168.5{-}</td>
</tr>
<tr>
<td>SBA-15</td>
<td>8-10</td>
<td>727.8{1.147}</td>
<td>125.4{0.311}</td>
</tr>
<tr>
<td>Fe-BTC</td>
<td>&lt;2</td>
<td>747.9{0.428}</td>
<td>240.5{0.173}</td>
</tr>
</tbody>
</table>

2.3.3 Chemical and Thermal Stability of the Scaffolds

The *in-situ* synchrotron XRD spectra show no change in the crystal structure of the bare MOF over the entire temperature range of hydrogen desorption from NaAlH₄. The spectra of Fe-BTC yield diffraction peaks at very low diffraction angles. Figure 2.13 [left] shows the high temperature XRD spectra of the bare Fe-BTC MOF and Figure 2.13 [right] shows Fe-BTC with infiltrated NaAlH₄ from room temperature to 200 °C. The peak positions are conserved over the entire temperature range in each case indicating thermal stability of the MOF, even after hydride infiltration. The broad bump at ~10° is an instrumental feature present in all investigated samples.
There are two important observations within the XRD data – one is that the peaks corresponding to sodium alanate are absent in the nano-confined sample. This disappearance of NaAlH₄ peaks upon confinement is due to a loss in long range order (a very good indication of spatial segregation of nano-sized particles and hence confinement); second, the reduction of peak intensities of the Fe-BTC scaffold upon sodium alanate infiltration (which is an indication that a secondary material (presumably NaAlH₄) is present within the highly ordered porous structure of the MOF resulting in a loss of signal. The isolated spikes in intensity (which appear as isolated lines) are not real and are artifacts introduced at the beam line.

Since the long range order of NaAlH₄ is lost, XRD is incapable of providing any further information on the desorption pathways of NaAlH₄ under confinement. In Chapter 4, an attempt has been made to study the local chemical structure around the metal sites in Fe-BTC to get more clues of the nature of co-ordination, if any, of the nano-confined NaAlH₄ with the metal sites of the MOF.
The chemical compatibility of NaAlH$_4$, THF and the scaffolds were verified by DSC experiments. The DSC data of micro NaAlH$_4$, bare Fe-BTC and nano NaAlH$_4$ (in Fe-BTC) samples, are shown in Figure 2.14 and that of micro-Ti-doped NaAlH$_4$, bare SBA-15 and nano-Ti-doped NaAlH$_4$ (in SBA-15) in Figure 2.15.

![DSC data](image)

**Figure 2.14:** DSC data to check compatibility of the Fe-BTC MOF with NaAlH$_4$ and THF.
The DSC clearly illustrates the thermal and chemical stability of the scaffold in the presence of sodium alanate. The scaffolds were also treated with only THF to check if there were any reactions in the temperature range of study. For these samples, the DSC results showed no features. All the distinct peaks in the DSC are attributed to NaAlH$_4$. While the micro NaAlH$_4$ sample shows an expected sharp endothermic peak at $\sim$185 °C, the data for nano-NaAlH$_4$ (in Fe-BTC) shows an early onset of the same peak ($\sim$175 °C). This feature (175 °C) arises from the un-confined NaAlH$_4$ particles that lie outside the mesoporous MOF particles. The slight reduction in temperature ($\sim$10 °C) may be attributed to a combined effect of smaller crystallite size (post THF infiltration) and possible scaffold interaction. In addition, the nano-NaAlH$_4$ samples in Fe-BTC (Figure 2.14) (and Ti-doped NaAlH$_4$ in SBA-15 (Figure 2.15)) show a very broad, less intense

**Figure 2.15:** DSC data to check compatibility of the SBA-15 with NaAlH$_4$, TiCl$_3$ doped NaAlH$_4$ and THF.
endothermic peak at \(\sim 100 \, ^\circ C\). This feature is expected to be a direct dehydrogenation process. This suggests that the nano-confined NaAlH\(_4\) may release hydrogen gas directly from NaAlH\(_4\) without the formation of Na\(_3\)AlH\(_6\) and can be attributed to a thermodynamic destabilization effect due to spatial confinement. This feature for both sample types is discussed in the next chapter.

### 2.4 Conclusions

The scaffolds chosen for this study possess distinctly different pore morphologies and collectively span three orders of magnitude in pore sizes. The morphologies were characterized by N\(_2\)-BET and SEM before and after infiltration of NaAlH\(_4\). The confinement of secondary material (NaAlH\(_4\)) in their pores has been justified by tracking losses in specific surface areas and scattered x-ray intensities. The most important requisite for an ideal scaffold is to be chemically compatible with sodium alanate in the presence of THF. Synchrotron XRD (with \textit{in-situ} heating) and DSC confirmed the chemical and thermal stability of the scaffolds in the presence of THF and NaAlH\(_4\).
CHAPTER 3

LATTICE DYNAMICS OF HYDROGEN IN NANOCONFINED SODIUM ALANATE

3.1 Introduction

A focus towards understanding the effect of nano-confinement on H-diffusion/dynamics of NaAlH₄ is discussed in this chapter. In the previous chapter, MOFs and SBA-15 were shown to possess unique pore morphologies and serve as stable scaffolds to confine nano-volumes of sodium alanate. It has been reported that nano-confinement results in faster hydrogen release [10-15, 27]. The faster release, by logic, is either due to shorter diffusion distances in nano-sized crystals or an overall increase in lattice jump diffusivities in the material itself. In order to elucidate if the latter is true, QENS experiments were performed on the nano-confined samples and compared to the lattice diffusion dynamics in pristine NaAlH₄ (micro NaAlH₄). The synergetic effect of Ti-doping and nano-confinement was also investigated and is reported in Section 3.3.6.

Unlike x-rays, which interact with the electrons in the sample, neutrons interact with the nuclei of the atoms. Being neutral, neutrons achieve a high penetration into the sample without being deflected by the charged electrons. For the reasons mentioned above, neutrons appear to have a high "visibility" for low Z elements like hydrogen, although the scattering power does not vary systematically with Z like in x-rays. Hydrogen (H) atoms offer the highest incoherent scattering cross-section of ~82 barns for
neutrons, making them the best probes for tracing hydrogen motion. Neutron spectroscopic techniques such as QENS are very useful tools to understand the spatial and temporal aspects of H-mobility in any hydrogenous material. Various materials like laves phase hydrides [28], complex metal hydrides [29], and chemical hydrides [30, 31] have been studied using the QENS technique successfully.

3.2 Experimental Methods

3.2.1 Quasi-elastic Neutron Scattering (QENS) Theory

QENS is a technique based on detecting the scattered neutrons that show a small distribution in energies around the elastic signal, which is appropriately called the quasi-elastic (QE) signal. While the elastic signal is due to static (or stationary relative to the thermal vibrations about equilibrium) H-atoms, this small QE signal is a result of neutrons that are scattered from the diffusing atoms (hydrogen in particular). The QE scattering leads to the broadening of the elastic peak, very analogous to how the XRD peaks broaden in a poorly crystalline sample. The broadening is modeled as a function of Q (wave number) and the type of diffusion is extracted along with all the quantitative parameters defining atomic diffusion (diffusivity, \( D \); jump length, \( L \); jump frequency, \( 1/\tau \)).

Typically, the data are fit using a Gaussian function for the elastic signal \( (A_0) \) and multiple resolution broadened Lorentzian functions \( (A_1 \) and \( A_2) \) to model the QE broadening. This is shown in Eq. 3.1:

\[
S(Q, \omega) = A_0(Q)\delta(\omega) + A_1(Q)L(\omega, \Gamma_1) + A_2(Q)L(\omega, \Gamma_2). \tag{3.1}
\]
Here, the sum of the amplitudes is unity (i.e., $A_o + A_I + A_2 = 1$) and the ratio of the elastic peak amplitude ($A_o$) to the total amplitude ($A_o + \sum A_i$) is the elastic incoherent structure factor (EISF). $L(\omega, \Gamma)$ is the Lorentzian function and the full width at half maximum (FWHM, $\Gamma$) is a direct representation of the time-scale of motion, $\tau$. The broader the FWHM, the faster are the dynamics.

The temporal and spatial metrics of hydrogen dynamics are extracted by modeling the widths of the two Lorentzian functions (FWHM, $\Gamma$) using mathematical diffusion models. A brief explanation of the diffusion models is furnished below with their respective equations (Eq. 3.2 to Eq. 3.4). The simulated curve shapes of the different models are shown in Figure 3.1.

![Simulated curve shapes of the various diffusion models with arbitrary variable values.](image)

**Figure 3.1:** Simulated curve shapes of the various diffusion models with arbitrary variable values.
The Chudley Elliott (CE) diffusion model is the simplest representation of an atomic jump diffusion process and is visualized as random jumps to the nearest site with a mean residence time ($\tau$) at each site. The isotropic CE model [32] can be written as:

$$\text{FWHM}, \Gamma(Q) = \frac{2h}{\tau} \left[ 1 - \frac{\sin(Ql)}{Ql} \right]. \quad \text{Eq. 3.2}$$

In contrast to the CE model, whose postulates are more suited to highly ordered crystalline materials, Singwi-Sjolander (SS) model quantitatively describes a two stage diffusion process comprising of successive translations (of time scale, $\tau_d$) and oscillations (of time scale, $\tau_o$). This approach is well-suited to address disordered systems such as hydrogen in metal and hydrogen dynamics in water, for which it was initially proposed [32-34], The Q-dependency of FWHM can be represented by SS model as follows [32]:

$$\text{FWHM}, \Gamma(Q) = \frac{2}{\tau_o} \left[ 1 - \frac{\exp(-2W)}{1 + DQ^2 \tau_o} \right]. \quad \text{Eq. 3.3}$$

Where $\tau_o$ is life time of oscillatory motion, $D$ is the diffusion co-efficient, and the expression $\exp(-2W)$ is the Debye-Waller term. Eq. 3.3 is derived for jump processes, under the condition that $\tau_d << \tau_o$, where $\tau_d$ is the time spent in translation between jumps. This restricts the use of this equation to data at low Q values only. At high Q values, $DQ^2 \tau_o >> 1$, which forces the broadening to tend to the asymptotic value of $(\tau_o)^{-1}$ (Q-independent).

When atomic diffusion process is more continuous (or when the diffusion rates are slower), the H-atom spends a significant time in translation mode (i.e. $\tau_d >> \tau_o$) because of which the data tends to show a Q-dependency at high Q values. In such situations, SS model (Eq. 3.3) cannot be applied directly since it assumes $\tau_d$ to be negligible. The
following expression (Eq. 3.4) is derived to include $\tau_d$ and thus explains the Q-dependence of FWHM at high Q-values [29]:

$$\text{FWHM}, \Gamma(Q) = \frac{2Q^2D(\tau_d + \tau_o)}{\sqrt{\tau_o^2D^2Q^2(\tau_d + \tau_o)^2 + 2\tau_d\tau_o}}, \quad \text{Eq. 3.4}$$

where 'l' is the jump length and

$$D = \frac{l^2}{6(\tau_d + \tau_o)}, \quad \text{Eq. 3.5}$$

3.2.2 QENS Instrumentation

All neutron scattering data reported here were obtained on two instruments located at the National Institute for Standards and Technology (NIST) Center for Neutron Research (NCNR) in Gaithersburg, MD, a backscattering spectrometer (High Flux Backscattering Spectrometer, NG-2 beam-line) and a time-of-flight spectrometer (Disk Chopper Spectrometer, NG-4 beam-line).

The samples for the QENS experiments were prepared by sprinkling a small amount of the powdered samples evenly (allowing 90% transmission of the neutron beam) between thin aluminum foils and wrapping the edges to make thin slabs. These slabs were placed upright in aluminum sample cans that were sealed with aluminum lids using lead wire as an edge seal. The can was introduced into the sample well oriented at 45° with respect to the incoming neutron beam. Such an orientation restricts in-plane shadow of the sample to only the corner detectors and ensures quality signal for the rest of the Q-range.

The use of two instruments extends the accessible time scale of hydrogen dynamics within the sample from 10 ns to 0.1 ps. The incident wavelength used for HFBS was 6 Å with an energy transfer of +/- 17 μeV. The HFBS offers an extremely fine
energy resolution of 1 μeV, but at the expense of a narrow frequency range (time-scale). The HFBS records spectra across 16 detectors covering a Q-range of 0.25 Å⁻¹ to 1.75 Å⁻¹. The incident neutron wavelength used for DCS was 4.8 Å with a corresponding energy resolution of ~110 μeV (FWHM). One sample was studied at 6.0 Å to assess the effect of a higher resolution. The accessible Q-range for DCS at neutron wavelength of 4.8 Å was 0.3 Å⁻¹ to 2.1 Å⁻¹ and at 6.0 Å, the upper limit of the Q-range reduced to ~1.7 Å⁻¹. Although the DCS has a very coarse energy resolution compared to HFBS, the frequency range is wide enough to track multiple distinct diffusion processes at a single temperature with a very good quasi-elastic (QE) signal. The data was reduced and analyzed using DAVE® (Data Analysis and Visualization Environment), a software package provided by NCNR [35].

3.3 Results and Discussion

3.3.1 Elastic Neutron Scans

Prior to QENS, the samples were subjected to fixed window scans (FWS). The FWS yield a preliminary indication of transition temperatures, at which the detected intensity drops rather quickly owing to faster hydrogen dynamics that exceed the energy/time window of the instrument (>10⁸ jumps/s). This is best illustrated by micro-NaAlH₄ (Figure 3.2) at ~450 K (the onset temperature of desorption), where the intensity precipitously drops between 450 K and 500 K, is characteristic of a zero order decomposition reaction. This characteristic drop in intensity however is not clearly evident in the nano-NaAlH₄ and bare Fe-BTC samples. The gradual negative slope in intensity with increasing temperatures in all three samples is due to the Debye-Waller factor. In order to confirm hydrogen desorption from the nano samples, a cooling
schedule was performed (blue trace in Figure 3.2). The observed intensities in the cooling curve will reduce if hydrogen is lost during the heating process, leading to a hysteresis between the two signals. The nano NaAlH₄ sample does show a clear difference in intensities of the heating and cooling curves, but the bare Fe-BTC does not, re-assuring that there is no hydrogen (or moisture) released from the scaffold during these experiments. Based on the FWS and thermal analysis, the QENS data were collected on both DCS and HFBS at multiple temperatures.

**Figure 3.2:** Fixed window elastic scan data from the HFBS instrument of (i) Fe-BTC empty scaffold, (ii) nano-NaAlH₄ in Fe-BTC and (iii) pristine micro-NaAlH₄.
3.3.2 Quasi-elastic Neutron Scans

Micro-NaAlH₄ was studied at 450 K on DCS, while measurements on nano-NaAlH₄ were done at 350 K & 400 K on the DCS, and at 125 K, 150 K, 300 K and 320 K on the HFBS. A large signal due to hydrogen dynamics was clearly evident in the energy contour plots from the DCS instrument (Figure 3.3), where the nano-NaAlH₄ showed a spectacular increase in QE signal (green area) even at temperatures as low as 350 K (80 °C). The broadening shows a strong Q-dependence at low Q values and appears to have a weaker Q-dependence for Q > 1.0 Å⁻¹. At even higher Q values (Q > 1.9 Å⁻¹), there appears to be a flat Q-independent signal of a lower amplitude. As discussed in the subsequent sections, the observed QE signal from Figure 3.3 (right) is a combination of two geometrically distinct dynamical processes.

![Figure 3.3](image)

**Figure 3.3:** Energy contour plots of NaAlH₄ in its pristine form (micro-NaAlH₄) (left) and nano-NaAlH₄ (in Fe-BTC) (right) obtained from the DCS instrument.

Examples of the actual QENS spectra at Q = 1.0 Å⁻¹ (and their corresponding fits) from the HFBS and DCS are shown in Figures 3.4 and 3.5, respectively. The data were fit using a Gaussian function (black / dotted) for the elastic signal and multiple resolution broadened Lorentzian functions (red / dashed) to model the QE broadening in accordance with Eq. 3.1.
Figure 3.4: The QENS spectra from the HFBS instrument of nano-NaAlH$_4$ (in Fe-BTC) at 125K (i), 150K (ii), 320K (iii) and empty Fe-BTC scaffold at 400K (iv).

Figure 3.5: QENS data from DCS instrument of (i) micro NaAlH$_4$ at 450 K, (ii) nano-NaAlH$_4$ in Fe-BTC at 350 K (iii) nano-NaAlH$_4$ in Fe-BTC at 400 K on HFBS and (iv) nano-NaAlH$_4$ in Fe-BTC at 350 K using neutrons of $\lambda = 6$ Å.
Figure 3.4 shows the QENS data for nano-NaAlH$_4$ at (i) 125 K, (ii) 150 K and (iii) 320 K; and (iv) bare Fe-BTC at 400 K investigated on the HFBS instrument. All spectra obtained from HFBS were well described by one elastic Gaussian and one Lorentzian functions. The bare Fe-BTC in Figure 3.4 (iv) shows negligible QE broadening on the HFBS, which confirms that the observed hydrogen dynamics in Figures 3.4 (i), (ii), and (iii) are indeed from the infiltrated NaAlH$_4$. All the hydrogen atoms in Fe-BTC are present in the organic linkers and are expected to be in rapid vibrations that are beyond the accessible timescale of QENS instruments. This is evident by the strong Debye-Waller contribution in the FWS.

The QENS spectra at Q = 1.0 Å$^{-1}$ from the DCS instrument are shown in Figure 3.5. One Lorentzian function was sufficient to fit the broadening in micro-NaAlH$_4$, while the data from the nano samples needed two separate Lorentzians. The broader Lorentzian originates from fast localized atomic hydrogen motion and the narrow Lorentzian can be attributed to slower, long range hydrogen diffusion [32, 33]. It is interesting to note that the two Lorentzians show Q-variation for both FWHM and EISF. The detailed analysis of the FWHM and EISF is provided in the specific context of long range diffusion (Sections 3.3.3) and localized diffusion (Section 3.3.5). A Q-dependency in EISF arises due to a spatially restricted geometry of the jump process and a Q-dependency in FWHM is because of the hydrogen atom spending appreciable time making translations between sites [32, 33].

Generally, long range diffusion tends to show a Q-dependency in FWHM, but is Q-independent in EISF, whereas it is the other way around for localized motion. A Q-dependent EISF for long range motion suggests that the distribution of jump sites is
spatially limited since the maximum diffusion length is restricted to dimensions less than the pore size itself. Likewise, the Q-dependence of the broad Lorentzian width is indicative that the hydrogen atoms perform a continuous rotation between sites rather than discrete jumps. The flowchart in Figure 3.6 gives an overview of the data reduction and analysis that follows in the subsequent sections.

**Figure 3.6:** Overview of QENS data reduction and analysis.

### 3.3.3 Long Range Diffusion of H-atoms

Figure 3.7 shows the $Q^2$-dependence of the narrow Lorentzian widths of the micro NaAlH$_4$ at 450K and the nano NaAlH$_4$ at 350 K and 400 K. The width of the narrow
Lorentzian rapidly increases with increasing $Q$ and reaches a saturation asymptotic value for $Q > 1.0$ Å$^{-1}$. Also, the broadening increases with temperature. These occurrences tend to confirm that the narrow Lorentzian represents hydrogen atoms involved in a slower jump diffusion process that occurs on a long range order. The FWHM of the nano NaAlH$_4$ at both 350 K and 400 K are lower in magnitude compared to that of micro NaAlH$_4$ at 450 K and the trend seems to suggest that the nano-confinement does not really cause a significant enhancement in the jump diffusion kinetics.

![Figure 3.7](image-url)

**Figure 3.7:** $Q^2$-variation of the narrow Lorentzian widths of micro and nano (in Fe-BTC) NaAlH$_4$ samples; data is from DCS instrument and lines are best fits to Singwi-Sjolander (SS) model.

The diffusivity of hydrogen atoms in nano NaAlH$_4$ at 350 K and 400 K are only marginally better than micro NaAlH$_4$ at 450 K but they also seem to have higher residence times ($\tau_0$) at each site compared to the micro NaAlH$_4$. The $Q$-dependent EISF for this process implies that the sites available are limited, but a larger mean residence
time at these sites suggest that hydrogen atoms are randomly making jumps between the same sites without leaving the system. At this stage of the discussion, it is clear that the limiting factor for hydrogen release is not the jump-diffusion kinetics of hydrogen atoms.

Figure 3.8 shows the $Q^2$-dependence of the single Lorentzian widths of nano NaAlH$_4$ at lower temperatures obtained from the HFBS experiments. The atomic mobility is significantly diminished at cryogenic temperatures and hence HFBS was used to track them. The data were fit using the CE diffusion model and SS model (not shown) separately.

![Figure 3.8: $Q^2$-variation of Lorentzian widths in nano-NaAlH$_4$ (in Fe-BTC); data was measured on HFBS and lines are best fits of Chudley-Elliott model.](image)

The parameters of the model fits are shown in Table 3.1. The goodness of fit for both models is identical, the CE model being only marginally better. The CE model fits the low Q very well, while the SS model has a better averaged fit. The suitability of CE model (representative of diffusion in an ordered lattice arrangement) at low temperatures
as opposed to SS model at high temperatures, for the same samples, indicates that the samples portrayed a more ordered structure at lower temperatures. This observation is possible only at low temperatures because of the lower mobility of constituent atoms, and this confirms that the structure of NaAlH₄ is still preserved on the local order even after confinement. It is important to note that the small crystallite sizes limited the applicability of x-ray diffraction to reach this same conclusion since XRD requires long range crystalline order. At higher temperatures, the lattice vibrations are severely enhanced owing to the small crystallite sizes because of which they tend to show a SS model type behavior.

Table 3.1: Long-range diffusion parameters of H-atoms in unconfined and nano-confined NaAlH₄ lattice obtained from best fits to SS model (for DSC data) and CE model (for HFBS data).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Jump Length, $l$ (Å)</th>
<th>Diffusivity, $D$ ($\times 10^{-5}$ cm²/ps)</th>
<th>Residence Time, $\tau_r$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro NaAlH₄</td>
<td>450</td>
<td>2.20</td>
<td>4.23</td>
<td>1.78</td>
</tr>
<tr>
<td>Nano NaAlH₄ (DCS)</td>
<td>400</td>
<td>2.80</td>
<td>6.70</td>
<td>2.13</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>2.45</td>
<td>4.55</td>
<td>2.19</td>
</tr>
<tr>
<td>Nano NaAlH₄ (HFBS)</td>
<td>320</td>
<td>2.80</td>
<td>0.05</td>
<td>260.00</td>
</tr>
<tr>
<td></td>
<td>150</td>
<td>2.32</td>
<td>0.02</td>
<td>440.00</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>2.27</td>
<td>0.01</td>
<td>500.00</td>
</tr>
</tbody>
</table>
The EISFs of the narrow Lorentzians of nano NaAlH$_4$ and the single Lorentzian of micro NaAlH$_4$ are shown in Figure 3.9. The long range diffusion process was best described by the isotropic six site model [32, 33] as shown in Eq. 3.6:

$$EISF_{6\text{site}} = 1 - p + \frac{p}{6} \left[ 1 + 2j_o(Ql) + 2j_o(Ql\sqrt{3}) + j_o(2Ql) \right]. \quad \text{Eq. 3.6}$$

The EISF of micro NaAlH$_4$ shows negligible variation with $Q$, clearly suggesting that the dynamical process tracked using the DCS instrument is a long-range jump process. It is also noteworthy that only 4% of the hydrogen atoms are in a mobile state, which concurs with the finding of previous experiments [29, 36] at similar temperatures. In comparison, the narrow Lorentzian of the nano NaAlH$_4$, which also represents long range diffusion, shows a distinct $Q$-dependent EISF with close to 21% of hydrogen atoms participating in long range jumps. The $Q$-dependence of the narrow EISF also signifies that the sites available for random jumps are spread in a limited space. This is a direct proof that the NaAlH$_4$ is confined within the nano-sized pores of MOF.
Figure 3.9: Q-variation of EISF of micro and nano (in Fe-BTC) NaAlH$_4$ samples; data was collected on DCS instrument; data points were calculated from the narrow Lorentzian amplitudes (refer Eq. 3.1) and full lines are best fits of the isotropic six site model (Eq. 3.6).

The EISF of the single Lorentzians of nano NaAlH$_4$ from HFBS experiments are shown in Figure 3.10. Even at sub-zero temperatures, 15% of hydrogen atoms were found to be in a mobile state although they were slower jumps. This diffusion process is different in the time-scale compared to those tracked on the DCS instrument. The jump lengths agree with the distance between H-sites in NaAlH$_4$, which validates the observed signal to be originating from the NaAlH$_4$ lattice.
Figure 3.10: Q-dependence of EISF of nano-NaAlH₄ (in Fe-BTC) measured; data was collected from HFBS instrument and data points were calculated from the amplitudes (Eq. 3.1); lines are best fits to the isotropic six site model (Eq. 3.6).

The HFBS data was fit using Eq. 3.6 and the fits (both DCS and HFBS) are shown in Table 3.2.

Table 3.2: Jump diffusion parameters of H-atoms in unconfined and nano-confined NaAlH₄ lattice evaluated by EISF fits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Model</th>
<th>Jump Length, l (Å)</th>
<th>p</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro NaAlH₄</td>
<td>450</td>
<td>6 site isotropic</td>
<td>2.46</td>
<td>0.04</td>
</tr>
<tr>
<td>Nano NaAlH₄ (DCS)</td>
<td>400</td>
<td>6 site isotropic</td>
<td>2.60</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>320</td>
<td>6 site isotropic</td>
<td>2.90</td>
<td>0.14</td>
</tr>
<tr>
<td>Nano NaAlH₄ (HFBS)</td>
<td>150</td>
<td>6 site isotropic</td>
<td>2.80</td>
<td>0.12</td>
</tr>
<tr>
<td></td>
<td>125</td>
<td>6 site isotropic</td>
<td>2.80</td>
<td>0.11</td>
</tr>
</tbody>
</table>
3.3.4 Effect of Neutron Wavelength

A small increase in incident neutron wavelength on the DCS instrument yields a sharp increase in energy resolution, but at the expense of a narrower accessible Q-range and weaker quasi-elastic signal intensity [37]. In order to explore the effect of resolution on our samples, nano-NaAlH₄ at 350 K was investigated using neutrons of wavelength 6.0 Å in addition to that of 4.8 Å (Figures 3.11 and 3.12). The QE broadening appeared to be less when measured at 6.0 Å, indicating that the dynamics observed were slower than what was measured using 4.8 Å. This difference in widths was more pronounced for the long range dynamics, where the asymptotic value of FWHM was almost half of that in the 4.8 Å measurements. While the improvement in energy resolution by switching to 6.0 Å was calculated to be around 50 µeV [37], the difference in the asymptotic values of FWHM is in the range of 400 µeV for the narrow Lorentzian (Figure 3.11). A very large increase in wavelength often facilitates a preferential analysis of the translational dynamics without the rotational part of the signal [38]. This is because the rotational contribution to the QE signal, which is often from the broader Lorentzian, may be viewed as a flat background at very high resolution [refer to Figure 3.5 (iv) for the QENS data and Lorentzians]. However, our data with neutrons of 6.0 Å was well represented by both Lorentzians. The Q²-dependence of broad Lorentzian widths are comparable when measured at the two different wavelengths, although the process appeared marginally slower when measured at 6.0 Å (Figure 3.12).
Figure 3.11: Effect of neutron wavelength on narrow Lorentzian widths (long range diffusion parameters) in nano-NaAlH$_4$ (in Fe-BTC) measured at 350 K.

Figure 3.12: Effect of neutron wavelength on broad Lorentzian widths (localized diffusion parameters) in nano-NaAlH$_4$ (in Fe-BTC) measured at 350 K.
3.3.5 Localized Dynamics of H-atoms in the Alanate Tetrahedron

Figure 3.13 shows the $Q^2$-dependence of the broad Lorentzian. The narrow Lorentzian distribution illustrated previously (Figure 3.7) is also included for comparison. The narrow Lorentzian FWHM fits well with Eq. 3.3 while the broader Lorentzian (typically $Q$-independent) shows strong dependence at higher $Q$ values and is fit using Eq. 3.4. The intensity of the QE signal from the broad Lorentzian, $A_2$, appears to increase with increasing $Q$ indicating that the motion is very fast and localized.

![Graph showing $Q^2$-variation of the broad Lorentzian widths of nano NaAlH$_4$ (in Fe-BTC); data is from DCS instrument and lines are best fits to Modified Singwi-Sjolander model; data at low FWHM are narrow Lorentzian widths provided for comparison.](image)

Figure 3.13: $Q^2$-variation of the broad Lorentzian widths of nano NaAlH$_4$ (in Fe-BTC); data is from DCS instrument and lines are best fits to Modified Singwi-Sjolander model; data at low FWHM are narrow Lorentzian widths provided for comparison.

The variation of FWHM with $Q$ also suggests that the hydrogen atoms have an appreciable timescale of translation ($\tau_d$) (or in lay terms - 'flight-time'). This could be due to two reasons: either due to low diffusivity of the diffusing species or due to a more
continuous motion rather than discrete jumps. The results in Table 3.3 show very small jump lengths (~0.6 Å) compared to the average distance between hydrogen sites (~2.6 Å). This atypical value for the localized dynamics are due to a combination of more than one re-orientation mechanism about multiple axes of symmetry or a reorientation coupled with a rotational motion about different axes of symmetry. The jump length is a common fit parameter between the SS model and the EISF model. It signifies the same dynamical process of the same hydrogen atom and hence should be consistent with either of the two approaches to evaluate it.

Table 3.3: Localized jump diffusion parameters of H-atoms in nano-confined NaAlH$_4$ lattice obtained from best fits of modified Singwi-Sjolander model to data from DCS instrument.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Jump Length, $l$ (Å)</th>
<th>Diffusivity, $D$($x 10^5 \text{cm}^2/\text{s}$)</th>
<th>Residence Time, $\tau_\rho$ (ps)</th>
<th>Translation Time, $\tau_\delta$ (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano NaAlH$_4$ (DCS)</td>
<td>400K</td>
<td>0.62</td>
<td>1.62</td>
<td>0.25</td>
<td>0.16</td>
</tr>
<tr>
<td></td>
<td>350K</td>
<td>0.58</td>
<td>1.70</td>
<td>0.16</td>
<td>0.17</td>
</tr>
</tbody>
</table>

The geometry of the localized motion is deduced by modeling the Q-dependence of EISF. As mentioned earlier, both Lorentzians used to fit the nano NaAlH$_4$ data showed Q-dependent EISF and FWHM. Generally, long range H-diffusion shows a flat Q-independent EISF and is often described by rigorously modeling the quasi-elastic peak shape, without any geometrical description of the jumps. This is true in the crystalline bulk samples that have long-range order.
Figure 3.14 shows an illustration of the crystal structure of the alanate tetrahedron. Sodium alanate comprises of $\text{AlH}_4^-$ anions that are coordinated with $\text{Na}^+$ cations. The H-H bond lengths in $\text{NaAlH}_4$ are in the order of $\sim 2.6$ Å and the Al-H distances are of the order of 1.6 Å.

Figure 3.14: Crystal structure of $\text{NaAH}_4$ [white spheres are H-atoms, violet spheres are Na and the Al atoms are at the center of the alanate tetrahedron].

The broader Lorentzians show a sharp Q dependence and clearly exhibit a larger fraction of H-atoms participating in dynamic motion, while the narrow Lorentzians show a smaller fraction of the mobile H-atoms (magnified plot was shown previously in Figure 3.9). The localized EISFs (broad Lorentzian) were compared to many re-orientation and continuous diffusion models [32, 33, 39-42]. The EISF model equations used are listed in Table 3.4 and are explained in detail in Appendix A.
Table 3.4: EISF models to characterize the geometry of localized diffusion dynamics of H-atoms.

<table>
<thead>
<tr>
<th>Model</th>
<th>Equation</th>
<th>Parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotropic Rotation</td>
<td>[ j_o^2(Qr) ]</td>
<td>( r ) = radius of sphere</td>
</tr>
<tr>
<td>(eq. iii)</td>
<td>[ \frac{1}{N^3 + N} \left{ \frac{1}{4} \left[ \frac{N}{3} + Nj_o \left( Qr \sqrt{3} \right) \right] \right} ]</td>
<td></td>
</tr>
<tr>
<td>High Temperature Model</td>
<td>[ \frac{3}{4} \left[ \frac{N}{3} j_o \left( Qr \sqrt{3} \right) \right] + \sum_{p=1}^{N} j_o \left( 2Qr \sin \left[ \frac{\pi p}{N} \right] \right) ]</td>
<td>( r ) = radius of circle</td>
</tr>
<tr>
<td>(eq. iv)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Tetrahedral Tumbling</td>
<td>[ \frac{1}{4} \left[ 1 + 3j_o(Qa) \right] ]</td>
<td>( a ) = jump length (( a/\sqrt{3} ) = Al-H bond)</td>
</tr>
<tr>
<td>(eq. v)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cubic Tumbling</td>
<td>[ \frac{1}{8} \left[ 1 + 3j_o(Qa) + 3j_o \left( Qa \sqrt{2} \right) + j_o \left( Qa \sqrt{3} \right) \right] ]</td>
<td>( a ) = jump length</td>
</tr>
<tr>
<td>(eq. vi)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

In the observed Q-range, all the models appeared to fit well with the data as shown in Figure 3.15. The correct EISF model was identified by comparing the fit parameters (jump lengths) with those obtained from modeling the Q-dependence of FWHM (refer to Tables 3.1 and 3.2). The ‘high temperature’ (HT) model, derived elsewhere to describe BH₄⁻ reorientations [39], was found to be the best descriptive model for the nano-samples. The HT model assumes that three out of four hydrogen
atoms in the alanate tetrahedron make jumps in a circular geometry about its trigonal axis and the other occupies the axial position. Each of the three hydrogen atoms in this circle is assumed to jump \((2\pi/N)\) radians, where \(N\) is the number of equidistant points on the circle. By choosing an appropriately large value for \(N\), the model will assume a diffuse distribution of hydrogen atoms on the circle and thus approximate a continuous rotation on this circle. The other hydrogen atom in the axial position is allowed to exchange positions with any of the three rotating hydrogen atoms by an appropriate ‘tumbling’ reorientation such as tetrahedral tumbling (details discussed in Appendix A).

Figure 3.15: Q-variation of EISF of nano NaAlH\(_4\) (in Fe-BTC); data was collected on DCS instrument; data points were calculated from the broad Lorentzian amplitudes (refer Eq. 3.1) and full lines are best fits of the diffusion models in Table 3.4; the EISF of narrow Lorentzians are included for comparison (curves (i) and (ii) fit with Eq. 3.6).

The EISF of the HT model is a weighted average (methodology described in [40]) of the EISF for tetrahedral tumbling (in Eq. v, Figure 3.15) [41] and the EISF for N
jumps about a circle [33]. For $N = 6$ (in Eq. iv, Figure 3.15), our data yields a jump length on the circle ($l_1$) of 1.33 Å ($r = 1.33$ Å). For $N = 12$, the evaluated jump length was $l_1 = 0.68$ Å ($r = 1.33$ Å). These values are reported in Table 3.5. This value is in excellent agreement with the jump length calculated from modeling the $Q^2$-variation of FWHM using SS model (Table 3.3). The distance between the axial H-atom and the orbiting H-atom is fixed at $r\sqrt{3}$ ($l_2 = 2.3$ Å), which agrees with the structural information of NaAlH$_4$ (H-H bond distance of ~2.6 Å). The calculations are addressed in Appendix A.

Table 3.5: Localized jump diffusion paramters of H-atoms in nano-confined NaAlH$_4$ lattice evaluated by EISF model fits.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>Model</th>
<th>Jump length, $l$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Nano NaAlH$_4$</td>
<td>400K</td>
<td>HT Model (N=12)</td>
<td>0.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HT Model (N=6)</td>
<td>1.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cubic Tumbling</td>
<td>0.94</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Tetrahedral Tumbling</td>
<td>1.35</td>
</tr>
</tbody>
</table>

3.3.6 Synergetic Effect of Ti-doping and Nano-confinement

A comprehensive report of QENS results is presented for samples that were nano-confined in SBA-15 after TiCl$_3$ doping. In a prior study by J.H. Bitter et al. [44], the dehydrogenation properties were found to be affected by the stage at which Ti was introduced into the nano-scaffolds: deposition of Ti before NaAlH$_4$ infiltration was found to be more favorable. Yet another study showed that the presence of TiCl$_3$ in the nano-confined NaAlH$_4$ helped the onset temperature for hydrogen release to be much lower.
than the nano-confined pristine NaAlH₄ [45]. In both these studies, NaAlH₄ and TiCl₃ were infiltrated in two separate stages and TiCl₃ impregnation was done first, such that the scaffold material was 'functionalized' with Ti before the hydride insertion. In our experiments, a ball milled mixture of NaAlH₄ and 4% (mol) TiCl₃ was infiltrated into SBA-15 in a single process using Tetrahydrofuran (THF). The main motive of this study is to elucidate the role of Ti in NaAlH₄ desorption particularly at the nano-scale. A second dimension to this study was proposed using the Ti-grafted SBA-15 discussed in Chapter 2. The Ti-grafted SBA-15 was supposed to be used as functionalized scaffolds to investigate the role of geometrical location of the catalyst (bulk vs. surface). However, since the Ti-grafted SBA-15 were not compatible with THF, it was not possible to complete this additional proposed study.

Until recently, most published literature investigated TiCl₃ doping and nano-confinement as two tactical approaches to address the thermodynamic and kinetic issues. In this study, a three-fold comparison of desorption trends are presented - pure NaAlH₄, TiCl₃ doped NaAlH₄ and Ti-doped NaAlH₄ confined within SBA-15. Desorption properties of pure NaAlH₄ and nano-confined NaAlH₄ has already been presented in the previous sections, which will be cited whereever appropriate. Figure 3.16 illustrates the elastic scans performed on the samples. The pure NaAlH₄ begins to decompose with an onset of fast hydrogen dynamics at 450+ K. Ti-doped NaAlH₄ shows a reduction of ~50 K to start desorbing at ~420 K. The nano-Ti-doped NaAlH₄ (in SBA-15) desorbs at an even lower temperature of ~350 K. In retrospect, nano-NaAlH₄ in Fe-BTC had a negative slope from a very low temperature as well, although the transition temperature was not sharply evident. The scaffold (SBA-15) neither showed any drop in intensity beyond
acceptable Debye-Waller induced slope, nor did it show any hysteresis between the heating and cooling curves.

![Graphs showing heating and cooling curves at different temperatures.](image)

**Figure 3.16:** Fixed window elastic scan data from the HFBS instrument of (a) SBA-15 (empty scaffold), (b) nano-Ti-doped NaAlH₄ in SBA-15, (c) micro-Ti-doped NaAlH₄, and (d) pristine micro-NaAlH₄.

Analysis of the QE broadening revealed a similar pattern observed for pure NaAlH₄, where the samples did not show an appreciably large increase in the diffusivities when nano-confined (Figure 3.17). However, the pure micro-NaAlH₄ data saturated at an asymptotic value of ~1 meV, while in the micro-TiCl₃ doped NaAlH₄, it was higher by a small margin at ~1.25 meV. The broader distribution of energies implies that Ti-doping only improved the H-diffusivities, which was expected. However, similar to the argument
presented in the previous sections for pure NaAlH₄, the nano-confinement did not enhance the diffusivities by an appreciable margin even for the Ti-doped NaAlH₄. In comparison to the nano-samples of pure NaAlH₄ in Fe-BTC and Ti-doped NaAlH₄ in SBA-15, the maxima (asymptotic value) were similar. If lattice diffusivities of hydrogen is considered the metric, synergetic effect of Ti-doping and nano-confinement is unlikely to be any better than either of the strategies adopted independently.

![Graph](image)

**Figure 3.17:** $Q^2$-variation of the narrow Lorentzian widths of micro and nano TiCl₃-doped NaAlH₄ samples; data was collected from DCS instrument and lines are best fits to Singwi-Sjolander model.

Table 3.6 shows the diffusion parameters of the micro and nano TiCl₃-doped NaAlH₄ samples. The jump lengths evaluated concur well with the known lattice structure of NaAlH₄, although the jump lengths in these samples appeared lower than pure NaAlH₄ samples. There have been studies that showed a decrease in lattice parameters following Ti-addition [46]. The nano samples show lower diffusivities and a
higher residence time than the bulk sample. The nano samples were measured at lower temperatures than the micro samples. However, these temperatures signify the onset of desorption (refer Figure 3.16) in the respective samples and hence justify the comparison. In an argument similar to that of nano pure NaAlH₄, the nano-confinement only improves the overall fraction of H-atom participation in dynamics but the lattice diffusivities are unaffected.

**Table 3.6:** Long-range diffusion parameters of H-atoms in unconfined and nano-confined (in SBA-15) TiCl₃-doped NaAlH₄ obtained from best fits to SS model (for DSC data).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Jump Length, ( I ) (Å)</th>
<th>Diffusivity, ( D ) (x 10⁻⁵ cm²/s)</th>
<th>Residence Time, ( \tau_r ) (ps)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro TiCl₃ doped NaAlH₄</td>
<td>420</td>
<td>2.27</td>
<td>6.13</td>
<td>1.40</td>
</tr>
<tr>
<td>Nano TiCl₃ doped NaAlH₄</td>
<td>400</td>
<td>2.09</td>
<td>5.96</td>
<td>2.09</td>
</tr>
<tr>
<td></td>
<td>350</td>
<td>2.16</td>
<td>4.54</td>
<td>2.16</td>
</tr>
</tbody>
</table>

The EISF (Figure 3.18) revealed an increase in the fraction of H-atoms participating in diffusive motion. Roughly 15% of H-atoms were actively participating in long range diffusion compared to the micro-sample and the generic trend was comparable to the micro and nano samples of pure NaAlH₄. Clearly, nano-confinement has an effect in increasing the fraction of mobile hydrogen despite not increasing the rates at which they diffuse.
Upon observing the localized dynamics of the H-atoms in the alanate tetrahedron in Figure 3.19, the EISF tend to flatten out at much higher values than pure NaAlH₄. This indicates that, unlike pure nano-NaAlH₄ samples, Ti-doped samples may have a different tumbling / reorientation mechanism. By tracking the change in the tumbling mechanism of the alanate tetrahedron, the position and hence the role of Ti in the NaAlH₄ lattice can be extracted. Ozolins et al. [47] showed that TiCl₃ doping has negligible effect on the structure of NaAlH₄. So, studying the alanate reorientation mechanisms in the presence and absence of Ti will give conclusive evidence of their lattice positioning. There have been a number of differing/contradicting theories related to the position and role of Ti [46-54]. Lee et al. suggest that it is totally unfavorable for Ti to substitute both Al and Na, but the formation of TiAl₃ is more favorable thermodynamically [46]. Arroyo et al.
support partial substitution of Ti in Na and Al sites [48]. Some researchers support the Ti substitution at Na sites [46, 49-52] while there are others who suggest that Ti substitution at Al sites are equally favorable [53]. Many experimental works have strongly suggested the formation of various Ti-Al intermetallic compounds [54-56].

**Figure 3.19:** Q-variation of EISF of nano TiCl$_3$-doped NaAlH$_4$ (in SBA-15); data was collected on DCS instrument; data points were calculated from the broad Lorentzian amplitudes (refer to Eq. 3.1) and full lines are best fits of the diffusion models in Table 3.4; the EISF of narrow Lorentzians are included for comparison (curves (i) and (ii) fit with Eq. 3.6).

Restricting the discussion to only those models which fit the data in Figure 3.19, there are four models that define the alanate reorientations mentioned in Table 3.4. The models are explained in Appendix A. The early saturation of EISF increases the possibility of having only 3 out of 4 hydrogen atoms that perform a circular continuous diffusion (rotation about a circle, Figure A.2), with the other axial H-atom either being stationary or wholly absent resulting in AlH$_3$ species (both of which leads to $p \sim 0.75$).
The immobility of the axial H-atom suggests a phenomenon involving either Ti-Al or Ti-Al-H interactions. The absence of the axial H-atom supports the proposed theory that the diffusing species in Ti-doped NaAlH$_4$ is AlH$_3$ [57] while the diffusing species in pristine NaAlH$_4$ is the (AlH$_4$)$^-$ tetrahedron. The isotropic rotation on an alanate sphere-equivalent is also likely to be a viable description and is only descriptive in terms of individual H-atoms.

In the investigated Q-range, all models exhibit a good fit as shown in Figure 3.19. However, unlike the nano-samples of pure NaAlH$_4$ where the $Q^2$-dependence of the FWHM allowed an indirect cross-comparison, the widths of the broader Lorentzian did not show a $Q^2$-dependence in Ti-doped nano samples and hence a conclusive justification on the correct model was not possible.

The early saturation of the EISF tends to support either the isotropic rotation or the high temperature model with a stationary axial H-atom description, but the jump lengths are higher than expected. The HT model as described for the nano NaAlH$_4$ samples offers the best geometrical representation of localized dynamics, owing to a closer match to the length scales discussed for nano-NaAlH$_4$ ($l = 0.6 \text{ Å}$). Table 3.7 contains the fit parameters of the various EISFs used to model the nano-Ti-doped NaAlH$_4$ (in SBA-15) samples. The goodness of fits for each curve mentioned here were comparable ($\chi^2$$<1$), making it difficult to favor any of these models mathematically. The identification of the correct model may be possible by performing experiments at higher Q-range. This would mean the experiments will need to be conducted at lower wavelengths and at the cost of energy resolution and hence the quality of data.
Table 3.7: Localized jump diffusion parameters of H-atoms in nano-confined TiCl$_3$-doped NaAlH$_4$ evaluated by EISF model fits; parameter $p$ represents the fraction of mobile H-atoms.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (K)</th>
<th>Model</th>
<th>Jump Length, $l$ (Å)</th>
<th>$p$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Micro TiCl$_3$-doped NaAlH$_4$</td>
<td>450</td>
<td>6-site isotropic ...... (eq. i)</td>
<td>2.60</td>
<td>0.05</td>
</tr>
<tr>
<td>Nano TiCl$_3$ doped NaAlH$_4$ (narrow Lorentzian)</td>
<td>400</td>
<td>6-site isotropic ....... (eq. ii)</td>
<td>2.78</td>
<td>0.15</td>
</tr>
<tr>
<td>Nano</td>
<td>400</td>
<td>Isotropic Rotation........ (eq. iii)</td>
<td>0.80</td>
<td>1.00</td>
</tr>
<tr>
<td>TiCl$_3$ doped NaAlH$_4$ (broad Lorentzian)</td>
<td></td>
<td>HT Model (stationary axial H-atom) ........ (eq. A-1)</td>
<td>1.00</td>
<td>0.75</td>
</tr>
<tr>
<td></td>
<td></td>
<td>HT Model (N=12) ...... (eq. iv)</td>
<td>0.75</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td></td>
<td>Cubic Tumbling ........... (eq. vi)</td>
<td>1.20</td>
<td>0.67</td>
</tr>
</tbody>
</table>

3.3.7 Kinetic Vs. Thermodynamic Destabilization

The results, so far, quantitatively illustrated that the nano-confinement has a positive effect in mobilizing a higher fraction of H-atoms but does not necessarily improve the net rates of diffusion of those mobile H-atoms. There has been a lot of interest in understanding if nano-confinement is a thermodynamic effect or a kinetic
effect [15, 18, 44, 58-61]. Many researchers acknowledge that the nano-confinement is a thermodynamic destabilization owing to the increase in surface energies associated by size reduction. The higher surface to bulk ratio destabilizes the material leading to the onset of hydrogen desorption to occur at lower temperatures. Other researchers tend to support a kinetic destabilization, i.e., faster H-atom diffusivities caused by lower activation energies. The improvement in kinetics of H-diffusion has been negated in the previous sections of this chapter. However, there were very strong clues supporting a thermodynamic destabilization upon nano-confinement based on the evaluated density of states (DOS) from inelastic neutron signal. Figure 3.20 shows the DOS and DSC of three pairs of data-sets representing three sets of samples. The ‘a’-pair is a comparison of the micro samples of pristine NaAlH₄ and Ti-doped NaAlH₄. The ‘b’-pair is a comparison of the micro NaAlH₄ and nano NaAlH₄ (in Fe-BTC). The ‘c’-pair corresponds to the micro TiCl₃-doped NaAlH₄ and nano TiCl₃ doped NaAlH₄ (in SBA-15). The following discussion is concentrated on the one distinct feature (marked) on the DOS spectra at $|E| \sim 10$ meV and the feature at $T \sim 100$ °C on the DSC curves. DOS is a measure of the entropy of the material, and features that occur at lower energies imply that there are unoccupied energy states which could promote a reaction at lower enthalpies. Figure 3.20 (a-1) shows distinctly emerging features upon TiCl₃-doping. This has sufficient support from the literature where TiCl₃ doping is shown to reduce the enthalpy and temperatures of desorption to $\sim 120$ °C compared to $\sim 180$ °C in pristine NaAlH₄. The DSC data (Figure 3.20 (a-2)) supports this argument as well.
Figure 3.20: Generalized density of states evaluated from QENS experiments (right) and differential scanning calorimeter data (right) illustrating the thermodynamic effect of TiCl₃-doping (a-1 and a-2), nano-confinement (b-1 and b-2) and synergetic effect of Ti-doping and nano-confinement (c-1 and c-2).
The nano-confinement of pure NaAlH\textsubscript{4} also results in a distinct feature in the
DOS spectrum, this time more pronounced and at an even lower energy as shown in
Figure 3.20 (b-1). There have been many reports recently that suggest a single step
reaction in nano-scale complex hydrides [58-61]. In a recent study, Bhakta et al. reported
studies of NaAlH\textsubscript{4} confined in Cu-BTC MOF where they estimated that each pore in the
MOF houses less than 8 formula units of NaAlH\textsubscript{4} [15]. They observed hydrogen release
at temperatures less than 100 °C. The data presented in Figure 3.20 (b-1 and b-2) are
direct proof supporting a single step reaction pathway. The DSC data shows a very broad
peak at ~100 °C. The width of this peak covers a temperature range of ~40 °C and the
intensity of the peak is too low to extract any quantitative information. Such broad peaks
are a qualitative indication of phase change processes such as sublimation or
vaporization. The feature quite convincingly addresses the direct desorption of gaseous
H\textsubscript{2} from solid NaAlH\textsubscript{4}.

The desorption reaction mechanism for pristine NaAlH\textsubscript{4} is shown in Eq. 3.7. The
NaAlH\textsubscript{4} desorbs in two stages releasing 3.7 wt. % of H\textsubscript{2} in the first step and 1.85 wt. %
H\textsubscript{2} in the second step at temperatures >180 °C.

\[
\text{NaAlH}_4 \leftrightarrow \frac{1}{3} \text{Na}_3\text{AlH}_6 + \frac{2}{3} \text{Al} + \text{H}_2 \leftrightarrow \text{NaH} + \frac{1}{3} \text{Al} + \frac{1}{2} \text{H}_2. \tag{Eq. 3.7}
\]

The small clusters of NaAlH\textsubscript{4} (diameter<52 nm) [59] are believed to desorb
directly to gaseous H\textsubscript{2} without the formation of intermediates in a single step as follows:

\[
(\text{NaAlH}_4)_n \leftrightarrow (\text{NaH})_n + (\text{Al})_n + \frac{3n}{2} \text{H}_2. \tag{Eq. 3.8}
\]
Majzoub et al. [60] also reports the dehydrogenation mechanism for small nano-clusters of Na-Al-H as follows:

\[(\text{NaAlH}_4)_n \rightarrow (\text{NaAl})_n + 2n\, \text{H}_2. \quad \text{Eq. 3.9}\]

The alternate reaction pathway when cluster sizes are low is an indication of thermodynamic destabilization.

It was very interesting to observe the behavior of nano TiCl\(_3\)-doped NaAlH\(_4\). The features present in micro TiCl\(_3\)-doped NaAlH\(_4\) vanished upon infiltration into SBA-15. The DOS spectrum in Figure 3.20 (c-1) illustrates this phenomenon. Although it is inconclusive to argue based on DOS alone, the nano-confinement of TiCl\(_3\)-doped NaAlH\(_4\) does not become thermodynamically destabilized by particle size reduction. However, the faint broad endothermic peak occurs at \(-100\) °C for this sample as well (Figure 3.20 (c-2)) suggesting an alternate desorption pathway. The vanishing of DOS features at \(|E|\sim 10\) meV was initially speculated to be due to the interaction (oxidation) of the confined hydride by silica of SBA-15. However, DSC does not support this argument, as there are no exothermic peaks in the entire desorption range supporting an oxidation reaction. An alternate explanation for this behavior can be attributed to the Ti interaction with SBA-15. In the previous section, AlH\(_3\) clusters were shown to be the preferred medium of bulk hydrogen diffusion in nano Ti-doped NaAlH\(_4\), owing to the fourth (axial) hydrogen atom being stationary or absent (in case of Ti-Al interaction). The loss of DOS peaks may be due to a binding of the Ti-capped AlH\(_3\) cluster to Si in SBA-15. This Si-Ti-AlH\(_3\) species would obviously have fewer degrees of freedom leading to the loss of features.
3.4 Conclusions

The QENS study on nano-confined NaAlH₄ and TiCl₃-doped NaAlH₄ illustrated the differences in dynamical behavior with size reduction and confinement. This chapter also presented a unique data analysis for materials that are nano-sized. By using both a time of flight and backscattering instrument, the scope of this study was improved. It was shown that the alanate tetrahedron displays reorientational disorder under confinement and the localized dynamics of AlH₄⁻ are a combination of flips and atomic rotations rather than plain liberations, as expected at lower temperatures. The quasi-elastic broadening of the localized motion was described using a modified form of Singwi-Sjolander diffusion model. The long range dynamics seemed to be unaffected by the confinement, as the diffusivities of the hydrogen in micro and nano NaAlH₄ were identical. Low temperature measurements were tracked on the HFBS instrument. There was a marked increase in the fraction of H-atoms participating in the dynamics both in the pristine and Ti-doped NaAlH₄ when nano-confined. It was also shown that Ti-doping may not be necessary when nano-confinement is adopted since there was negligible improvement in H-atom jumps in the lattice. The Ti-doped samples also seemed to stabilize upon confinement leading to a loss in the low energy DOS, while additional low energy features emerged when pristine NaAlH₄ was nano-confined.
CHAPTER 4

LOCAL CHEMISTRY AROUND METAL SITES IN POROUS METAL ORGANIC FRAMEWORKS

4.1 Introduction

In Chapter 2, various scaffolds including MOFs were characterized and the MOFs, Basolite F (Fe-BTC) and Basolite C (Cu-BTC or HKUST-1) were shown to possess unique pore morphologies. In addition to the crystalline / ordered pore framework, these MOFs also offer significant functionality due to the exposed metal sites that form the peripheral nodes of the micropores. NaAlH₄, when confined into these pores, desorbed quickly and at lower temperatures and a thorough investigation of the lattice diffusion of hydrogen atoms was done using QENS and reported in Chapter 3. Clues for an alternate desorption pathway as an effect of nano-confinement in MOFs were provided by qualitative observations of emerging features in the DOS spectrum. In addition to the effect induced by nano-confinement, the unsaturated metal sites in MOFs offer an additional possibility of catalytically influencing the desorption properties of NaAlH₄. Synchrotron XRD of nano-NaAlH₄ in Fe-BTC proved to be insufficient to identify the chemical changes occurring in NaAlH₄ because of a loss in long range order (both due to confinement and due to segregation of unconfined NaAlH₄ particles). The x-ray absorption spectroscopy analysis permits studies on the local order without the need for a material to be crystalline. This chapter presents the details of the experiments
designed to study the change in local chemistry around the metal sites (Fe) in Fe-BTC after sodium alanate is infiltrated into the pores. The choice to study the MOF's metal sites rather than that of Al or Na of NaAlH₄ was made because not all NaAlH₄ particles in the precursor solution manage to 'seep' through the pores of the MOF. Since there are unconfined NaAlH₄ particles on the surface (ppm levels) in addition to those confined within the pores (since pore loading is ~60%), it would be difficult to differentiate between the absorber atoms (Na or Al) in confined and unconfined NaAlH₄. On the other hand, studying the local chemistry of the Fe-sites in Fe-BTC MOF enables an indirect, yet more accurate analysis of the catalytic activity of the Fe-sites.

4.2 Experimental Methods

4.2.1 X-ray Absorption Spectroscopy (XAS) Theory

X-ray absorption spectroscopy (XAS) techniques have been developed widely for structural research of materials with the availability of synchrotron radiation sources. EXAFS (Extended X-ray Absorption Fine Structure) and XANES (X-ray Absorption Near Edge structure) are subsets of XAS (X-ray Absorption Spectroscopy). These techniques are based on photoelectric absorption phenomena and are used to investigate the local chemical structure around selected atoms (called absorber atom) in the sample.

The photoelectric x-ray absorption phenomenon occurs when an atom absorbs the incident x-ray energy to get ionized. This usually results in the emission of an electron and the interaction of this photo-emitted electron with neighboring atoms is quantized by the EXAFS technique. When an electron gets photo emitted, its interaction with the neighboring atoms (referred to as backscattering atoms) results in the constructive and destructive interference of the absorption signal. These constructive and destructive
interference events are referred to as “fine structure”. The “K-edge” refers to the energy absorbed by the atom to eliminate a ground shell (K) electron. The technique is represented by a single yet highly important equation (so called EXAFS equation) which describes the entire phenomenon and yields parameters that define the local chemistry around the absorber atom. The equation may be written as [62]:

\[ \chi(k) = \sum_j N_j f_j(k) e^{-2k^2\sigma_j^2} \frac{1}{kR_j^2} \sin[2kR_j + \delta_j(k)]. \]  

Eq. 4.1

where \( f_j(k) \) is the electron scattering factor; \( \delta_j(k) \) is the phase shift of the photoelectron; \( R_j \) is the distance to neighboring atom; \( N_j \) is the coordination number (number of neighboring atoms) and \( \sigma_j^2 \) is the mean square disorder of neighbor distance (Debye Waller factor). The data is fit using this equation to extract the values for \( N \) and \( R \) leading to structural information.

The summation term accounts for the scattering contribution of all neighbors since, in general, there are more than one next nearest neighbor to the absorber atom. The atoms of the same element that are within the same radial distance contribute to the same EXAFS signal component. This collection of atoms together forms a coordination shell. The number of atoms in the coordination shell is \( N_j \). ‘\( j \)’ refers to the number of such shells and represents the number of shells being considered in the collective EXAFS signal. Usually, the EXAFS technique can provide useful and reliable information of atomic positions and coordination for up to 8 Å in radial distance and hence the number of shells within that distance. The phase shift arises because of a mismatch in the distance between the absorber and backscatterer often caused by structural disorder and thermal excitations. The disorder, when small and possesses a Gaussian distribution, is quantized
by the mean square displacement of the atoms from their respective positions, which is popularly known as the Debye Waller factor.

4.2.2 XAS Instrumentation

The instrumentation used was the XAFS set up at CAMD’s DCM beam-line. There are several reasons to pursue these experiments at synchrotron facilities. The flux and brilliance of the photons at synchrotron facilities is orders of magnitude higher than conventional lab scale x-ray instruments (CAMD’s radiation intensity is $10^9$ photons/s). The synchrotron radiation has a continuous spectrum of energies that can be tuned to the desired edge energy. The DCM’s representative feature is the double crystal monochromator, whose angular range is 12.5° to 72°. The energies are tuned in by pitching the two crystals back and forth such that a parallel geometry is achieved while driving towards maximum intensity. The DCM beam-line at CAMD-LSU operates between 1.0 keV to 12 keV [63]. The absorption data of the bare MOFs were collected in transmission mode and that of SAH-infiltrated MOFs was collected in fluorescence mode, with the energies of incident photons tuned to about 1000eV above the K-edge of the respective metals contained in each of the MOFs. The energy resolution achieved was 0.5 eV to 1.5 eV. The scans were done to accommodate one million intensity counts in total from the 14 slots in the high purity germanium array detector. Integration time was set to five seconds and the energy step size adopted was 0.3 eV for both MOFs. The step sizes were smaller at the near edge energies and larger at the higher end of the energy range. The samples in fluorescence mode requires up to one hour per scan including calibration, sample set up, etc. Multiple scans were measured per sample to get an
amplified signal. On average, each sample would take two hours (assuming two scans per sample).

EXAFS data was analyzed using the open source "Ifeffit" software package which consists of specific software needed to handle raw data. Data reduction (i.e. background subtraction, normalization, and Fourier transform) was done using the Athena software, and data analysis (i.e. calculating fits using EXAFS equation) was done using the Artemis Software [64].

4.3 Results and Discussion

4.3.1 Local Chemistry of Metal Sites in MOFs

MOFs offer a very unique pore morphology that contains unsaturated metal sites. These sites are primary interaction zones for guest molecules, making them suitable for a variety of applications [64-67]. Cu-BTC (Basolite C) has been well studied by many researchers in the recent past [65, 68], while Fe-BTC (Basolite F) is a relatively less known material. The EXAFS spectra of these two MOFs along with the standard reference materials are shown in Figures 4.1 and 4.2. As reported in the literature, the Cu sites in Cu-BTC were found to be in a "+2" oxidation state. This was elucidated by comparing the XANES spectrum to standard references comprising of Cu$^{2+}$ ions (Copper (II) Acetate and Copper (II) Oxalate). XANES analysis is qualitative but a match in the near edge features/positions is a very good indicator of the electronic state of the absorbing atom. The threshold absorption energy ($E_\alpha$) for the Cu-BTC MOF was found to be 8991.4 eV at an edge jump of 1.5 eV. In comparison, Cu in Cu-foil has an edge energy value of 8979 eV. The sodium aluminum hydride (SAH) infiltrated Basolite C showed slightly reduced threshold absorption energy of 8989.5 eV and data was collected at 0.07
eV. The value of $E_0$ was obtained from the peak position of the first derivative at threshold absorption after alignment and energy calibration.

**Figure 4.1:** EXAFS spectra of Basolite C (Cu-BTC) before and after NaAlH$_4$ infiltration; EXAFS spectra of several Cu standards are included for comparison.
The XANES spectrum of Fe-BTC best matched iron (III) acetate and thus Fe sites are believed to be in a +3 oxidation state. Another group [66] reports the same oxidation state based on their studies. The near edge features of the Basolite F before and after infiltration were identical, indicating that there were no changes in the oxidation state of the Fe sites remained in a +3 state. The edge positions of Fe-BTC before and after infiltration were 7125.4 eV and 7125.5 eV, respectively. In comparison, the edge of Fe in Fe-foil was 7112 eV. The edge step for bare Fe-BTC was 0.16 eV and that for SAH/Fe-BTC was 0.32 eV.

4.3.2 Effect of Sodium Alanate Infiltration

The $k^2$ weighted Fourier filtered EXAFS data of Cu-BTC (Basolite C) before and after sodium alanate (SAH) infiltration is plotted in Figure 4.3. The amplitude envelope of the SAH/Basolite C nano sample is lower than pure Basolite C. There are two reasons
for a damped amplitude envelope. The first is that this often occurs because of distance heterogeneity between the absorber and backscatterer atoms in the samples [67]. The other reason could be that the number of interactions (waves) between the absorber atom and backscattering atoms in the sample may decrease. The former reason arises because of faulty synthesis procedures or mishandling (e.g. exposure to air). The latter reason is more comprehensible for the current scenario since there are secondary atoms in the vicinity of the absorber atom that could damp the signals. Such an observation on the local order is a highly reliable confirmation that the sodium alanate particles do indeed reach the pore interiors.

![Graph](image)

**Figure 4.3:** The $k^2$-weighted Fourier filtered EXAFS spectra in k-space of Basolite C before and after infiltration.

The Fourier Transform (FT) of the EXAFS spectra $|\chi(R)|$ of Cu-BTC before and after infiltration is plotted in Figure 4.4. A $k$-weight of two was multiplied to enhance the signal of the farther Fourier peaks. For this experiment, the local chemistry of the Cu$^{2+}$
sites remained unchanged even after infiltration, as interpreted from a very identical near
edge structure. Based on published literature [65, 68], the data in Figure 4.4 matches a
dehydrated structure of Cu-BTC or HKUST or Basolite C. The first Fourier peak in
Figure 4.4 thus represents the Cu-O distance, which was found to be 1.95 Å with a
coordination number (N) of 3.92 [65]. The distance of the first peak in Figure 4.4 is
roughly 0.5 Å lower than the actual distance calculated because the phase factors in the
EXAFS equation vary with energy [69]. The sample after infiltration shows no change in
the first peak distance. However, the amplitude of the first Fourier peak, representing the
radial distribution of the atoms in the inner most coordination shell is lower in the SAH
infiltrated Basolite C. The local chemistry of the MOF Basolite C is preserved up to 2.2
Å that covers two coordination shells. The third peak in Figure 4.4 is more pronounced
and is closer in the SAH-infiltrated sample. This seems to suggest the hydride atoms are
at least three coordination shells away from the absorber Cu atoms, which eliminates any
possible contribution of the Cu atoms in catalyzing the sample. This was the main reason
for choosing Fe-BTC (Basolite F) as a scaffold for further detailed investigation.
Figure 4.4: Fourier transformed EXAFS spectra in $R$-space of Basolite C before and after sodium alanate infiltration.

Figure 4.5 illustrates the crystal structure of Cu-BTC. As clearly evident, the Cu-O$_1$ coordination dominates the first coordination shell with degeneracy (N) estimated to be around four [65, 68]. The hydrated sample (e.g. by exposure to atmosphere) causes another O-atom to coordinate with the Cu absorber, which is at a slightly higher distance. Our samples clearly showed a radial distribution of a dehydrated Cu-BTC environment in comparison to the published data [65].
Figure 4.5: Structure of Cu-BTC MOF (left) [67] and local structure around the absorbing metal (right) [64].

The crystal structure of Fe-BTC (Basolite F) is not known, as mentioned before. The interpretation was based on finding the most identical material structure. It was found that Fe (III) Acetate provided the nearest match to the local structure around the absorber (Fe) atoms. Figure 4.6 shows the $k^2$-weighted Fourier filtered EXAFS data in $k$-space. The SAH infiltrated Basolite F showed a damped amplitude envelope compared to the pure Basolite F and Fe (III) Acetate. The damping, as suggested earlier, hints at the presence of secondary material (in this case, sodium alanate particle) in the local environment of the Fe-absorber atoms, reiterating that the confinement was successful. A first shell fit was performed on the Fe-BTC samples using a starting structure of Fe (III) acetate, which is discussed in the next section. The Fe (III) acetate, in fact, has a very similar local structure around the Fe$^{3+}$ absorber atom, at least in the first shell. The $k$-edge of Fe (III) acetate is 7125.3 eV and the near edge structure too is very identical to Fe-BTC.
Figure 4.6: The Fourier filtered EXAFS spectra in $k$-space of Basolite C before and after infiltration; Fe (III) Acetate is included for comparison.

Figure 4.7 shows the Fourier transformed EXAFS data in R-space. There is a dramatic difference in the radial distribution of the Basolite F before and after SAH infiltration. The most evident difference is that the first Fourier peak is severely distorted in the SAH-infiltrated sample. In addition to the lower amplitude, the emergence of pre-edge features and an apparent splitting of the first coordination shell suggest that the infiltrated SAH particles directly coordinate with the innermost shell of Fe-BTC. The position of the first peak was lowered due to the SAH-infiltration from $\sim 1.5 \text{ Å}$ in the pure Basolite F to $1.25 \text{ Å}$ with an additional pre-edge at $\sim 1.0 \text{ Å}$. A $k$-weight of three actually split the first peak into two distinct peaks. The second Fourier peak of SAH-infiltrated Basolite F is significantly lowered to $\sim 2.0 \text{ Å}$ compared to $2.2 \text{ Å}$ in the pure Basolite F. However, the second peak position matched the Iron (III) Acetate's second peak signifying that the Basolite F after infiltration showed an identical local structure at the
second coordination shell. There is an additional peak in the SAH-infiltrated Basolite F before the third shell positions match in all three samples.

![Graph](image)

**Figure 4.7:** Fourier transformed EXAFS spectra in $R$-space of Basolite F before and after sodium alanate infiltration; Fe (III) Acetate is included for comparison.

### 4.3.3 Local Structure of Fe-BTC

**MOF - First Shell Fitting**

The $E_0$ value was carefully chosen from the peak position of the first derivative of the absorption k-edge from the EXAF data. An uncertainty in choosing $E_0$ often reflects in an uncertainty in k-space values. However, in the course of refinement, this is accounted for and refined to the right value since the EXAFS analysis is based on $\Delta E$ (energy shift). The $\Delta E_0$ was one of the parameters that were varied, but it was assumed to be the same value for all coordination shells. The first shell fitting of Fe-BTC was done with a starting structure of Fe (III) Acetate whose crystal structure is shown in Figure 4.8. The first coordination shell in Fe (III) Acetate consists of one oxygen atom (hydrated – red oval) and the second shell consists of four O-atoms and the third consists of Fe atoms.
The CIF file was downloaded from the crystallography database and the paths were extracted. A total of 22 paths out of the full crystal structure were recognized when a fitting scheme was attempted. The "guess" parameters and their uncertainties were reasonable and are reported in Table 4.1. The first shell fit yielded an $R$-factor of 0.0324 and a measurement uncertainty (in $R$) of 0.0003 Å, which indicate an excellent fit. They appear to be good fits visually, too (Figures 4.9 and 4.10). The $R$ evaluated for the first coordination shell was 1.90 Å with a degeneracy of one. This corresponds to the hydrated O-atom. The next four paths yielded the same $R$~1.99 Å and all of them were O-atoms comprising the second coordination shell.

![Crystal structure of Fe (III) Acetate](image)

**Figure 4.8:** Crystal structure of Fe (III) Acetate [70]; red sphere: O; Chrome: Fe; Black: C; white: H.
Figure 4.9: Fourier transformed EXAFS spectra in \(R\)-space of Fe-BTC; Full line is the best fit of the first shell to the EXAFS equation.

Figure 4.10: Fourier filtered EXAFS data in \(k\)-space of Fe-BTC; Full line is the best fit to the EXAFS equation.
Table 4.1: EXAFS fit parameters of Basolite F.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplitude</td>
<td>0.708</td>
<td>0.07</td>
</tr>
<tr>
<td>$E_o$</td>
<td>-0.066</td>
<td>-</td>
</tr>
<tr>
<td>$\delta R$</td>
<td>-0.0098</td>
<td>0.01</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>0.005</td>
<td>0.02</td>
</tr>
</tbody>
</table>

The SAH-infiltrated Basolite F showed an excellent fit as well to the first Fourier peak. The starter structure used was again Fe (III) Acetate. In comparison to the bare Basolite F samples, the SAH-infiltrated samples showed a closer structural identity to Fe (III) Acetate, and this is clearly evident in the fits (Figures 4.11 vs. 4.9 and Figures 4.12 vs. 4.10). The fit parameters are listed in Table 4.2 and there are no ambiguous fit values. The paths chosen were the same as those chosen to fit bare Fe-BTC. The first coordination shell R-value 1.93 Å, which is slightly more than the first shell of bare Fe-BTC. This looks contradicting to the observed curves (in Figure 4.7) where the distorted first peak of SAH infiltrated Fe-BTC is lower in amplitude and distance. The second shell O-atoms are at a distance of ~2.02 Å (again higher than bare Fe-BTC) from the absorber Fe atoms although the radial distribution function in Figure 4.7 suggests the opposite. The reason for this disparity is yet to be interpreted. However, the only obvious difference between the two was that the data of bare Fe-BTC samples were collected in transmission mode, while the SAH-infiltrated samples were examined in fluorescence mode. The latter adds a significant threat of multiple scattering.
Figure 4.11: Fourier transformed EXAFS data in R-space of Fe-BTC infiltrated with NaAlH₄; Full line is the best first shell fit to the EXAFS equation.

Figure 4.12: Fourier filtered EXAFS data in k-space of Fe-BTC infiltrated with NaAlH₄; Full line is the best fit to the EXAFS equation.
Table 4.2: Fit parameters for SAH infiltrated Basolite F.

<table>
<thead>
<tr>
<th>SAH/Bas-F</th>
<th>Value</th>
<th>Error</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amplitude</td>
<td>0.611</td>
<td>0.067</td>
</tr>
<tr>
<td>$E_o$</td>
<td>3.755</td>
<td>0.93</td>
</tr>
<tr>
<td>$\delta R$</td>
<td>0.023</td>
<td>0.015</td>
</tr>
<tr>
<td>$\sigma^2$</td>
<td>0.0057</td>
<td>0.002</td>
</tr>
</tbody>
</table>

4.4 Conclusions

The MOF samples (Fe-BTC and Cu-BTC) were examined at their respective metal sites for any local chemical changes occurring due to SAH infiltration. While Cu-BTC showed negligible changes, Fe-BTC was fairly interesting with an added disparity of un-matched qualitative and quantitative observations. In addition to understanding the role of these metal sites for a possible catalytic effect on the infiltrated hydride, this study has also proved to be a step forward in establishing the crystal structure of this promising material for the very first time. The damping effect on the EXAFS signal of the SAH-infiltrated MOF samples are yet another finding to validate nano-confinement.
CHAPTER 5

MORPHOLOGY OF SODIUM ALANATE

5.1 Introduction


Many underlying challenges in developing reversible complex metal hydrides, such as hysteresis or choosing the right catalysts and mill times, can adequately be addressed by examining their morphology. To study complicated morphologies, small angle scattering of light and x-rays is an invaluable tool since it covers almost seven orders of magnitude on the length scale [73]. Measuring x-ray scattering at small angles can yield information on large scale electronic inhomogeneities of the size of colloidal particles. The ultra-small angle x-ray scattering finds use when there is a need to extend the length scales to micron or sub-micron levels while small angle x-ray scattering is limited to the nanometer scale [74]. NaAlH₄ is comprised of colloidal particles with extremely complex surface fractal pore morphology and the USAXS technique is well suited for such materials [75]. The present work is intended to show some unique applications of ultra-small angle x-ray scattering technique that address some of the unanswered problems in the development of reversible complex metal hydrides.
Catalysis, hysteresis, optimization of process parameters (e.g. mill time), and characterization for complex metal hydrides are some of the vital questions that need further investigation.

5.2 Experimental Methods

5.2.1 Ultra-Small Angle X-ray Scattering (USAXS) Theory

The unified model fits complicated SAXS data having multiple Guinier regions and power law regions without introducing any additional parameters than those used for local fits [76]:

\[ I(Q) = G \exp \left( -\frac{Q^2 R_g^2}{3} \right) + B \left\{ \frac{\text{erf} \left( \frac{QR_g}{\sqrt{6}} \right)^3}{Q} \right\}^p. \]  

Eq. 5.1

The unified model fit yields the power law slope (p) and the radius of gyration (R_g) for each structural level present. For colloidal particles, the power law slope represents the degree of surface roughness, which is defined by a parameter commonly called surface fractal dimension (D_s). The power law slopes are related to the surface fractal dimension by the relation [77]:

\[ D_s = p + 2D. \]  

Eq. 5.2

Where D = 3 for colloidal particles. The values for D_s vary between two and three with a corresponding variation of p between -4 and -3. D_s = 3 (or p = -3) represents the high specific surface area particles either due to agglomeration of smaller particles or due to very coarse surfaces and/or a lot of internal pores, while D_s = 2 (or p = -4) represents the smooth spherical particle [77]. The value of the exponent (p) may be less than -4 for diffuse interfaces and more than -3 for mass fractals. The exponent p = -1 represents
elongated rod like mass fractals and $p = -2$ represents flat disc like particles [77]. The surface fractal dimension is related to the surface area of the particle by Eq. 5.3:

$$S \sim R^{D_s}.$$  \hspace{1cm} \textbf{Eq. 5.3}

$R$ is the radius of the colloidal particle. For spherical particles, $R$ can be deduced from the radius of gyration ($R_g$) by the relation [77]:

$$R = \frac{5}{\sqrt{3}} R_g.$$ \hspace{1cm} \textbf{Eq. 5.4}

The specific surface area of the particle was evaluated by dividing the calculated surface area from the volume of an individual spherical particle with radius determined from the $R_g$ value as done in Eq.5.4.

5.2.2 **USAXS Instrumentation**

USAXS data were collected at Sector 32ID, Advanced Photon Source - Argonne National Laboratory (IL) using incident photon energy of 16.9 keV. The beam size employed for these experiments was 0.3 mm x 0.3 mm. Powder samples were on the order of 0.2mm thick and the template samples were approximately 0.1 mm in thickness, including the two layers of Kapton tape. Data reduction, slit-smear correction and analysis were made using IGOR Pro (a data analysis software product of WaveMetrics, Inc.) combined with sets of macros Indra [78] and Irena [79] to analyze and fit the data. The scattering intensity was fit by the unified model (Eq. 5.1), developed by Beaucage [76].

For the USAXS experiment, small amounts of each sample was packed between two layers of Kapton film and the edges further sealed with Kapton tape to avoid any exposure to air. Two “blank” samples were made each for the powdered and template
samples. Here “blank” refers to the background material that holds the actual sample whose scattering needs to be subtracted to evaluate the scattering from the sample during the USAXS data analysis. The “blank” for the powdered samples was just a bilayer of the Kapton tape. In the case of nanostructured NaAlH$_4$, the empty template packed in Kapton was treated as the “blank” sample.

5.3 Experimental Methods

5.3.1 Morphology of Sodium Alanate

Prior reports of USAXS data have shown that a five min milled sample creates more surface area than a 25 min milled sample or a one min milled sample [75]. Figure 5.1 shows a unified fit for a five min milled sample of NaAlH$_4$. The curve is characterized by two power law slopes corresponding to a large population (at low Q) and a smaller population of particles (at high Q) separated by an exponential shoulder known as the Guinier shoulder. This Guinier region characterizes the small population of particles (referred to as primary colloids) by a parameter called radius of gyration. The radius of gyration for the primary colloidal NaAlH$_4$ particles is found to be approx. 6.5 nm, which translates to a particle radius of approx. 8.0 nm using Eq. 5.4.
Figure 5.1: Two-level unified fit for NaAlH₄ USAXS data; Level 2 Guinier region is excluded from the fit by approximating a very large radius of gyration [72].

To address the hysteresis phenomena (that reduces the cyclic capacity), the morphology of the particles before and after heat treatment has been evaluated. Figure 5.2 shows the SEM micrographs of NaAlH₄ before and after one complete dehydrogenation (heated to 180 °C). Figure 5.3 illustrates the changes in particle radius due to heat treatment for the un-milled NaAlH₄ and the five min milled NaAlH₄. It can be seen that there is more than a two-fold increase in the particle size after heat treatment, indicating agglomeration of particles due to heat, regardless of whether the particles were milled or not. Agglomeration of particles leads to densification which reduces the overall surface area available for re-adsorption, thus reducing the hydrogen up-take capacity with every subsequent cycle. This is a feasible explanation to the hysteresis phenomena in NaAlH₄.
Figure 5.2: SEM micrograph illustrating powder densification at the end of thermal dehydrogenation; pristine NaAlH₄ particles (left) and heat treated NaAlH₄ (right); scale (red line) in the micrographs is 300 μm.

Figure 5.3: Crystal growth of milled and un-milled NaAlH₄ at the start and end of the first desorption run; sample A is pristine NaAlH₄ and sample B is TiCl₃-doped NaAlH₄.

In order to avoid the agglomeration and the associated loss in the total surface area, nano-confinement of NaAlH₄ is suggested. Particle size measured by USAXS can also be used as a reference when choosing the pore-size for nano-confinement.
applications. While it is a widely accepted idea that “the smaller the pore size, the better the desorption properties,” it should also be noted that nano-confinement becomes increasingly difficult as one goes down in size. Therefore, in reality, one should be choosing an optimum pore size that is both reasonably easy to load and also enhances the (re)hydrogenation properties. This idea can be generalized for all of the metal hydride systems as a tool to decide on the best possible size of the nanostructures.

5.3.2 Effectiveness of Treatment Procedures

Specific surface area of a material is a collective indication of the extent of porosity and surface roughness prevalent in the material [78]. Specific surface area can thus be increased by the creation of internal pores by desorbing gaseous elements occupying interstitial sites, by aggregating smaller particles to make a rough surface, or by breaking down a larger particle to expose new surfaces. In this study, the effectiveness of a treatment aimed at improving desorption properties is thus decided based on the extent to which it increases the particle’s surface area. Figure 5.4 shows the changes in power law slopes and the accompanying changes in specific surface areas of the particles due to the various treatments employed for NaAlH₄.
Figure 5.4: Effectiveness of treatments assessed by power law slope from USAXS data and calculated specific surface areas; Sample A is pristine NaAlH₄; sample B is ball-milled for 5 min; sample C is NaAlH₄ doped with 4 mol% TiCl₃ (5 min milled); sample D is heat-treated to 180 °C.

Table 5.1: Specific surface area and absolute power law slope (|p|) calculated after each treatment to assess its effectiveness.

<table>
<thead>
<tr>
<th></th>
<th>NaAlH₄ Un-milled</th>
<th>After 5 min of milling</th>
<th>After TiCl₃ doping</th>
<th>After first desorption</th>
</tr>
</thead>
<tbody>
<tr>
<td>Specific Surface Area (nm⁻¹)</td>
<td>0.05</td>
<td>0.09</td>
<td>0.14</td>
<td>0.24</td>
</tr>
<tr>
<td></td>
<td>power law slope</td>
<td>3.60</td>
<td>3.46</td>
<td>3.26</td>
</tr>
</tbody>
</table>

The un-milled NaAlH₄ (as received) particles which are of the order of 12.5 nm in the effective radius yield an absolute power law slope value of 3.6 corresponding to a calculated specific surface area of 0.05 nm⁻¹. High energy ball milling reduces the particle size, thus creating new surfaces due to reduction of the absolute slope to 3.46
indicating an increase in the specific surface area. The addition of the catalyst (4 mol% TiCl₃) and ball milling further reduces the absolute value of the exponent to 3.26. This decrease in the absolute value of the slope can be attributed to the loss of interstitial hydrogen due to the combined effect of the catalyst and heat generation during ball milling. Catalyzed NaAlH₄ desorbs at 180°C and USAXS data for heat-treated samples at this temperature indicates particles with a totally rough surface ($p = -3$) and a significantly increased specific surface area that is evidence to the aggregation of the particles. This work confirms the proposition that USAXS is a potentially robust technique to arrive at effective processing treatments (e.g. ball milling) and their parameters (e.g. mill time) by studying the morphological changes induced during the course of desorption.

5.3.3 Identifying Confined Sodium Alanate in the Scaffold-Hydride Mixture

As pointed out earlier, the background chosen for the nanostructured NaAlH₄ was the combination of a bilayer of Kapton and an empty template, whose scattering was subtracted to identify confined NaAlH₄. The USAXS data for nanostructured samples revealed that the primary particles on the porous template had absolute power law slope values less than three, indicating a mass fractal morphology. The template wetting technique involved dissolution of the NaAlH₄ particles in the volatile THF solution and re-crystallizing NaAlH₄ back by allowing the THF to evaporate. The NaAlH₄ re-crystallizes into tightly packed particles (negligible internal porosity), thus possessing significant material (mass) within a shape acquired by the terrain of the template. This explains the mass fractal morphology detected by USAXS. The data was collected from
six different positions on the template containing NaAlH₄. Some positions revealed slopes of \( p = -1.41 \) (Figure 5.5) indicating rod like particles and other positions revealed slopes of \( p = -2.72 \) (Figure 5.6) indicating flat disc like particles. It can be inferred that the particles acquire the shape of an elongated rod due to their confinement inside the pore well. The particles that do not enter the pore wells due to clogging of the pores rest in a flat disc-like configuration atop of the pore wall.

**Figure 5.5:** Absolute power law slope of \( 1 < |p| < 2 \) indicating one dimensional rod like morphology of NaAlH₄ nano-confined within the pore wells of Alumina [72].
Figure 5.6: Absolute power law slope of \(2<|\rho|<3\) indicating two dimensional disc like morphology of un-confined NaAlH\(_4\) on the surface of the porous membrane [72].

### 5.4 Conclusions

The changes in morphological features during desorption have been studied. Morphological metrics such as SSA and particle radius were shown to be useful in illustrating the effectiveness of the various treatments procedures such as ball milling, TiCl\(_3\) doping, and heat treatment. Phenomena such as reversible hysteresis can be adequately explained by tracking the changes in morphology and the morphological features measured by USAXS were reported. The particles agglomerated to twice their size during heat treatment resulted in a loss of surface area for the next rehydrogenation cycle. USAXS was also used to distinguish the confined phase from the unconfined phase in a two-phase mixture by virtue of shape and fractal morphology.
CHAPTER 6

CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

Wet synthesis procedures were successfully developed to confine sodium alanate in porous scaffolds of various dimensions and morphologies using wet infiltration techniques.

- The confinement was quantitatively studied using N$_2$-BET adsorption analysis. A significant reduction in specific surface area and pore volume was reported, and the pore loading was estimated to be between 60% in MOFs to ~73% in SBA-15.

- The MOFs were shown to be structurally stable over the entire desorption range both in the presence and absence of NaAlH$_4$ by XRD measurements. A marked decrease in the scaffolds’ peak intensity (presence of guest molecules inside the pores) and the complete loss of NaAlH$_4$ peaks after infiltration (loss of long range order) confirmed confinement.

- The chemical compatibility of the wet reagent (THF), NaAlH$_4$ and the porous scaffolds (MOF, SBA-15 and Alumina) was confirmed by DSC experiments. The lattice jump diffusion of H-atoms in nano-confined NaAlH$_4$ was studied using QENS technique.
• The nano-samples were found to possess enhanced mobility of hydrogen in the lattice. More than 20% of the H-atoms of nano-NaAlH$_4$ were involved in long range diffusion at ~350 K compared to a mere 4% mobile hydrogen in micro NaAlH$_4$ at 450 K.

• The nano-confinement clearly resulted in an early (temperatures less than 80 °C) onset of lattice diffusion of hydrogen atoms.

• A significantly higher fraction (>75%) of H-atoms were found to be involved in a localized diffusional process within their host tetrahedron, whose diffusivities were at least 10 times faster than the long range diffusivities.

• Various models were explored to describe the localized mechanism and the best quantitative description was obtained from the high temperature model.

• The synergetic effect of TiCl$_3$ doping and nano-confinement was shown to have the same effect as nano-confinement alone. In addition, the QENS measurements provided further proof for a Ti-Al interaction upon TiCl$_3$-doping.

• Generalized density of states (GDOS) showed significantly distinct low energy features in the nano-samples, indicating an alternate reaction pathway. This was complimented by the DSC data which showed a distinct endothermic feature at ~100 °C indicating a direct dehydrogenation from NaAlH$_4$, as proposed by many researchers.

The local chemistry of the metal sites in the MOFs (Basolite C and Basolite F) was characterized using EXAFS analysis.
• The oxidation state of the metal sites remains unchanged before and after infiltration. However, the NaAlH₄ molecules were shown to be present in the second coordination shell of both MOFs.

• The EXAFS amplitude envelope was reduced in the MOFs upon infiltration, thus showing that the NaAlH₄ molecules were found in the vicinity of the unsaturated metal sites of the MOFs.

• The EXAFS analysis provided the first clues to solving the crystal structure of Fe-BTC MOF.

The morphology of pristine, doped, milled, heat treated, and nanostructured NaAlH₄ was studied using USAXS.

• The effectiveness of various treatment procedures adopted for NaAlH₄ (Ti-doping, ball milling, heat treatment) were assessed by virtue of surface area changes.

• The feature sizes of NaAlH₄ was found to increase two fold upon a single cycle of desorption leading to a reduced accessible surface area and hence reversible hysteresis.

• The nano samples showed dense mass-fractal morphology compared to the surface-fractal morphology exhibited by the as-received NaAlH₄.

• A unique method of identifying confined and un-confined NaAlH₄ was developed based on the differences in the morphological shape.

6.2 Future Work

The results presented so far were focused on addressing the thermodynamics and kinetics of various phenomena (diffusion, chemical reaction, solid-solid phase change,
This section is aimed at laying a foundation to develop unique microstructure/chemistry relationships for hydrides in general. The motive driving this synopsis is to correlate seemingly un-related phenomena at various length-scales by virtue of their common driving factors (e.g. Morphology evolution at micron scale and phase evolution and growth at the nano scale are driven by the diffusion of the same constituent atoms). A clear understanding of these phenomena and their relationships would enable a much more robust approach in the discovery and development of solid hydrogen storage materials. The field of research, based on microstructure-chemistry relationships, is vast. This section is limited only to laying the foundations required to develop correlations between morphology evolution (at μm scale) and phase evolution (at nm scale). This work acknowledges the fact that atomic diffusion is the mediator for both these phenomena. The working hypothesis to develop a correlation between the two phenomena is: “the rate of phase transformation (chemical reaction) is influenced by the rate of morphology evolution and vice-versa.” The results shown in this section are preliminary and do not prove or refute the hypothesis yet.

The grand objectives of this dissertation research are best illustrated in Figure 6.1. The various aspects of the study are:

a. To understand how size affects the thermodynamics and kinetics in these materials by experiments and theory
b. To design high-throughput experiments that can measure the various multi-scale phenomena
c. To develop unique empirical models to describe micro-structure/chemistry relationships
The results presented in prior chapters of this dissertation were aimed at the first two aspects. Thermodynamics and kinetics of various phenomena (diffusion, reaction, phase change, morphology evolution) were addressed. Several advanced instrumentation were used to track various properties/parameters. This section sheds light on the third aspect of relating these multi-scale phenomena.

6.2.1 Sintering Kinetics

Sintering is a ceramic processing step that produces dense polycrystalline ceramic products. It involves heating the material to high temperatures (also known as firing) in order to arrive at the desired morphology / microstructure. It is quite easily one of the most important stages in ceramic processing because by controlling the sintering process, the microstructure can be tuned to obtain the desired product. Although in a very different scenario, processing of complex hydrides and metal hydrides is very analogous, if not similar to ceramic sintering. The interest in treating complex hydrides as ceramics emerges from the very same need to be able to manipulate the material chemistry to get
the desired product. This section reviews the main aspects of modeling a sintering phenomenon.

Various atomic diffusion mechanisms contribute to the densification process during sintering. Figure 6.2 shows a pictorial depiction of the various kinds of diffusion mechanisms that lead to a two-particle sintering. The study is restricted to an ideal case of two perfectly spherical particles of the same radii. In reality, this is not true. One of the metrics used to track the progress of sintering is the neck size formed at the interface of the two particles. The neck size grows in accordance to a power law model which is discussed here. Nichols [80] provides the power law equations (Eq. 6.1 to 6.4) for the mass transport mechanisms shown in Figure 6.2, which are the major ones, contributing to sintering:

\[
Lattice \text{ Diffusion:} \quad x^2 = \frac{40\gamma \delta^3 a^2}{k\theta} D_v t, \quad \text{Eq. 6.1}
\]

\[
Surface \text{ Diffusion} \quad x^2 = \frac{56\gamma \delta^4 a^3}{k\theta} D_s t. \quad \text{Eq. 6.2}
\]

Where \( x = \) neck radius, \( a = \) initial radius; \( \gamma = \) surface tension; \( t = \) time; \( \delta = \) interatomic spacing; \( k = \) Boltzmann constant; \( \theta = \) absolute temperature; \( D_v = \) volume diffusion constant (lattice); \( D_s = \) surface diffusion constant.
Figure 6.2: Various transport mechanisms that contribute to sintering [79].

A comprehensive study of the sintering phenomenon is very elaborately explained by Hadrian Djohari [79]. The models developed for the description and analysis of particle sintering are robust in ref [79]. Figure 6.3 shows the different stages of sintering in a crystalline material with a contour map of vacancy concentrations. Our interest was to extend the scope of these models to non-ceramic substances and those undergoing chemical changes in the same conditions simultaneously.
The hypothesis stated earlier warrants a model that is able to track both these phenomena simultaneously. In the next section, phase transformation kinetic models are discussed and the goal is to finally club both the models to predict the relationship between the two models.
6.2.2 Phase Transformation Kinetics

Kolmogorov-Johnson-Mehl-Avrami (KJMA) model is one of the most widely accepted kinetic models to quantify phase transitions [81-84]. In its simplified form, the theory assesses the transformed phase fraction as a function of time as follows:

\[ f = 1 - \exp(-(kt)^n). \]  

Eq. 6.3

where \( f \) is the fraction transformed, and \( n \) is called the Avrami constant.

Despite the widespread use of KJMA model, it has a few inherent drawbacks. Multiple studies have shown that the KJMA model often under-predicts the amount of converted phase fraction [85]. The KJMA model behaves differently when the case of continuous nucleation is considered over a site saturation case. The following equation represents the KJMA model under continuous nucleation [85]:

\[ \varphi = 1 - \exp\left(-\frac{N G^2}{12\pi} t^3\right). \]  

Eq. 6.4

And under the case of site saturation nucleation for \( N=1 \),

\[ \varphi = 1 - \exp\left(-\frac{G^2}{4\pi} t^2\right). \]  

Eq. 6.5

In this section, experimental data of the NaAlH\(_4\) \( \rightarrow \) Na\(_3\)AlH\(_6\) phase transformation has been modeled using the conventional KJMA model and also the relatively new concept of phase-field modeling. The two equations above are fit to the experimental data in Figure 6.4. Both versions of the KJMA model under-predict the phase fraction which confirms the arguments presented elsewhere [85]. Figure 6.4 also shows the 'phase-field model' which offers the best fit. This relatively new technique has garnered a lot of interest. The main motive to develop a phase field model is to make lesser assumptions regarding solid-solid phase transformations. The difference between the two models is
that the phase field model incorporates atomistic details such that the structure is tracked as it evolves. The phase field model is also not based on a random growth process unlike the KJMA model [86], but relies on satisfying thermodynamic constraints involved in new phase nucleation and growth. The model allows for the new phase to evolve freely without the need to track the diffusivity of individual atoms across the interface.

![Experimental Data vs. Phase-Field Model Fit](image)

**Figure 6.4:** Comparison of KJMA and phase-field model fits.

6.2.3 **Unified Model**

Based on the kinetic models discussed above, a phase-field simulation was done as shown in Figure 6.5 on COMSOL. The phase field module in COMSOL only allows the analysis of physical problems involving liquids. To simulate a solid-solid transformation as shown in the next section, the parameters were approximated to the best define a solid. It should be noted that this is only a preliminary work and must be resolved before any accurate, quantitative information can be extracted. Phase evolution
is demonstrated for different ‘shapes’ of the 2D domain consistent with the sintering stages reported in Figure 6.3. If both phenomena are coupled, the spatial distribution of the evolving phases may change considerably. This is because the atomic diffusion would be a result of a combination of curvature-driven mass transport as well as phase growth-driven mass transport. The new phases could have concentrated growth along the contours shown in Figure 6.3. For this collection of discrete simulations, the actual process may, at best, be approximated by the arrow in Figure 6.5. The future work may be concentrated on developing this unified model, such that the simulations can predict the role of either phenomenon on the rates of the other.
Figure 6.5: Representative phase-field simulation phase evolution at various stages of sintering (t' is dimensionless time).
APPENDIX A

REORIENTATIONAL MODELS
The geometrical models to describe the localized alanate tetrahedron dynamics (arising from the broad Lorentzian EISFs) are discussed here and the parameters are evaluated from the geometry of the jumps. The various models described are isotropic rotation, cubic tumbling, tetrahedral tumbling and the high temperature (HT) model.

The isotropic rotation model describes a mechanism where hydrogen atoms do not make discrete jumps to crystallographic sites, but instead make random jumps on a sphere-equivalent of the alanate tetrahedron. This does not yield a definitive jump length but reflects on the size of the alanate cluster in terms of the Al-H bond distances. The hydrogen atoms are at all times, present on a spherical cloud, whose radius is extracted from the EISF modeling.

Figure A.1 shows a schematic to illustrate the geometry of any tetrahedron re-orientation. There lines in red and blue are the axes of symmetry. It can be stated that, for a cube, there are four C3 axes and six C2 axes. The tumbling mechanism is easier to explain with the reference of a boundary-cube. The cubic tumbling model describes tetrahedral re-orientation with a reorientational disorder. It explains the tumbling of a tetrahedron about the C2 axis, i.e., a 90° flip (in Figure A.1), such that the H-atom at one vertex of the cube jumps to the immediate adjacent vertex of the cube. The symmetry about C2 axis is preserved but it becomes disordered along C3 axis. The parameter evaluated is ‘a’=2*r/sqrt (3), which is the jump distance (length of one edge of the cube) and ‘r’ is the Al-H distance.
The tetrahedral tumbling mechanism is caused when the tetrahedron is tumbling about all four C3 axes. This, in effect, represents hydrogen atoms making jumps among their own four tetrahedral sites. This mechanism is indicative of an ordered structure as the symmetry about all axes is preserved. The parameter evaluated is 'a', which is the jump length and is equal to \( r \sqrt{3} \), where 'r' is the Al-H distance.

The High Temperature (HT) model was shown to describe the BH$_4^-$ dynamics in LiBH$_4$ with exceptional fits even at high Q values [39]. The HT model is illustrated in Figure A.1. For explanatory purposes, sites numbered one, five and nine may be assumed to be the initial positions of the three hydrogen atoms; sites two, four, six, eight, ten and twelve are the positions for HT model (N = 6) and sites one to twelve be the hydrogen positions for HT model (N = 12). The center of the circle is the position of the Al atom and in the same axial position; the fourth H atom is present at a distance of 1.6 Å from the Al atom. HT model assumes three of the four hydrogen atoms perform a continuous diffusion in a circle and the parameter N is an approximation that is chosen to mimic
continuous diffusion. The fourth hydrogen exchanges position with the H-atoms of the circle by a tetrahedral tumbling mechanism. The parameter \( r \) is obtained from the fit to EISF data and is the radius of the circle (in top view). The radius is not the actual Al-H bond distances and is expected to be approximately 0.8 \( d_{Al-H} \) from geometry. The evaluation of jump lengths in the case of \( N = 6 \) and \( N = 12 \) is possible by simple geometry and is shown in Figure A.2. When \( N = 6 \), the jump sites are equidistant from the center (Al atom) and also from each other, as is the case with a regular hexagon. When \( N = 12 \), the jump distances are approximately 0.518*r. Based on this formulation, the jump distances for the HT model (\( N = 12 \)) is evaluated to be 0.518*(1.33) \( \sim \) 0.68 Å. The H-H bond distances is evaluated to be \( \sqrt{3} \)*r. This yields the distance between the axial H atom and the H-atoms on the circle.

![Figure A.2: Continuous diffusion of H-atoms in high temperature (HT) model.](image)

There is an additional variation to the HT model, where the fourth axial H-atom is stationary. This mechanism is modeled using the HT model (Equation (iv) in Table 3.4) with an additional term as shown in Eq. A.1 [39]:

\[ EISF_{\text{stationary axial } H} = \frac{1}{16} \left[ 4 + \sum_{N=1}^{12} j_0 \left[ 2Qr \left[ \sin \frac{\pi N}{12} \right] \right] \right]. \quad \text{Eq. A.1} \]

This model, by definition, assumes that only three of the four H-atoms in the alanate tetrahedron are in a mobile state. This model was used to describe the localized dynamics in nano-Ti-doped NaAlH₄ (in SBA-15).
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