Application 2050

Synthesis and characterisation of novel metal amidoboranes

Nikola Biliskov

Rudjer Boskovic Institute, Division of Materials Chemistry, Zagreb

The aim of the proposed project is to contribute the development of a highly efficient chemical system for solid-state hydrogen storage, with a high potential to be transferred to a technology applicable for mobile on-board use.

Among the materials under consideration as systems for hydrogen storage, metal amidoboranes (hereafter denoted as MAB) are charaterised by extremely high both gravimmetric and volumetric hydrogen capacity and faster kinetics as compared to ammonia borane. Thus, nowadays they attract a considerable research attention with respect of improvement of thermodynamics and prevention of emission of unwanted gaseous byproducts, such as ammonia and diborane. Recent experimental and computational studies show a strong correlation of dehydrogenytion rate on the ionicity as well as size of metal species in MABs. On the other hand, one of the main characteristcs of these systems is the fact that not only their solid-state structure, but also dehydrogenation properties, are largely determined by dihydrogen bonding of the NH---HB type. Perturbation of this dihydrogen bonding network, for example by introduction of aducts can lead to improvement of dehydrogenation performance of given materials. Along with numerous published examples of MAB ammoniates, Wu et al. prepared LiAB.AB adduct [Wu et al. Chem. Mater. 22 (2010) 3], which shows a considerably adventageous behaviour. Among all experimental techniques vibrational spectroscopies are the most sensitive to hydrogen bonding. Thus, they can be utilized to obtain a thorough insight into the mechanistic details of dehydrogenation process.

Endothermic dehydrogenation process is a prerequisite for achieving an energetically efficient hydrogenation (regeneration) of the spent material. In this respect bimetallic amidoboranes of the general composition M_2MgAB_4 are of considerable interest. Namely, in the hydrogen release from MABs, metal M mediates hydride transfer from boron to amino-proton by formation of MH. However, production of H_2 molecules can follow two different mechanistic pathways, which competes to each other and are dependent on the properties of M. Furthermore, this competition also plays a key role in determining intermediates and products [Kim et al. PCCP 12 (2010) 5446]. Dehydrogenation properties of MABs are related to changes in the bonding nature of AB^- when it interacts with metal cations. Therefore, introduction of multiple metals with various sizes, charges, electronegativities and coordination preferences could increase the number of possible bonding interactions of M with AB^-, ultimately allowing tailoring the more favourable materials as compared to single-metalic MABs. Since the first representative of this family, Na_2MgAB_4 [Wu et al. ChemComm 47 (2011) 4102, Chua et al. Chem. Mater. 24 (2012) 3574] is found to dehydrogenate endothermically, which is a strong incentive to prepare related systems.

Thus, the objectives of this project are as follows:

1. synthesis of MAB adducts with ammonia borane of general composition MABn.mAB (where n is determined by charge of M);
2. synthesis of bi- and trimetallic amidoboranes of the generaL composition M'M''M'''AB4 (where M' and M'' are alkaline, while M''' is an alkaline earth metal, preferably Mg);
3. characterisation of prepared compounds by means of XRD and vibrational spectroscopy;
4. characterisation of their dehydrogenation by means of variable-temperature vibrational spectroscopy.

For synthesis, high-energy ball milling will be used. A typical synthesis include ball milling of stoichiometric mixtures of metal hydrides, such as NaH, LiH, MgH_2 and CaH_2 with AB for 1 hour in 1 bar argon atmosphere. All sample preparations and measurements will be done in a glove box filled with argon. The instrument usage time cannot be precisely estimated, because it depends on both predictable and unpredictable experimental parameters. Thus, here I give just a rough estimation:

1. Ball milling - 1.5 h per sample (altogether around 30 h);
2. Use of glove box - 70 h
3. IR spectroscopy - 30 h
4. XRD - 1.5 h per sample (altogether around 30 h)
5. Raman spectroscopy - 15 days

Laboratory for Solid Hydrogen Storage Materials is well equipped with all instrumentation needed for successful realisation of this project. Concretely, their instrumentation include MBraun glove box for sample handling in inert atmosphere, Spex 8000 mixer/mill, Bruker Alpha IR spectrometer equipped with accessories for DRIFT, ATR and gas-phase measurements, Bruker Senterra Raman spectrometer and Bruker D8 Advance X-ray diffractometer. Also, they have long-term experience in the field of solid-state hydrogen storage materials, especially complex hydrides.

The proposer has an extensive experience in hydrogen bonding investigations in liquid and solid state by means of vibrational spectroscopies, especially IR spectroscopy. His recent work is focused to utilisation of variable-temperature IR spectroscopy, together with TG/DTA and XRD for investigation of complex solid systems and ordered liquids. Nowadays, his research includes investigation of hydrogen sorption properties of $LaNi_5$ type intermetallic compounds. Now he is entering the field of complex hydrides as potential solid-state materials for hydrogen storage. For successfull investigation of these systems his expertise in vibrational spectroscopy is crucial, but it purports also introduction of new techniques in which he does not have any experience. Thus, the visit to Laboratory for Solid Hydrogen Storage Materials at EMPA will considerably advance his research experience, for sure to the satisfaction of both sides. It is expected that this visit will result in several publications in high impact factors journals, but also in further collaboration of the two groups through mutual projects.