Appendix A

Effect of porous texture on hydrogen adsorption in activated carbons

A.1 Introduction

Physisorption-based hydrogen (H$_2$) storage in microporous carbons has a trade-off between adsorption capacity and adsorption enthalpy [5]. Conceptually, this problem is best illustrated in terms of the ideal slit pore formed from two parallel, semi-infinite graphite slabs. Packing density is maximized when the pore width is several times larger than the diameter of the H$_2$ molecule, since it permits the formation of several hydrogen monolayers within the pore [16]. At supercritical temperatures, however, condensation within pores does not occur. Characteristic H$_2$ adsorption enthalpies associated with large slit pores therefore approach the enthalpy of H$_2$ adsorption on carbon, typically measured between 4 kJ mol$^{-1}$ to 6 kJ mol$^{-1}$ [15, 121]. With smaller pores, the adsorption enthalpy increases due to the overlap of potentials fields from each face of the pore. The packing density begins to decrease, though, when the pore is no longer wide enough to accommodate two H$_2$ monolayers. *Ab initio* calculations of hydrogen adsorption in ideal slit pore carbons

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are largely consistent with this picture [16, 122]. The fundamental limitations of hydrogen storage in activated carbons are difficult to study experimentally because uniform slit pore structures do not occur in nature. To extend the slit pore concept to realistic carbon adsorbents, the distribution of pore sizes must be understood.

Due to their microporosity, activated carbon fibers (ACF) are an excellent material for a fundamental study of \( \text{H}_2 \) adsorption capacity and enthalpy. ACFs are synthesized from polymeric carbon precursors and contain narrow pore size distributions [6, 123]. Images of ACFs from scanning tunneling microscopy have revealed networks of elongated slit-shaped and ellipsoid-shaped pores [124, 125]. Edge terminations in graphitic layers are thought to be the most reactive sites during the physical activation process, resulting in a gradual lengthening of slit shaped pores as a function of burn-off [126]. ACFs subjected to less burn-off will have smaller pore volumes and a greater abundance of narrow pores widths. With longer activation times, the pores grow larger resulting in a larger amount of mesopores. This offers a convenient control for an experimental study of pore structure and hydrogen adsorption.

In the current study, the pore size distributions (PSD) of ACFs are compared to the hydrogen adsorption enthalpy and adsorption capacity. Two ACF samples subjected to different degrees of activation are characterized. The microstructure of the activated carbon samples is investigated first with high resolution transmission electron microscopy (HRTEM). Then the PSD is obtained from argon adsorption measurements using the density functional theory method. Supercritical hydrogen adsorption isotherms are measured, and the enthalpies and capacities are determined. Measurements are also performed on a microporous, coconut-derived activated carbon as a control sample.
A.2 Experimental Methods

Kynol™ activated carbon fiber samples ACF-1603-10 (ACF-10) and ACF-1603-20 (ACF-20) were obtained from Kynol Inc. These ACFs are produced by carbonization and gasification of a phenolic resin precursor. The last two digits in the labels are an approximate indication of surface area in hundreds of m$^2$ g$^{-1}$. The commercial, coconut-shell-derived activated carbon CNS-201 (CNS-201) was purchased from A.C. Carbon Canada Inc. Since CNS-201 is known to be highly microporous (90% of pores are smaller than 1.3 nm), it is a useful reference material for the microporous ACFs. Textural parameters were obtained from Ar isotherms (87 K) for ACF-10 (0.2811 g) and ACF-20 (0.3222 g), and from a N$_2$ isotherm (77 K) for CNS-201 (0.1019 g). For illustration, the Ar isotherm for ACF-10 is displayed in Fig. A.1a. Surface areas and saturation pore volumes are calculated from the BET equation, given by

$$\frac{p/p^\circ}{n (1 - p/p^\circ)} = \frac{1}{n_mC} + \frac{C - 1}{n_mC} (p/p^\circ).$$  \hspace{1cm} \text{(A.1)}

The monolayer capacity, $n_m$, is determined from the slope and $y$-intercept of the fitted line in Fig. A.1c. We can then calculate the BET surface area, $a$(BET), from the molecular cross-sectional area ($\sigma$) using the formula,

$$a$(BET) = $n_mN_a\sigma, \hspace{1cm} \text{(A.2)}

where $N_a$ is the Avogadro constant.

Total pore volumes are calculated from the Dubinin-Astakhov equation, given by

$$\log (n) = \log (n_p) - D [\log (p^\circ / p)]^x, \hspace{1cm} \text{(A.3)}$$
Figure A.1: Surface texture analysis for sample ACF-10. (a) Ar isotherm measured at 87 K. (b) Dubinin-Astakhov transformed isotherm plot. (c) BET surface area plot.

where $D$ are $x$ are empirical constants.\(^1\) The pore capacity, $n_p$, is determined from the $y$-intercept of the fitted line in Fig. A.1b. It is then used to calculate the pore volume

$$V_p = n_p \times M/\rho,$$

(A.4)

where $M$ and $\rho$ are the molar mass and liquid density (at 87 K) of Ar. Pore size distributions were calculated using the original DFT method as implemented in Micromeritics ASAP 2020 Version 3.01 software.\(^2\)

\(^1\)Note that $x$ was optimized as 2.0771 for ACF-10, as indicated on the $x$-axis of Fig. A.1b.

\(^2\)Ar and $N_2$ isotherms, and DFT modeling performed by Micromeritics Analytical Services.
High resolution TEM micrographs were acquired on a Tecnai F30-UT operated at 300 keV. Sample preparation consisted of grinding about 10 mg of the sample in isopropanol and dispersing it on a carbon grid. High-pressure H\textsubscript{2} isotherms were measured with the custom-built Sieverts apparatus at temperatures of 77 K, 87 K, and 195 K. This instrument was described in detail in Sec. 3.1.3. The sample weights used for the hydrogen adsorption measurements were 0.1782 g (ACF-10), 0.2114 g (ACF-20) and 0.903 g (CNS-201). Prior to adsorption measurements, samples were degassed by heating at 200 °C under vacuum for 12 h. Sample masses were measured again after the adsorption experiment to check for changes in mass due to removal of residual water. The void volume of the sample was estimated by assuming a skeletal density of 2.1 g ml\textsuperscript{-1}, which is typically sufficient for most carbon samples.

A.3 Results

An HRTEM micrograph of ACF-10 is presented in A.2. ACFs are known to be more graphitic than typical activated carbons [126], but this is not obvious from the image. The microstructure appears similar to the highly disordered microstructures typically observed for activated carbons. Micropore structures were not visible in the HRTEM analysis. However, the combination of finite sample thickness and non-periodicity tends to conceal micropore structures.

The BET surface areas and total pore volumes for ACF-10, ACF-20, and CNS-201 are listed in A.1. As expected, ACF-10 (subject to less burn-off than ACF-20) has a smaller pore volume and smaller BET surface area than ACF-20. The activated coconut carbon CNS-201 appears to have a BET surface area and pore volume which is intermediate between the two
ACFs. Calculated surface areas of activated carbons are often unrealistically high, since the micropore adsorption mechanism is not equivalent to the multilayer process assumed in the BET model. Nevertheless, the BET method is useful for comparisons between different materials.

Pore size distributions obtained from the DFT method are displayed in Fig. A.3. The pore width is defined as $L - d$, where $L$ is the internuclear spacing between the walls of the slit pore and $d$ is the van der Waals diameter of carbon (3.4 Å). Since graphite has an interlayer spacing of $L = 3.35\,\text{Å}$, a slit pore formed from a single missing graphene plane has a width of 3.3 Å. A slit pore formed from two missing graphite planes has a width of 6.7 Å, and a pore formed from three missing graphite planes has a width of 10 Å. Taking into account the finite diameter of Ar (2.8 Å) and $N_2$ (3.0 Å), the cutoff in the pore spectrum

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3Note that textural parameters were obtained from Ar isotherms for the ACFs and from $N_2$ isotherms for CNS-201. For direct comparison between samples it would have been better to have used the same adsorptive. Textural parameters obtained by Ar and $N_2$ data are still sufficient for the qualitative comparison done here.
Table A.1: Surface texture parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (m² g⁻¹)ᵃ</th>
<th>V_pore (cm³ g⁻¹)ᵇ</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF-10</td>
<td>801</td>
<td>0.296</td>
</tr>
<tr>
<td>ACF-20</td>
<td>1817</td>
<td>0.706</td>
</tr>
<tr>
<td>CNS-201</td>
<td>1158</td>
<td>0.452</td>
</tr>
</tbody>
</table>

ᵃ Specific surface areas obtained by the BET method.
ᵇ Total specific pore volumes obtained from the Dubinin-Astakhov equation.
ᶜ The textural parameters of ACF-10 and ACF-20 were obtained from Argon measurements at 87 K while those of CNS-201 were obtained from N₂ measurements at 77 K.

must be above 3 Å.⁴

The pore size distributions displayed in Fig. A.3 all show a sharp increase in intensity just below 5.0 Å, which corresponds to a width that is between the predicted pore widths for one or two removed graphite planes. This may simply reflect the smallest pore width which is measurable by the specific probe molecule. Another possibility is that after the removal of two layer planes, the slit pore structure relaxes to the observed 5 Å spacing. The pore distribution of ACF-10 is narrow, consisting of the single large peak at 5 Å. Since burn-off in ACF-10 was minimized, larger pore structures did not develop fully, and are present only as a small tail in the PSD. For ACF-20 there is a broad distribution of pore widths from 5 Å to 20 Å with a small positive skew. Since ACF-20 was subject to a greater degree of burn-off, larger pores were formed during the activation process.⁵ The activated carbon CNS-201 also appears to have a distribution of pore widths between 5 Å and 20 Å with a positive skew. This broad distribution of pore widths in ACF-20 and CNS-201 may reflect the presence of slit pores formed from the removal of up to six graphite planes.

⁴ Smaller probe molecules, such as helium, could measure pore widths below this cutoff.
⁵ The minima near 6 Å and 10 Å are likely to be model-induced artifacts which are independent of the actual sorbent material [127]. The minima in the distributions have been proposed to originate from packing effects where the pore width transitions from being able to support one adsorbed layer to two, and from two layers to three. This width is governed by the functional form used for the adsorbing molecule, for example, a Lennard-Jones potential. However, the fact that the maxima in the distributions are separated by integrals of the graphite layer spacing distance suggests that the maxima may be real and correspond to pores formed from removal of one, two, three, etc, graphitic planes.
Figure A.3: Pore size distributions determined by the DFT method for (a) ACF-10, (b) ACF-20, and (c) CNS-201. The bottom axis is shown in logarithmic scale.
Supercritical H\textsubscript{2} isotherms are displayed in Fig. A.4. As discussed in Sec. 1.6.7, comprehensive studies of H\textsubscript{2} adsorption in activated carbons typically report a linear dependence of \( n_{\text{max}} \) at 77 K with specific surface area [19, 20, 128]. An increase of approximately 1 wt\% hydrogen for every 500 m\textsuperscript{2} g\textsuperscript{-1} of surface area is the rule-of-thumb. As shown in the inset of Fig. A.4, the hydrogen adsorption capacities of ACF-10, ACF-20, and CNS-201 at 77 K roughly follow the rule-of-thumb, although ACF-10 does show a substantial positive deviation. Since ACF-10 is almost exclusively microporous, with little contribution from mesopores,\textsuperscript{6} this may explain why it shows a large positive deviation from the 500 m\textsuperscript{2} g\textsuperscript{-1} per 1 wt\% rule. On the other hand, ACF-20 has a wider distribution of both mesopores

\textsuperscript{6}Small mesopores can produce large BET surface areas, but contribute little to hydrogen adsorption capacity.
Table A.2: Hydrogen adsorption parameters

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\Delta \hat{h}_0$ (kJ mol$^{-1}$)$^a$</th>
<th>$\Delta H_{avg}$ (kJ mol$^{-1}$)$^b$</th>
<th>$n_{max}$ (wt%)$^c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>ACF-10</td>
<td>8.92</td>
<td>6.64</td>
<td>2.1</td>
</tr>
<tr>
<td>ACF-20</td>
<td>7.63</td>
<td>5.85</td>
<td>3.5</td>
</tr>
<tr>
<td>CNS-201</td>
<td>8.59</td>
<td>6.07</td>
<td>2.5</td>
</tr>
</tbody>
</table>

$^a$ Enthalpy of hydrogen adsorption in the zero-coverage limit.
$^b$ Average isosteric heats between 0 wt% and 1.8 wt%.
$^c$ Maximum hydrogen adsorption capacity at 77 K.

and mesopores, which may explain why it does not show the same positive deviation from the rule-of-thumb.

Accurate adsorption amounts were measured in the low-pressure region using a high-resolution pressure gauge. Henry’s law constants were then calculated at 77 K, 87 K, and 195 K from the zero-order virial coefficient $C_0 = \ln(k_H)$ in Eq. 3.11. The differential enthalpy of adsorption was calculated from the temperature variation of $k_H$ using the van’t Hoff expression (Eq. 3.12). For all the samples we find that $\ln(k_H)$ varies linearly with $1/T$, and an accurate estimate of $\Delta \hat{h}_0$ is obtained from the slope. Values of enthalpy in the zero coverage limit are summarized in Table A.2. The largest adsorption enthalpy (8.92 kJ mol$^{-1}$) is observed for ACF-10, which has the greatest fraction of narrow pores. In ACF-20, which has larger pore widths, the adsorption enthalpy (7.32 kJ mol$^{-1}$) is smaller. An intermediate enthalpy is observed for the activated carbon CNS-201.

The isosteric heat was calculated by fitting the 77 K and 87 K isotherms to the virial-type thermal equation (Eq. 3.8). As displayed in Fig. A.5, all of the samples are energetically heterogeneous, and the enthalpy decreases substantially with increasing $n$. Heterogeneity is especially pronounced for ACF-10. In the inset to Fig. A.5, the isosteric heat is also plotted against the fractional adsorption amount. When viewed as a function of fractional adsorption, the isosteric heat of ACF-10 remains higher than ACF-20 until a fractional
Figure A.5: The $\text{H}_2$ isosteric enthalpy of adsorption for ACF-10, ACF-20, and CNS-201 as a function of surface excess adsorption. Inset: The isosteric heat is plotted as a function of the fractional amount of adsorption (excess adsorption divided by the saturation adsorption amount at 77 K).

filling of about 0.7. For comparison between the different samples, the isosteric heats were averaged from 0 mmol g$^{-1}$ to 9.5 mmol g$^{-1}$, and these values are summarized in Table A.2.

A.4 Discussion

Heterogeneity in the adsorption potentials of microporous carbons is modeled using a distribution of widths of the slit pores. Recent studies have also stressed the importance of fluctuations in pore wall thickness on the adsorption potential [5,129]. Narrow pores have deeper potential wells and should be filled at the lowest pressures. This is followed by the gradual filling of larger pores at higher pressures. At a given equilibrium pressure, $p$, there should be a critical pore width, below which all pores are filled and above which all pores
are vacant [73]. The zero coverage heat of H$_2$ adsorption, $\Delta \tilde{h}_0$, reflects the initial filling of pores and therefore should depend on the PSD of the three samples.

Since ACF-10 contains a narrow peak at 5 Å in the PSD, the filling of these small pores presumably leads to the large zero coverage H$_2$ adsorption enthalpy. ACF-10 also contains a small fraction of wider pores, and it is the filling of these larger pores that apparently causes the steep decrease in the isosteric heat of adsorption at higher coverage. In ACF-20, there is a broad distribution of pore widths. In theory, the smallest 5 Å pores should fill first, leading to a similar zero coverage H$_2$ adsorption enthalpy as ACF-10. Measurements indicate, however, that ACF-20 has a significantly smaller zero coverage enthalpy than ACF-10. The exclusive filling of the smallest pores at low pressures, in isolation from the larger pores, may not be a realistic view. Simultaneous filling of pores with widths from 5 Å to 20 Å, on the other hand, might explain this smaller-than-expected zero coverage adsorption enthalpy. Therefore it is the relative abundance of the smallest pores relative to the larger pores which seems to have the greatest influence on the zero-coverage enthalpy.

In all three samples, the isosteric heat of adsorption decreases with the excess adsorption amount. Since the samples have different adsorption capacities, a better comparison can be made by plotting the isosteric heats as a function of fractional adsorption. This is displayed in the inset to Fig. A.5. The isosteric heats of both ACF-10 and ACF-20 decrease almost uniformly at low filling, but ACF-10 eventually falls below ACF-20 at a fractional filling of 0.7. At least some of the decrease in isosteric heat can be attributed to repulsive interactions between the adsorbed H$_2$ molecules. These unfavorable interactions are likely to be greater in small slit pores than in larger slit pores, leading to the observed behavior.

Heats of adsorption in the Henry’s Law region (listed in Table A.2) are considerably greater than the 4–6 kJ mol$^{-1}$ heats typically observed for H$_2$ adsorption on the surface of
carbon. This is due to strong interactions between adsorbed hydrogen molecules and the slit pore potential fields. Average isosteric heats of adsorption fall between 5.8–6.7 kJ mol$^{-1}$ for the three samples, closer to the characteristic values for carbon. The H$_2$ adsorption enthalpy (ACF-10 > CNS-201 > ACF-20) is negatively correlated with the total H$_2$ adsorption capacity (ACF-20 > CNS-201 > ACF-10) for the three samples that were studied.

A.5 Conclusion

Pore size distributions and supercritical H$_2$ isotherms for two microporous activated carbon fibers and one coconut-derived activated carbon were measured and compared. The low surface area sample, ACF-10, has a narrow peak in the PSD at 5 Å with a very small tail at larger widths. The high surface area sample, ACF-20, has a broad PSD which contains widths from 5 Å to 20 Å and has a small positive skew. The coconut-derived activated carbon CNS-201 also has a broad PSD with widths from 5 Å to 20 Å. The zero coverage enthalpy of hydrogen adsorption depends strongly on the relative intensity of the smallest pore widths in the PSD. Zero-coverage enthalpies vary from 8.92 kJ mol$^{-1}$ for low surface area ACF-10 to 7.63 kJ mol$^{-1}$ for high surface area ACF-20.
Appendix B

Hydrogen absorption behavior of the ScH$_2$-LiBH$_4$ system

B.1 Introduction

Complex metal hydrides are basically salts consisting of an anionic complex [MH$_n$]$^-$ and a cation A$^+$ to balance the charge. Complexes containing light elements have been the focus of most research, due to their favorable gravimetric hydrogen densities. One such complex metal hydride is LiBH$_4$, which can release up to 13.8 wt% hydrogen by thermal decomposition:

\[
\text{LiBH}_4 \rightarrow \text{LiH} + \text{B} + \frac{3}{2}\text{H}_2.
\]  

Like most complex metal hydrides, LiBH$_4$ is a very stable compound. It requires temperatures well above 200°C to release hydrogen. The standard reaction enthalpy is 61 kJ mol$^{-1}$, which translates to 1 bar equilibrium pressure at 400°C [130,131].

Chemical destabilization of LiBH$_4$ offers a versatile way to lower the desorption enthalpy [132–136]. Recent work has focused on adding an additional metal or metal hydride species which reacts to form a stable metal boride phase, lowering the overall reaction enthalpy.

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Vajo et al. demonstrated that adding MgH$_2$ to LiBH$_4$ lowered the dehydrogenation enthalpy by 25 kJ mol$^{-1}$ [131]. Motivated by such successes, a comprehensive evaluation of potential chemically destabilized metal hydride systems was initiated, using density functional theory to evaluate formation and reaction enthalpies [137–139]. A significant result from this study was the identification of ScH$_2$ as a destabilizing agent with ideal thermodynamics [140]. The following decomposition pathway

$$\text{ScH}_2 + 2 \text{LiBH}_4 \rightarrow \text{ScB}_2 + 2 \text{LiH} + 4 \text{H}_2$$  \hspace{1cm} (B.2)

has a calculated reaction enthalpy of 34.1 kJ mol$^{-1}$ at room temperature. This system can release up to 8.9 wt% upon completion. An equilibrium pressure of 1 bar is calculated to occur at 57 °C.

It is important to note, however, that first principles DFT calculations provide no direct information about either the reaction mechanism or the activation barriers. It is likely that the rate limiting steps would involve the breakdown of ScH$_2$ ($\Delta H_f = 200$ kJ mol$^{-1}$) and the formation of ScB$_2$ ($\Delta H_f = 248$ kJ mol$^{-1}$), both of which are stable compounds. While first-principles calculations have proved accurate in reproducing experimental PCT diagrams for the destabilized MgH$_2$-LiBH$_4$ system, it is uncertain whether similar success will be achieved for a system in which the reactant and product phases have considerably larger formation enthalpies. High energy ball-milling can improve reaction kinetics to some degree by reducing diffusion distances and increasing the concentration of reaction interfaces. It does not necessarily mitigate the large activation barriers to ScH$_2$ and ScB$_2$ decomposition however.

The aim of the present work is to experimentally investigate the importance of kinetic
barriers in determining hydrogen absorption and desorption behavior. Isothermal kinetic H₂ adsorption and desorption of the ScH₂/LiBH₄ system was measured at various temperatures. Reaction products were characterized using powder XRD, magic angle spinning NMR, and Raman spectroscopy. We were unable to verify the formation of ScB₂ in the product phase, and there was no evidence for the proposed reaction pathway (Eq. B.2). Rather, the LiBH₄ was found to decompose independently into LiH and amorphous boron without the reaction of ScH₂.

B.2 Experimental Details

Samples of ScH₂ were synthesized by heating small scandium pieces (99.9% purity, Standford Materials Corporation) in ultrahigh purity H₂ at approximately 350°C. The resulting formation of scandium hydride was rapid and highly exothermic. This is illustrated in Fig. B.1, where the hydrogenation reaction is shown to complete within a minute or so. The large amount of released heat is evident from the spike in reactor temperature. Hydrogenation was allowed to proceed for 3 h to ensure equilibration. Volumetric analysis and X-ray diffraction both indicate that the reaction product is ScH₂. Roughly 10 g of a 2:1 molar mixture of LiBH₄ (95% purity, Sigma Aldrich) and freshly-prepared ScH₂ was loaded under argon atmosphere into a sealed 80 mL stainless steel vessel containing five 0.5 in. diameter stainless steel balls. The vessel was sealed with a rubber gasket and clamp and loaded into a planetary mill (Fritsch-pulverizette 6). Different mixtures were milled at 400 rpm for either 1 h or 10 h. For possible catalytic enhancement of the reaction rates, 2 mol% TiCl₃ (Sigma Aldrich) was added to several samples prior to milling. All samples were handled in argon atmosphere gloveboxes to prevent air and moisture contamination.

Isothermal kinetic desorption measurements were conducted on a custom built stainless
Figure B.1: Synthesis of scandium hydride. Top: Molar ratio of H to Sc in the solid scandium-hydrogen phase versus time. Bottom: Pressure of free H$_2$ in the reactor system versus time.

steel Sieverts apparatus. In a typical experiment, a 1 g sample was loaded into a 14 mL stainless steel reactor assembly sealed with a 0.5 in. Swagelok VCR filter gasket connection. The reactor was then mounted on the Sieverts system and enclosed in a thick, tight-fitting aluminum collar to maintain temperature uniformity. The furnace setup included a Watlow band heater fastened around the aluminum collar, with two thermocouples inserted into dedicated ports in the aluminum heat sink. The quantity of desorbed hydrogen was determined by volumetric measurements. Weight percents are reported with respect to the fully
hydrogenated samples, excluding the weight of the added catalyst. Powder XRD and Raman spectroscopy measurements were collected on samples sealed in 1.0 mm glass capillary tubes, following the procedure described in Sec. 2.6.

Solid-state magic angle spinning nuclear magnetic resonance (MAS NMR) measurements were performed using a Bruker Avance 500 MHz spectrometer equipped with a Bruker 4 mm boron-free cross-polarization (CP) MAS probe. The spectral frequencies were 500.23, 160.5, 121.6, and 73.6 MHz for the $^1$H, $^{11}$B, $^{45}$Sc, and $^6$Li nuclei, respectively. Samples were loaded into 4 mm ZrO$_2$ rotors, and each was sealed with a tight-fitting kel-F cap under argon atmosphere and spun at 13 kHz. The one-dimensional $^{11}$B, $^{45}$Sc, and $^6$Li NMR spectra were acquired after a short (0.5 $\mu$s) single pulse (i.e., $\frac{\pi}{12}$ for $^{11}$B) with application of a strong $^1$H decoupling pulse of the two-pulse phase modulation (TPPM) scheme [141]. The NMR shifts were reported in parts per million (ppm) with respect to “zeroes” set to standard external references: tetramethylsilane (TMS) for $^1$H, BF$_3$–Et$_2$O for $^{11}$B, 1.0 M LiCl aqueous solution for $^6$Li, and 1.0 M Sc(NO$_3$)$_3$–HNO$_3$ aqueous solution for $^{45}$Sc nuclei.

**B.3 Results**

The hydrogen desorption behavior for the as-prepared ScH$_2 + 2$ LiBH$_4$ mixtures were studied with kinetic desorption measurements using a series of temperature steps (Fig. B.2). Samples were heated inside a 72 mL volume to a final temperature of 450 °C. For samples maintained at this temperature, there was a release of 4.5 wt% hydrogen over 20 h. This is roughly half of the theoretical capacity of 8.91 wt% predicted for Eq. B.2. Longer milling times resulted in a small enhancement of the desorption capacity (an increase of less than 0.5 wt%) with no observable change in desorption kinetics. The composition of the desorbed gas was sampled using a residual gas analyzer (SRS, model RGA200) and found to
Figure B.2: Kinetic desorption data for the ScH$_2$ + 2 LiBH$_4$ system. Top: Desorption into initially evacuated volume. Bottom: Desorption into 100 psi hydrogen backpressure.
contain over 99% hydrogen. Significant hydrogen desorption began at 350 °C, close to the
temperature range at which the thermal decomposition of LiBH₄ is known to occur [142].
The 4.5 wt% of H₂ released at 450 °C is consistent with decomposition due solely to LiBH₄.¹

Desorption measurements were also performed with an initial hydrogen backpressure
of 100 psi, which was not found to enhance kinetics or to increase the hydrogen gas yield.
Desorption from a ScH₂ + 2 LiBH₄ + 0.02TiCl₃ sample was studied to assess the effect of a Ti
catalyst on the reaction kinetics. At 280 °C, the desorption capacity was increased five-fold
in the Ti-containing sample compared to the uncatalyzed sample. It should be noted that
overall desorption capacity was still low, at 0.5 wt%. However, at 350 °C and 450 °C, the
presence of TiCl₃ did not enhance either the kinetics or capacity.

The reverse direction of Eq. B.2 was also studied. A ball-milled ScB₂ + 2 LiH + 0.02TiCl₃ sample was prepared and its hydrogen adsorption properties were studied. Starting with
a 135 bar hydrogen pressure, a 0.8 g sample was heated to 300 °C for 48 h. No statistically
significant hydrogen uptake was determined from a volumetric analysis. Powder XRD and
MAS NMR analysis also failed to detect the formation of the expected product phases:
LiBH₄ and ScH₂. A subsequent absorption experiment was performed with an 896 bar
hydrogen pressure, with the sample kept at 460 °C for 48 h. A ¹¹B MAS NMR spectrum
(see Fig. B.4a) of this sample revealed the presence of a small peak at −41 ppm, indicating
a very limited LiBH₄ formation (about 3 mol%) in the reaction product. We note, however,
that this pressure falls well out of the range of interest for technologically relevant metal
hydride storage systems.

Figure B.3 shows the powder XRD measurements of the ScH₂ + 2 LiBH₄ system before
milling, after milling for 10 h, and after desorption at 450 °C for 20 h. The XRD pattern of

¹Excluding the mass of the unreacted ScH₂, this would give 9 wt%, which is consistent with desorption measurements taken on unmixed LiBH₄.
the 450 °C desorption product reveals the presence of LiH and unreacted ScH$_2$. Since LiH is also an expected decomposition product of unmixed LiBH$_4$ [142], this does not provide evidence that the ScH$_2$ has participated in the reaction. A large background was also present due to the abundance of amorphous phases, presumably originating from the melting and re-solidification of LiBH$_4$ as well as from the formation of amorphous intermediate phases [143]. No peaks from the expected ScB$_2$ phase could be detected in the desorbed material.

Because a large fraction of the desorption product was amorphous, MAS NMR was utilized to complement the powder XRD results. Figure B.4 shows the $^{11}$B, $^{45}$Sc, and $^6$Li MAS NMR data for the ScH$_2 + 2$LiBH$_4$ system after milling and after dehydrogenation (450 °C for 20 h). From $^{11}$B NMR spectra, no noticeable change of the LiBH$_4$ peak was observed after ball-milling. The $^{11}$B MAS and CPMAS spectra (Fig. B.4a and b) show the
Figure B.4: NMR spectra of milled and dehydrogenated $\text{ScH}_2 + 2\text{LiBH}_4$. (a) Bloch decay $^{11}\text{B}$ MAS NMR spectra with neat LiBH$_4$ added as reference. Note that a spectrum of the ScB$_2 + 2\text{LiH}$ system after absorption treatment at high H$_2$ pressure (896 bar; see text) is also included, where the broader spinning sidebands in this spectrum are due to unreacted ScB$_2$. (b) $^{11}\text{B}$ MAS and CPMAS NMR spectra (contact time = 0.1 ms) of desorbed sample. (c) $^{45}\text{Sc}$ MAS NMR spectra with pure ScB$_2$. (d) $^6\text{Li}$ MAS NMR spectra.

formation of elemental boron in the amorphous phase (broad shoulder at $\sim$ 5 ppm) and the formation of an intermediate phase (with peak at $-12$ ppm) that was recently identified as an $[^{12}\text{B}]_{12}^{12}\text{H}^{2-}$ species [144]. We note also that some unreacted LiBH$_4$ is still present (seen from the peak at around $-40$ ppm) in the dehydrogenated product.

While unreacted ScH$_2$ is still present in the desorption products, ScB$_2$ is not detectable in the $^{45}\text{Sc}$ MAS NMR spectra presented in Fig. B.4c. Note that the $^{45}\text{Sc}$ signal was
Figure B.5: Left: Raman spectra of the dehydrogenation products of (a) ScH$_2$+2 LiBH$_4$ system and (b) neat LiBH$_4$. Spectrum (a) corresponds to the white particles shown in the optical micrograph. The solid down-triangle, open circle, and open up-triangle identify Raman modes from Li$_2$B$_{12}$H$_{12}$, LiBH$_4$, and amorphous boron, respectively. Right: Optical micrograph of a ScH$_2$ + 2 LiBH$_4$ system after desorption.

significantly reduced after the desorption reaction, which we tentatively attribute to the inhomogeneous separation of the solid ScH$_2$ phase and LiBH$_4$ melt, and the correspondingly nonuniform distribution of ScH$_2$ particles in the resulting NMR sample. The $^6$Li MAS NMR spectra (shown in Fig. B.4d) also provide a distinctive signature of phase changes from LiBH$_4$ ($-1.1$ ppm) to Li$_2$B$_{12}$H$_{12}$ ($-0.5$ ppm). The presence of LiH was confirmed by independent $^6$Li CPMAS NMR measurements (not shown) because extremely long spin-lattice relaxation behavior inhibited its observation during recording of the MAS spectra in Fig. B.4d. As with the XRD data, the NMR results identify the decomposition products of LiBH$_4$, but provide no evidence that ScH$_2$ has reacted to form the ScB$_2$ product.

Raman spectroscopy was used to probe the chemical composition of a ScH$_2$ + 2 LiBH$_4$ mixture desorbed at 400°C for 20 h. The results are shown in Fig. B.5. It was found that the desorption product segregated into two phases, which are visible in Fig. B.5 as white particles and dark particles. The dark particles and the as-milled ScH$_2$ + 2 LiBH$_4$ mixture
did not have any Raman-active modes. However, the spectrum of the white particles bears a strong similarity to that of dehydrogenated LiBH$_4$. The B–H bending and stretching modes of LiBH$_4$ around 1300 cm$^{-1}$ and 2300 cm$^{-1}$ are present in both samples and, as observed previously, are not affected by decomposition at temperatures below 400°C [143]. The broad peak at 1100 cm$^{-1}$ corresponds to vibrations in amorphous boron. The additional B–H bending and stretching modes around 500–1000 and 2500 cm$^{-1}$ are consistent with the calculated and measured B–H vibrational modes in Li$_2$B$_{12}$H$_{12}$ [145]. These results lead us to believe that the ball-milled ScH$_2$ + 2 LiBH$_4$ mixture segregates back into its initial components upon the melting and solidifying of LiBH$_4$. The dark particles consist mainly of ScH$_2$, while the white particles consist mostly of LiBH$_4$ and its thermal decomposition products.

B.4 Discussion

The rate limiting steps of the absorption and desorption reaction of simple metal hydrides such as MgH$_2$ have been identified [146], but the reaction pathways of most destabilization-based reactions are still not well understood. Based on calorimetric and in situ XRD measurements, desorption in the MgH$_2$ + 2 LiBH$_4$ system has been found to proceed in two distinct steps [147]:

\[
\text{MgH}_2 \rightarrow \text{Mg} + \text{H}_2 \quad \text{(B.3)}
\]

\[
\text{Mg} + 2 \text{LiBH}_4 \rightarrow \text{MgB}_2 + 2 \text{LiH} + 3 \text{H}_2. \quad \text{(B.4)}
\]

An equivalent reaction pathway for the ScH$_2$ + 2 LiBH$_4$ system would not work for the temperature range investigated here. Decomposition of ScH$_2$ does not occur until 900°C.
Well below this temperature, thermal decomposition of LiBH$_4$ should have already occurred independently. In principle, nanocrystalline ScH$_2$ may have a lower decomposition temperature due to excess surface energies and excess grain boundary enthalpies in the hydride phase. Reductions in the heat of formation of MgH$_2$ up to 30% have been estimated for crystallites smaller than 5 nm [150]. In practice, crystal grains with a minimum size of 10–15 nm are typically obtained with high energy ball-milling. Our own measurements of XRD peak broadening after ball-milling indicate an average ScH$_2$ crystallite size larger than 20 nm in the experiments. Moreover, the effect of nanocrystalline ScH$_2$ is complicated by the fact that LiBH$_4$ melts at 280°C. Our results indicate that, above this melting temperature, the milled ScH$_2$ + 2LiBH$_4$ mixture segregates back into distinct phases. Another important insight is obtained by studying the desorption of a Sc + LiBH$_4$ system, which does not require the initial dehydriding of ScH$_2$. Significantly, it has been found that this reaction results in the formation of ScH$_2$ rather than ScB$_2$ [136]. From these results, it can be summarized that ScH$_2$ is not effective in destabilizing LiBH$_4$. Until the reaction mechanism is better understood, there is no simple way to surmount the significant reaction barriers present in this system.

**B.5 Conclusion**

Hydrogen sorption studies were performed on the ScH$_2$ + 2LiBH$_4$ system, identified by first-principle calculations as having favorable thermodynamics. Our experimental results demonstrate that H$_2$ desorption is consistent only with independent decomposition of LiBH$_4$. Extensive spectroscopic characterization (XRD, MAS NMR, Raman) failed to detect the ScB$_2$ product of the destabilization reaction. Due to the stability of ScH$_2$ and ScB$_2$, activation barriers in both directions appear to inhibit the predicted reaction at tem-
peratures below 450°C. Sluggish kinetics mean that the destabilization reaction is unfavorably compared to competing reactions such as the independent decomposition of LiBH$_4$. Application of a H$_2$ pressure of $\sim$ 900 bar to a heated ScB$_2$ + 2 LiH mixture was found to yield a minimal amount (i.e., $\sim$ 3 mol%) of the desired LiBH$_4$ phase. Furthermore, our findings suggest that the ball-milled LiBH$_4$-ScH$_2$ mixture segregates back into LiBH$_4$-rich and ScB$_2$-rich phases, due to the melting of LiBH$_4$. There was no indication that TiCl$_3$ assisted the destabilization reaction, although there was an improvement in the desorption kinetics.