Complex hydrides: from salts, via coordination chemistry to hybrid materials

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Light-weight hydrides, such as borohydrides, are considered as promising materials for hydrogen storage. Their stability is determined by electron transfer from metal atoms to the BH_4 anion: the lower the electropositivity of the metal atom the lower the decomposition temperature. Consequently, alkali metal borohydrides are mere ionic salts, too stable for practical applications.

Combination of two metals in "bimetallic borohydrides" allowed to extend the series to many more elements. Structural chemistry of bimetallic borohydrides is much more versatile – the less electropositive metal forms a complex anion with BH_4 groups, while the more electropositive metal is donating electrons to the complex anion. The decomposition temperatures are mostly determined by the electropositivity of the complex-forming metal [1]. Remarkably, the structural chemistry of this wide group of compounds can be rationalized using concepts of coordination chemistry, where the borohydride group acts as a ligand.

Recently the first porous hydride, γ-$Mg(BH_4)_2$, featuring so-called "borohydride framework" capable to store reversibly guest species was discovered [2]. This example clearly shows that the covalently bound hydride moieties, such as borohydride, amide, ammonia borane, amidoborane etc can act as directional ligands, capable to form molecular and polynuclear complexes, as well as framework structures typically occurring in classical coordination chemistry. We suggest that the auxiliary building blocks, such as azolates can drastically expand the chemistry of hydrides, creating the means to change their stability, reactivity and possibly to tune hydrogen storage properties.

The other aspect of our work is understanding the nature of guest-host interactions in the hydride porous frameworks. The unique character of the hydride anions exposed into the pores should lead to materials with new gas sorption properties, such as adsorption enthalpy, capacity, selectivity or even enable some reactions inside the pores. By the synergy of techniques used by hydrogen storage community and by coordination chemists, we are trying to explore the fundamental potential of designing new solids for hydrogen storage, gas adsorption and back-conversion of CO_2 into fuel.

[1] Rude L.H., Nielsen T.K., Ravnsbæk D.B., Bösenberg U., Ley M.B., Richter B., Arnbjerg L.M., Dornheim M., Filinchuk Y., Besenbacher F., Jensen T.R. *Phys. Stat. Sol. A.* 208 (2011). 1754-1773.

[2] Y. Filinchuk, B. Richter, T.R., Jensen V. Dmitriev, D. Chernyshov, H. Hagemann, *Angew. Chem. Int. Ed.* 50 (2011) 11162-11166.