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Complex Transition Metal Hydrides Incorporating Ionic Hydrogen: Thermal decomposition pathway of Na$_2$Mg$_2$FeH$_8$ and Na$_2$Mg$_2$RuH$_8$

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Complex transition metal hydrides have potential technological application as hydrogen storage materials, smart windows and sensors. Recent exploration of these materials has revealed that the incorporation of anionic hydrogen into these systems expands the potential number of viable complexes, while varying the countercation allows for optimisation of their thermodynamic stability. In this study, the optimised synthesis of Na$_2$Mg$_2$TH$_8$ ($T$ = Fe, Ru) has been achieved and their thermal decomposition properties studied by ex situ Powder X-Ray Diffraction, Gas Chromatography and Pressure-Composition Isotherm measurements. The temperature and pathway of decomposition of these isostructural compounds differs considerably, with Na$_2$Mg$_2$FeH$_8$ proceeding via NaMgH$_3$ in a three-step process, while Na$_2$Mg$_2$RuH$_8$ decomposes via Mg$_2$RuH$_4$ in a two-step process. The first desorption maxima of Na$_2$Mg$_2$FeH$_8$ occurs at ca. 400 °C, while Na$_2$Mg$_2$RuH$_8$ has its first maxima at 420 °C. The enthalpy and entropy of desorption for Na$_2$Mg$_2$TH$_8$ ($T$ = Fe, Ru) has been established by PCI measurements, with the $\Delta H_{des}$ for Na$_2$Mg$_2$FeH$_8$ being 94.5 kJ/mol H$_2$ and 125 kJ/mol H$_2$ for Na$_2$Mg$_2$RuH$_8$.

Introduction

Transition metals are renowned for their diverse range of valence states and structural conformations.$^{1,2}$ As such, in the last five decades a swathe of homoleptic transition metal hydrides have been synthesised to determine their potential for technological applications. Mg$_2$NiH$_4$ was first realised for its reversible hydrogenation properties in 1968,$^3$ and has since been investigated for a variety technological applications including smart windows and sensors.$^4$-7 Mg$_2$FeH$_6$, with a gravimetric hydrogen storage content of 5.5 wt% has since been developed,$^8$-14 along with a host of other transition metal hydride congeners and derivatives.$^{1,2,15-22}$

The transition metal hydrides of Group 8 often form octahedral [TH$_6$]$^{4-}$ anions, of which are limited to four-fold coordination by counterions (M) in the form of $M'M''M'''M''''$, $M''M'''M''''$, $M''M'''''M'''$, $M''M''''M'''$. Expanding the diversity of coordination can be achieved by increasing the anionic charge of the system, for instance by the inclusion of $H^-$. A recent DFT study by Takeshi et al. established that the incorporation of anionic hydrogen into complex transition metal hydride compounds enables inclusion of a wider variety of cations, thereby allowing tuning of these materials in order to optimise their thermodynamic properties or hydrogen storage capacities.$^{23}$ To date, a variety of quaternary complex hydrides have been synthesised and their structural and physical properties explored, these include LaMg$_2$NiH$_7$ (La$^{3+}$:2Mg$^{2+}$:3H$^-$:[NiH$_4$]$^{4-}$)$^{18,24}$ Na$_2$Mg$_2$NiH$_6$ (2Na$^{+}$:2Mg$^{2+}$:2H$^-$:[NiH$_4$]$^{4-}$)$^{19,19}$ Na$_2$Mg$_2$TH$_8$ (2Na$^{+}$:2Mg$^{2+}$:2H$_2$-[TH$_6$]$^{4-}$) ($T$ = Fe, Ru)$^{20}$ M$_2$Mg$_2$FeH$_{12}$ (M$^{2+}$:2Mg$^{2+}$:2H$_2$-[TH$_6$]$^{4-}$) ($M$ = Ba, Ca, Sr; $T$ = Fe, Ru, Os)$^{6,15,26}$ and M$_2$Mg$_2$Fe$_2$H$_{12}$ (4Ca$^{2+}$:4Mg$^{2+}$:4H$_2$-[FeH$_3$]$^{4-}$) ($M$ = Ca, Yb)$^{27,28}$ Thermodynamic data for these materials are scarce, although some experimental$^{20,28}$ and DFT calculated$^{13}$ values have been determined. SrMg$_2$FeH$_8$ and BaMg$_2$FeH$_8$ decompose at ca. 440 and 450 °C under 0.1 MPa H$_2$, respectively, while Ca$_2$Mg$_4$Fe$_3$H$_{12}$ and Yb$_2$Mg$_4$Fe$_3$H$_{12}$ decompose at ca. 395 and 420 °C, respectively. The enthalpy of desorption of Ca$_2$Mg$_4$Fe$_3$H$_{12}$ and Yb$_2$Mg$_4$Fe$_3$H$_{12}$ to their corresponding binary hydrides has been calculated to be 122 and 137 kJ/mol H$_2$, respectively.$^{28}$ These values are significantly larger than those determined for the ternary Mg$_2$FeH$_6$ at 87 kJ/mol H$_2$, which decomposes at ca. 300 °C,$^{13}$ and indicates the increased stabilisation offered by the incorporation of anionic hydrogen and varied cations into these quaternary compounds.

The isostructural compounds of Na$_2$Mg$_2$FeH$_6$ (5.1 wt% H) and Na$_2$Mg$_2$RuH$_6$ (4.0 wt% H) hold potential as hydrogen storage materials.$^{20}$ To make a fair assumption of their prospective
application, a true understanding of the physical properties of these novel quaternary complex transition metal hydrides must be determined, unto which the data is extremely sparse. As a consequence, the influence of H\textsuperscript{+} on the thermal stability and decomposition process of these materials is generally unknown and must be understood. As such, ex situ powder X-ray diffraction (PXD) and Pressure-Composition Isotherm Measurements (PCI) have been conducted. Their temperatures and pathways of decomposition have been established and the associated enthalpies and entropies of H\textsubscript{2} desorption have been calculated and compared to literature values.

**Experimental**

All preparation and manipulation was performed in a Miwa glove box filled with purified argon (<1 ppm O\textsubscript{2} and the dew point of H\textsubscript{2}O below 190 K) to avoid contamination. The synthesis of Na\textsubscript{2}Mg\textsubscript{2}FeH\textsubscript{6} was carried out by two methods: S1 followed a four step process, which first required the synthesis of Mg\textsubscript{2}FeH\textsubscript{6}. This was achieved by mechanically milling (Fritsch Pulverisette 7) MgH\textsubscript{2} (hydrogen storage grade, Sigma Aldrich) and Fe (99.99%, Misuwa) powders at a molar ratio of 2:1 for 2 h at 400 rpm (ball-to-powder ratio 40:1), under argon with subsequent heat treatment of the pelletised powder at 400 °C for 20 h under 30 MPa H\textsubscript{2}. The resultant olive green powder was then mechanically milled with NaH (95%, Sigma Aldrich) at a molar ratio of 1:2 for 20 h under argon (S1-BM) with subsequent heat treatment of the pelletised powder at 400 °C for 20 h under 30 MPa H\textsubscript{2}. The product was yielded as an olive green powder. The synthesis of S2 (Na\textsubscript{2}Mg\textsubscript{2}FeH\textsubscript{6}) followed a two-step process. NaH, MgH\textsubscript{2} and Fe powders at a molar ratio of 2:2:1 were mechanically milled for 20 h at 400 rpm (ball-to-powder ratio 40:1), under argon (S2-BM) with subsequent heat treatment of the pelletised powder at 400 °C for 60 h under 30 MPa H\textsubscript{2}. The product was then milled with NaH (S2)BM, followed by hydrogenation at 30 MPa H\textsubscript{2} at 400 °C (Eq. 3), with an associated time requirement of 80 h. The products after milling and hydrogenation of S1 and S2, identified by PXD, are not altered during milling.

**Results and Discussion**

The synthesis of Na\textsubscript{2}Mg\textsubscript{2}FeH\textsubscript{6} was first reported to utilise Mg\textsubscript{2}FeH\textsubscript{6} as a starting material, which was consequently milled for 20 h with NaH (S1-BM), followed by hydrogenation at 30 MPa H\textsubscript{2} at 400 °C (Eq. 1 and 2).\textsuperscript{20} Overall, this method is time intensive (in excess of 100 h due to the requirement of two milling and two hydrogenation procedures), and the final product also contains Fe, NaH, and Mg\textsubscript{2}FeH\textsubscript{6} impurities. In order to reduce the time requirements and levels of impurities, alternative synthetic routes were investigated. It was determined that successful synthesis is achievable by ball milling 2NaH + MgH\textsubscript{2} + Fe (S2-BM), followed by hydrogenation at 30 MPa H\textsubscript{2} at 400 °C (Eq. 3), with an associated time requirement of 80 h. The products after milling of each material differ considerably (Figure 1), the constituents of S1-BM, identified by PXD are not altered during milling.
(Mg$_2$FeH$_6$ + NaH) despite a broadening of the peaks due to a decrease of crystallite size (or reduced crystallinity). The products of S2-BM were NaMgH$_3$ + Fe.

Hydrogenation of the ball milled samples S1-BM and S2-BM under standard conditions (30 MPa H$_2$ and 400 °C for 60 h), resulted in the formation of Na$_2$Mg$_2$FeH$_8$ as the major phase (Figure 1). Analysis of hydrogenated S1 by Reitveld refinement indicates that the sample is 80.3(9)% pure and as such contains residual Mg$_2$FeH$_6$ (8.9(4) %), Fe (7.9(2) %), NaMgH$_3$ (2.5(3) %) and NaH (2.7(2) %) starting materials. Analysis of hydrogenated S2 indicates that the sample contains 90.6(4) % Na$_2$Mg$_2$FeH$_8$ and 9.4(3) % Fe, without residual Mg$_2$FeH$_6$ or NaH. This indicates that the optimal method of synthesis is via the S2 method due to the elimination of the prerequisite Mg$_2$FeH$_6$ synthesis (Eq. 1) and overall decrease in impurities compared to S1, primarily due to the initial (complete) formation of NaMgH$_3$ during the milling reaction. Milling initiates the breaking of the strong Na-H bonds, which is required to ensue during the annealing phase when synthesised via Mg$_2$FeH$_6$ (S1). This ultimately leads to the observation of unreacted NaH and Mg$_2$FeH$_6$ starting materials.

The synthesis of Na$_2$Mg$_2$RuH$_8$ follows a two-step reaction, where stoichiometric quantities of Ru, NaH and MgH$_2$ are milled for 5 h (S3-BM) before hydrogenation under 30 MPa H$_2$ at 500 °C for 20 h (S3) (Eq.4). The composition of the milled material is unchanged from the starting materials (Figure 1), whereas after hydrogenation the sample appears to be mostly Na$_2$Mg$_2$RuH$_8$, but also comprises of some residual Ru. An unknown material is also identifiable within the Na$_2$Mg$_2$RuH$_8$ powder (S3), of which only a few reflections are discernible. These occurrence of these additional Bragg peaks were also noted previously.

Thermal Decomposition of Na$_2$Mg$_2$TH$_8$ ($T$ = Fe, Ru)

In order to determine the thermal decomposition temperatures of Na$_2$Mg$_2$TH$_8$ ($T$ = Fe, Ru), aliquots of each material were heated at a rate of 5 °C/min with GC detecting the...
Figure 3. PCI analysis of Na$_2$Mg$_2$FeH$_8$ (a) and Na$_2$Mg$_2$RuH$_8$ (b) at selected temperatures. van’t Hoff plot of H$_2$ desorption equilibrium pressures and the linear fit to the data for Na$_2$Mg$_2$FeH$_8$ (c) and Na$_2$Mg$_2$RuH$_8$ (d). Ex situ PXD analysis of Na$_2$Mg$_2$FeH$_8$ (S1) (e) and Na$_2$Mg$_2$RuH$_8$ (S3) (f) for samples collected after PCI analysis and after rehydrogenation ($\lambda$ = CuK$\alpha$). * = Na$_2$Mg$_2$TH$_8$ ($T$ = Fe, Ru); # = Mg$_2$FeH$_6$; @ = NaH; $\chi$ = Na$_2$Mg$_2$TH$_8$ ($T$ = Fe, Ru); $\gamma = $ NaMgH$_3$; ^= NaOH; += Mg; $\Delta = $ Na; $\alpha = $ Mg$_3$Ru$_2$; $\delta = $ Mg$_2$RuH$_4$; ! = unknown phase; $\Omega = $ unknown phase; $\xi = $ unknown phase.

corresponding desorbed H$_2$. The chromatograms obtained (Figure 2a) are similar, with two stages of H$_2$ desorption being observed for both materials (S1 and S3). The onset of decomposition for Na$_2$Mg$_2$FeH$_8$ occurs at ca. 280 °C, with the first maxima being observed at ca. 400 °C, and the second at ca. 430 °C. Decomposition concludes at ca. 475 °C. Conversely, the onset of H$_2$ desorption for Na$_2$Mg$_2$RuH$_8$ occurs at ca. 325 °C, with the first maxima being observed at ca. 421 °C, and the second at ca. 460 °C. H$_2$ is no longer detected after ca. 500 °C. To ascertain the pathway of decomposition, ex situ PXD was conducted on samples heated to selected temperatures in vacuo (Figures 2b and e). Analysis of Na$_2$Mg$_2$FeH$_8$ after heating at 360 °C indicates a miniscule quantity of Na$_2$Mg$_2$FeH$_8$ residues, although the majority has decomposed into NaH, Mg and Fe.
while NaMgH$_3$ is also detected. By 400 °C NaH has decomposed, while only Mg and Fe are observable by PXD. Na is not observed due to the low vapor pressure of Na at elevated temperatures. No further changes to the material are observed at higher temperatures. Therefore the decomposition of Na$_2$Mg$_3$FeH$_8$ is determined to occur according to Eqs. 5-7.

Na$_2$Mg$_3$FeH$_8$ → 2NaMgH$_3$ + Fe + H$_2$ (1.3 wt%)

2NaMgH$_3$ + Fe → 2NaH + 2Mg + 2H$_2$ + Fe (2.5 wt%)

2NaH + 2Mg + Fe → 2Na + 2Mg + Fe + H$_2$ (1.3 wt%)

Na$_2$Mg$_5$RuH$_8$ was first heated to 320 °C, where PXD determined that decomposition has not yet started. By 420 °C full decomposition appears to be complete, with Mg, Ru and Fe being the products. At this temperature, NaH instantly decomposes to Na and evaporates from the sample. As a result, the decomposition of Na$_2$Mg$_5$RuH$_8$ is determined to occur according to Eqs. 8 and 9. Presumably the excess Ru required to form Mg$_2$Ru$_2$ (without leaving excess Mg) comes from the excess Ru that remained in the starting material.

Na$_2$Mg$_5$RuH$_8$ → 2NaH + $\frac{5}{2}$Mg$_2$Ru$_2$ + 3H$_2$ (3.0 wt%)

2NaH + Mg$_2$Ru$_2$ → 2Na + Mg$_3$Ru$_2$ + H$_2$ (1.0 wt%)

PCI analysis of Na$_2$Mg$_5$TH$_8$ ($T$ = Fe, Ru) (Figures 3a and b) enables the intricacies of the decomposition process to be truly understood. The experiments on Na$_2$Mg$_5$FeH$_8$ were conducted at initial pressures of 30 MPa and 400 °C, mimicking conditions used for synthesis. Consequently, it was ascertained that the first thermal reaction according to Eq. 5, occurs at an equilibrium pressure of 15.5 MPa, releasing ca. 0.8 wt% H$_2$ at 400 °C (Figure 4a). PXD analysis of the products recovered at 6 MPa characterised the products to be NaMgH$_3$ and Fe (Figure 3e). $\Delta$H$_\text{des}$ for this process was determined by means of a van’t Hoff plot of H$_2$ desorption equilibrium pressures and the linear fit ($R^2 = 0.975$) to the data to be 93 kJ/mol H$_2$ (Figure 3c), while the corresponding $\Delta S_{\text{des}}$ was calculated as 180 J/mol K H$_2$. However, at lower temperatures this step is kinetically hindered and as a result $\Delta H$ and $\Delta S$ may be obscured. The values reported above are an average of the plateau pressures. The further two equilibrium plateaus below 1 MPa H$_2$ correspond to the decomposition of NaMgH$_3$, exhibiting mass losses of 2.5 and 1.5 wt% for Eqs. 6 and 7, respectively. The overall hydrogen content released was therefore determined to be 4.7 wt% at 400 °C (theoretical maximum of 5.1 wt%). $\Delta$H$_\text{des}$ was calculated to be 87 and 111 kJ/mol H$_2$ for the latter two processes, in accord with the literature values.\textsuperscript{36} The corresponding $\Delta S_{\text{des}}$ also agreed with literature values with 132 and 158 J/mol K for Eq. 6 and 7, respectively. Therefore $\Delta$H$_\text{des}$ for the entire system is surmised to be 378 kJ/mol (94.5 kJ/mol H$_2$). The identity of the species at each decomposition stage was determined by PXD by ending selected PCI experiments at specified pressures. Figure 3e illustrates the final products after the PCI experiments conducted at 360 and 400 °C and also those observed after the first and during the second equilibrium step (Eq. 6). During the second equilibrium step, NaMgH$_3$, Fe and NaH, and Mg are observed, indicating that NaMgH$_3$ is decomposing. After the third equilibrium (final products), Na, Mg and Fe are the main constituents, although residual NaH is also observed. Therefore the decomposition process can be described according to Eqs. 5-7 and Figure 4. The thermal stability of Na$_2$Mg$_5$FeH$_8$ is enhanced compared to that of Mg$_2$RuH$_6$, which exhibits a H$_2$ desorption maxima at ca. 360 °C (Figure 2) with an associated $\Delta$H$_\text{des}$ of 261 kJ/mol.\textsuperscript{29} The additional stability achieved by the incorporation of Na" and H" into the compound, induces a significant increase in desorption temperature maxima to 400°C and a total $\Delta$H$_\text{des}$ of 378 kJ/mol (Figure 4). This value correlates very well with the previous DFT calculations conducted on this compound, which determined $\Delta H$ to be ~328 kJ/mol.\textsuperscript{23} In contrast to Na$_2$Mg$_5$FeH$_8$, Na$_2$Mg$_5$RuH$_8$ is stable above pressures of 0.19 MPa H$_2$ and T >500°C (Figure 3a). PXD analysis of material annealed at 6 MPa H$_2$ and 450 °C (Figure 3f) indicates that the only modification is the disappearance of the unknown phase (observed after initial synthesis (Figure 1)) which is replaced by another unknown phase. This material can be indexed to an orthorhombic unit cell of $a = 14.5331$, $b = 7.9841$ and $c = 6.2429$ and crystallises in a possible space group of Pmmn, although structural identification is inhibited by the low concentration and weak intensity of the Bragg peaks. As was observed from the GC results (Figure 1), decomposition is also noted to follow a two-step decomposition route by PCI. At 500 °C, the first plateau is observed at an equilibrium pressure of 0.19 MPa, while the second occurs at ca. 0.07 MPa. Each step was determined to have an associated mass loss of ca. 1.9 wt%, with a total of 3.8 wt% H$_2$ being desorbed out of a maximum theoretical capacity of 4.0 wt%. This process was also carried out at 475 and 450 °C. This allowed for $\Delta$H$_\text{des}$ and $\Delta S$ to be determined to be 131 kJ/mol H$_2$ and 176 $\Delta S$ (J/mol H$_2$K), respectively for step 1 ($R^2 = 0.984$) and $\Delta$H$_\text{des} = 119$ kJ/mol H$_2$ and $\Delta S = 151$ $\Delta S$ (J/mol H$_2$K) for step 2 ($R^2 = 0.999$) (Figure 3d). Therefore $\Delta$H$_\text{des}$ for the entire system is surmised to be 500 kJ/mol (125 kJ/mol H$_2$). PXD of the products at each stage allows a greater insight into those determined by ex situ heating in vacuo. After the first plateau, a substantial level of Mg$_2$RuH$_4$ is identifiable in the powder,
along with Ru, NaOH and a small quantity of MgRu2. The highly oxidisable Na (residual after evaporation) is the source of NaOH (occurring during PXD analysis), while the thermally unstable Mg3RuH8 is the source of MgRu2. An unknown phase is also observed at this temperature and pressure, which due to the low intensity of the Bragg peaks associated with this material, indexing and as such, structural refinement was not possible. After the second plateau, the remaining powder consists of Mg3Ru2 and Ru. Presumably the excess Ru required to form Mg3Ru2 (without leaving excess Mg) comes from the excess Ru that remains in the starting material (Figure 1). Therefore the decomposition process can be described according to Eqs. 10 and 11 and Fig. 4.

\[
\begin{align*}
Na_2Mg_2RuH_8 & \rightarrow 2Na + Mg_3RuH_4 + 2H_2 \quad (2.0 \text{ wt.} \% H_2) \quad (10) \\
Mg_3RuH_4 & + 2Na \rightarrow Mg_3Ru_2 + 2Na + 2H_2 \quad (2.0 \text{ wt.} \% H_2) \quad (11)
\end{align*}
\]

The decomposition pathway of these materials differ significantly in that NaMgH3 is the intermediate for Na2Mg2RuH8, while Na2MgRuH4 disassembles via Mg3RuH4 (Figure 4). The optimised syntheses of Na2Mg2RuH8 have been studied by PCI measurements. The total enthalpy of desorption for Na2Mg2RuH8 is 94.5 kJ/mol H2 and 125 kJ/mol H2 for Na2Mg2RuH8.

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