

Miniaturized Hydrogen Production by Decomposition of Ammonia Stored in Metal Ammines

Claus H. Christensen^{1*}, Rasmus Z. Sørensen¹, Asbjørn Klerke¹,
Ulrich Quaade² and Jens K. Nørskov³

¹Center for Sustainable and Green Chemistry, Department of Chemistry, Building 206, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark ²Center for Individual Nanoparticle Functionality, Department of Physics, Building 307, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

³Center for Atomic-Scale Materials Physics, Department of Physics, Building 307, Technical University of Denmark, DK-2800 Kgs. Lyngby, Denmark

*chc@kemi.dtu.dk

Efficient and safe storage of hydrogen for energy conversion has received significant attention over the last decades. However, it still remains a substantial challenge for the prospects of a hydrogen economy to provide a safe, reversible and dense storage method for hydrogen. Most research is currently focused on the so-called complex hydrides based on aluminates or borates. Some hydrides have promising properties, but most still suffer from a too low hydrogen density, too slow kinetics or lack of reversibility. In addition, hydride materials are very reactive towards oxygen and water, which causes the handling to be very challenging. Ammonia is an efficient hydrogen carrier [1]. The “reforming” of ammonia into hydrogen and nitrogen, the reverse ammonia synthesis, is well-understood and can be performed at temperatures close to 600K. However - in terms of safety - it might not be desirable to drive directly with liquid ammonia fuel in a pressurized container. However, a hydrogen economy based on ammonia appears promising, if it was combined with a safe, high density storage method.

We have demonstrated the use of solid metal ammine complexes as such an indirect hydrogen storage material [2]. Ammonia can be chemically coordinated to a metal salt, and we have shown a number of salts to be viable indirect hydrogen storage materials. With focus on $MgCl_2$ as one of the most promising materials; we will outline the potential of such a storage

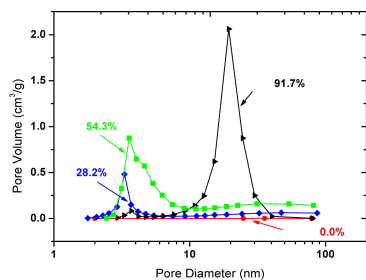


Figure 1: Development of nano-porous structure during desorption of NH_3 from $Mg(NH_3)_6Cl_2$.

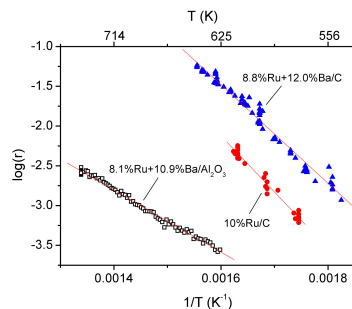


Figure 2: Activities of Ru based catalysts for decomposition of ammonia.

Table 1: Gravimetric and volumetric hydrogen storage capacities of two ammine complexes compared to the goals for hydrogen storage for fuel cell vehicles set by US Department of Energy.

	Gravimetric H ₂ density (wt % H ₂)	Volumetric H ₂ density (kg H ₂ /l)	Energy density (MJ/l)
$Mg(NH_3)_6Cl_2$	9.1	0.11	13.0
$Ca(NH_3)_8Cl_2$	9.7	0.12	14.4
DOE 2015	9.0	0.081	9.72

approach. $Mg(NH_3)_6Cl_2$ contains 9.1 % hydrogen by weight in the form of ammonia. Table 1 gives hydrogen densities of other possible salts. Furthermore the ammine complexes can be compacted to above 90% of their crystal density without compromising their ability to release ammonia. Ammonia is released from the salts upon heating, and the kinetics of this release is only limited by heat transfer to the salt. When ammonia is desorbed from compact bodies of ammine complexes, the crystals shrink and give rise to development of a nano-porous structure through which ammonia from the center of the compact body can desorb. No change in size of the compact body is observed. The change in pore diameter and volume during desorption is shown in fig. 1.

Ammonia stored in this way is a dense indirect hydrogen storage material, but for use in low temperature fuel cells, the ammonia must be catalytically decomposed to the elements before it can be utilized as a fuel.

One perceived area where fuel cells show importance is for miniaturized systems known as “lab on a chip”. Often, power supplies or batteries for such systems are very bulky compared to the system it supports. Thin fuel cells would be optimal for solving this problem, if the fuel could be delivered from an equally compact system.

Promoted Ru catalysts on porous graphitized carbon is generally recognized as the most active for decomposition of ammonia [3, 4]. So far, it has not been possible to integrate significant amounts of porous graphitized carbon support in micro-fabricated reactors, and the best miniaturized systems have thus used less optimal supports [5, 6]. As seen in Fig. 2, the use of graphite support makes the catalyst far more active for the decomposition of ammonia.

Here, a method for such incorporation is presented, and the very high activities for ammonia decomposition are demonstrated. Furthermore, micro-fabricated reactors are well suited for catalyst studies, as the reactors can be kept absolutely isothermal under reaction conditions and the gas flow stays laminar over a large range of space velocities. This has been used to investigate promotion of the Ru/C system with Cs and Ba.

References

1. Metkemeijer, R., and Achard. P. *Int. J. Hydrogen Energy*, 19, 535 (1994)
2. Christensen, C. H., Sørensen, R. Z., Johannessen, T., Quaade, U., Honkala, K., Elmøe, T. D., Kjøhler, R., and Nørskov, J. K. *J. Mater. Chem.* 15, 4106 (2005)
3. Rarog-Pilecka, W., Szmigiel, D., Komornicki, A., Zielinski, J., Kowalczyk, Z., *Carbon* 41, 579 (2003)
4. Yin, S.F., Xu, B.Q., Zhou, X.P., Au, C.T. *Applied Catalysis A: General* 277, 1 (2004)
5. Ganley, J.C., Seebauer, E.G., Masel, R.I. *J. Power Sources* 137, 53 (2004)
6. Sørensen, R. Z., Nielsen, L. J. E., Jensen, S., Hansen, O., Johannessen, T., Quaade, U., Christensen, C. H. *Catal. Commun.* 6, 229 (2005)