Metal ammine complexes for hydrogen storage

Claus Hviid Christensen,[a] Rasmus Zink Sørensen,[b] Tue Johannessen,[c] Ulrich J. Quaade,[b] Karoliina Honkala,[b] Tobias D. Elmøe,[c] Rikke Køhler[a] and Jens K. Nørskov*[b]

The hopes of using hydrogen as an energy carrier are severely dampened by the fact that there is still no safe, high-density method available for storing hydrogen. We investigate the possibility of using metal ammine complexes as a solid form of hydrogen storage. Using $Mg(NH_3)_6Cl_2$ as the example, we show that it can store 9.1% hydrogen by weight in the form of ammonia. The storage is completely reversible, and by combining it with an ammonia decomposition catalyst, hydrogen can be delivered at temperatures below 620 K.

Storing hydrogen in a safe, high-density, condensed phase is a notoriously difficult problem.[1] Storage in the form of metal hydrides has been studied for decades,[2] and most recently attention has been focused on the so-called complex hydrides based on alanates[3] or borates.[4] Several of the hydrides have promising properties, but most of them also suffer from problems relating to the density of hydrogen being too low, the kinetics of hydrogen release being too slow, or the regeneration of the hydride being too difficult.[5] Another possibility that has also attracted considerable attention lately is storage by physisorption on high surface area solids.[6] Here again, more work is needed to establish whether or not this is a feasible method.[5]

In the present paper we explore a new way of storing hydrogen in the form of metal ammine complexes. They decompose thermally by evolving ammonia at a temperature which can be varied by changing the composition of the complex. By combining such complexes with an ammonia decomposition catalyst one obtains a very versatile hydrogen source. We consider $Mg(NH_3)_6Cl_2$ (Fig. 1) in some detail, and show that the kinetics of ammonia adsorption and desorption are reversible and fast, and that the complex is easy to handle.

Metal ammine complexes of the form $M(NH_3)_nX_m$, where M is a metal cation like Mg, Ca, Cr, Ni, and Zn, and X is an anion like Cl or SO_4, have been know for more than a century.[8] For the divalent metal ions, ammine complexes are generally formed easily by leading ammonia over the anhydrous MX_m salt. The heat of formation depends on M and X and can be varied between 40 and 80 kJ mol^{-1} NH_3.[9]

$Mg(NH_3)_6Cl_2$ was prepared by leading 1 bar of ammonia (Hede Nielsen, >99.9%) over anhydrous $MgCl_2$ (Merck, >98%) at 300 K.

The purity and phase composition was verified by X-ray powder diffraction.[10] The saturated salt can be compacted into, e.g., a pellet to obtain a high volumetric density. The saturated salt was then put in a small cell, where the rate of ammonia desorption from the sample could be measured quantitatively. This was done by absorbing the ammonia immediately at the outlet of the cell in a miniaturized scrubber using a small flow of distilled water. The ammonia content was then determined using an on-line conductivity cell. Fig. 2 shows a thermal desorption spectrum of $Mg(NH_3)_6Cl_2$. Decomposition of the complex starts around 350 K

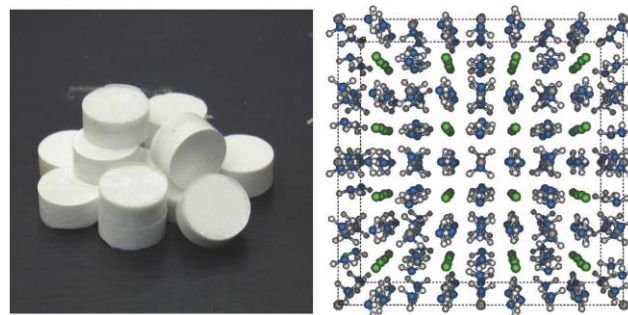Fig. 1 Pellets of $Mg(NH_3)_6Cl_2$ (left). The skeleton density is 1.25 g cm^{-3} and the pellets have a density within 5% of this. It crystallizes in a cubic unit cell with a lattice constant of 10.19 Å.[7] The atomic structure of the crystalline complex is shown to the right, as it comes out of an energy minimization using density functional theory calculations. Mg^{2+} is shown grey, Cl^- is green, nitrogen blue, and hydrogen is white.
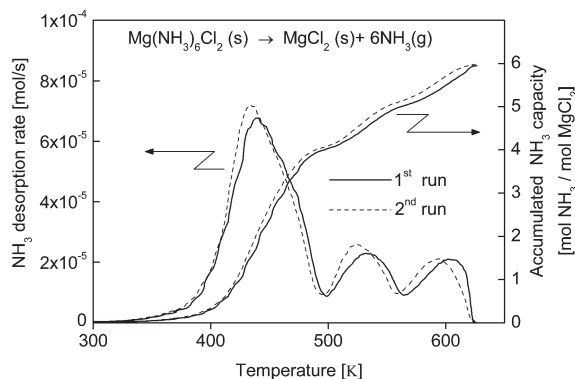

Fig. 2 Thermal decomposition spectra for $Mg(NH_3)_6Cl_2$ recorded by ramping the temperature at 10 K min^{-1} against a pressure of ca. 0.1 bar. Both the desorption rate and the integrated amount of ammonia is shown. After all ammonia was desorbed, the complex was again saturated with ammonia and a second desorption spectrum was recorded to show the reversibility of the process.

[a]Center for Sustainable and Green Chemistry, NanoDTU, Department of Chemistry, Technical University of Denmark, Building 206, DK-2800 Lyngby, Denmark
[b]Center for Atomic-scale Materials Physics, NanoDTU, Department of Physics, Technical University of Denmark, Building 307, DK-2800 Lyngby, Denmark. E-mail: norskov@fysik.dtu.dk
[c]NanoDTU, Department of Chemical Engineering, Technical University of Denmark, Building 229, DK-2800 Lyngby, Denmark

and at 500 K, 2/3 of the ammonia has been released. The remaining 1/3 is released below 620 K.

After desorption, the MgCl$_2$ was again saturated with ammonia and the desorption experiment was repeated. It can be seen in Fig. 2 that the second desorption trace is essentially the same as in the first desorption experiment, indicating that the absorption–desorption process is reversible. This is confirmed by X-ray diffraction patterns obtained after one and two cycles.[10] We have done the same loading and decomposition experiments at the kg scale to show that there are no system size effects.

It is a fairly simple matter to convert the ammonia desorbed from the solid storage medium into H$_2$ and N$_2$ by leading the ammonia over an ammonia decomposition catalyst.[11–13] A number of catalysts can be used, and the kinetics are well understood.[14] Present catalysts can be operated down to around 600 K. The ammonia decomposition catalyst can be integrated into the metal ammine container since the desorption temperature is below or at the catalyst operating temperature. This gives a compact system for hydrogen delivery. A schematic illustration of the process of making and decomposing Mg(NH$_3$)$_6$Cl$_2$ to produce hydrogen is shown in Fig. 3.

Compared to metal hydrides,[16] the metal ammine system is characterized by more facile absorption and desorption kinetics. There are three possible reasons for this. One is that, while H$_2$ needs to dissociate before absorbing to form the hydride, NH$_3$ absorbs molecularly. Instead, the hydrogen dissociation or recombination takes place at an ammonia synthesis or decomposition catalyst. This is a process, which is extremely well optimized—in fact the synthesis of ammonia from natural gas costs essentially the same energy as the synthesis of hydrogen.[17,18]

The other reason is that the concentration of ammonia in the complex can vary quasi-continuously. This is evident in the thermal decomposition spectra in Fig. 2. The first four ammonia
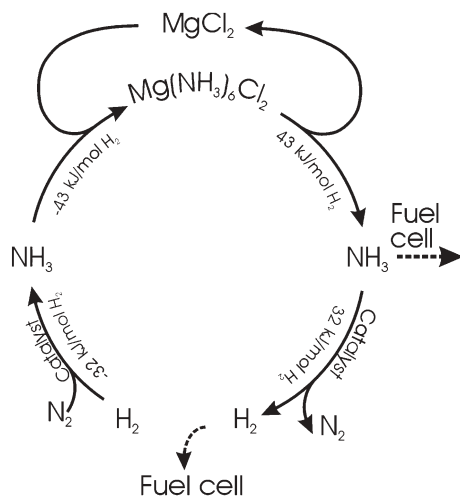

Fig. 3 Schematic illustration of the process whereby hydrogen can be transformed into ammonia, which is stored as Mg(NH$_3$)$_6$Cl$_2$. The Mg(NH$_3$)$_6$Cl$_2$ can be transported safely and when needed ammonia is released and decomposed into molecular hydrogen and nitrogen. The standard enthalpies of formation and decomposition are indicated.[9,15] If all the enthalpy needed for decomposition (43 + 32 = 75 kJ mol^{-1} H$_2$) has to be taken from the H$_2$ produced, about 30% of the heating value of the H$_2$ (242 kJ mol^{-1} H$_2$[15]) is lost.

molecules desorb at the same temperature and the last two at only slightly higher temperatures. We have also checked this using density functional theory calculations. The calculations were carried out using a plane wave pseudopotential approach employing the RPBE generalized gradient approximation to describe exchange and correlation effects.[19] The experimentally determined crystal structure[7] was used as a starting point, and all the atomic positions were fully relaxed to obtain the minimum energy structure, see Fig. 1. We find that both the vacancy formation energy and the activation energy for vacancy diffusion in Mg(NH$_3$)$_x$Cl$_2$ is of the order 50 kJ mol^{-1} NH$_3$ meaning that it is simple to transport ammonia molecules through the lattice through formation and hopping of ammonia vacancies.

Finally, we have found that Mg(NH$_3$)$_6$Cl$_2$ develops its own pore system during decomposition. After all the ammonia has been released, a pellet like the ones shown in Fig. 1 retains its form, but becomes very porous. BET measurements of the specific surface area after decomposition gives 32 m^2 g^{-1}, showing that there is a well developed nanopore system formed during decomposition. The average size of the MgCl$_2$ nanoparticles is *ca.* 80 nm. This also makes it easy to reabsorb ammonia. After reabsorption the Mg(NH$_3$)$_6$Cl$_2$ can again be compacted.

The Mg(NH$_3$)$_6$Cl$_2$ complex shows a high hydrogen content, see Table 1. It is important to note that these are measured values, on large samples, and the loading of the complex is reversible. The only drawback is that metal ammine complexes deliver hydrogen in the form of ammonia. This can be used directly as fuel for a solid oxide fuel cell without further reaction.[20] In connection with alkaline[21] or low temperature (PEM) fuel cells, the ammonia must be decomposed. For the PEM cell the trace amounts of ammonia left in the gas after decomposition must also be removed.[22] This can be done easily by leading the gas over a small amount of unsaturated MgCl$_2$. At 80 °C where PEM fuel cells are typically operated, the equilibrium ammonia pressure over MgCl$_2$ is 1.5 × 10^{-6} bar[9] corresponding to an ammonia content of 1.5 ppm at 1 bar pressure.

Using metal ammine complexes for hydrogen storage involves ammonia as an intermediate energy carrier.[11,23] In principle, pure ammonia could be used as a storage medium—it can be condensed to a liquid by 8 bar at room temperature, and today ammonia is transported as such in large quantities as a fertilizer. Ammonia is, however, a strong irritant and excessive emissions to the environment must be avoided.[24] This puts strong demands on the storage container. Mg(NH$_3$)$_6$Cl$_2$ has the property that, while it has the same volume density as liquid ammonia, it is considerably more stable—the equilibrium ammonia pressure at room temperature is only 2 × 10^{-3} bar.[9] It is therefore considerably simpler to design a safe container for the metal ammine complex, and even if it is outside a container it is simple to handle at room

Table 1 Measured hydrogen storage capacity in terms of the gravimetric and volumetric hydrogen density and the energy density in the Mg(NH$_3$)$_6$Cl$_2$ complex. For comparison we also give the corresponding values calculated for Ca(NH$_3$)$_8$Cl$_2$

	Gravimetric H$_2$ density (% H$_2$)	Volumetric H$_2$ density/ kg H$_2$ l^{-1}	Energy density MJ l^{-1}
Mg(NH$_3$)$_6$Cl$_2$	9.1	0.11	13.0
Ca(NH$_3$)$_8$Cl$_2$	9.7	0.12	14.4

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temperature due to the slow kinetics, see Fig. 2. The pellets in Fig. 1a have a desorption rate so low that one cannot smell ammonia at room temperature even if one holds a pellet right under the nose, indicating that the concentration is less that 50 ppm.[25]

Ammonia is a chemical storage medium for hydrogen just like hydrocarbons (gasoline or diesel) or alcohols (*e.g.*, methanol). The main advantage of ammonia in this connection is that it is considerably easier to decompose than hydrocarbons and alcohols. Ammonia has the additional advantage that the only by-product is N_2. There is no CO_2 emission during operation. If the ammonia is synthesized on the basis of hydrocarbons, there is of course CO_2 produced, but since this is done in large plants, often in connection with natural gas fields, centralized sequestration of the CO_2 is considerably simpler than in, *e.g.*, individual automotive units or portable devices.

In summary, we have shown that metal ammine complexes, in combination with an ammonia decomposition catalyst, provide a new solid hydrogen storage medium, working below 620 K. The system has a considerably higher measured reversible hydrogen content than any system considered until now.[1,5]

Acknowledgements

Notes and references

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