(Bi)Metallic amidoboranes – synthesis, characterisation and perspective for hydrogen storage

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Metallic and bimetallic amidoboranes can be easily synthesized by liquidless mechanochemical technique. By using the mechanical ball milling technique, solventless solid state reaction between ammonia borane (NH_3BH_3, AB), alkali metal hydrides (NaH, LiH) and alkaline earth metal hydrides (CaH_2 and MgH_2) is absolutely possible [1-3].

Using the Raman spectroscopy for solid state operando monitoring of reaction between ammonia borane and hydrides we sucessfully synthesized two monometallic ($NaNH_2BH_3$, $LiNH_2BH_3$) and four bimetallic amidoboranes ($Na_2Mg(NH_2BH_3)_4$, $Li_2Mg(NH_2BH_3)_4$, $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$. As a milling equipment we used PMMA (plexiglass) jars and stainless steel balls. Mentioned approach allowed real time observation of key intermediate phases and a straightforward follow-up of the reaction course. Detailed analysis of time-dependent spectra revealed a two-step mechanism through formation of $MNH_2BH_3{\cdot}NH_3BH_3$ adducts as key intermediate phases which further reacted with MgH_2, giving $M_2Mg(NH_2BH_3)_4$ as final products (M are Li or Na) [1]. We have also developed a new green and rapid mechanochemical procedure for the synthesis of Ca-containing alkaline metal amidoboranes [2], $Na_2Ca(NH_2BH_3)_4$ and $Li_2Ca(NH_2BH_3)_4$, using a similar approach. Also, the tandem technique - operando X-Ray diffraction with temperature profile measurement was used for monitoring of mechanochemical syntheses. On such a way we revealed how the course of the reactions and their thermal profiles strongly depend on the starting alkali metal hydride. For instance, NaH induced a sudden and dramatic increase in temperature of the reaction mixture (sometimes followed by explosion), which induced a partial or total decomposition of thermally labile AB+NaH system and influenced the yield and composition of reaction products. The changing of milling reactor material from insulating plastics (PMMA) to thermally conductive stainless steel readily amended this issue (through more effective heat dissipation). In summary, solid state stainless steel equipment for bimetallic amidoborane synthesis is shown in Figure 1.

In all cases, as a products, only mixed metal amidoborane and hydrogen gas are obtained, without usage of any solvent, fulfilling all aspects of green chemistry.

Having in mind all the problems with rehydrogenation and practical irreversibility of metallic amidoboranes (only indirect rehydrogenation is possible by using the hydrazine [4]), there is only one question - are these compounds very prominent materials for solid state hydrogen storage?

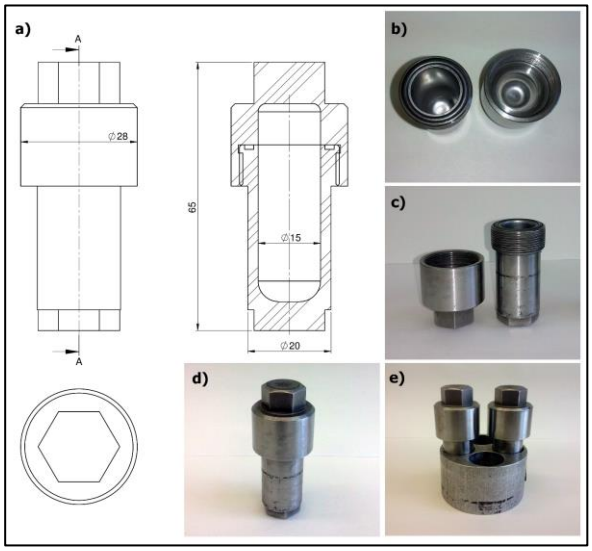

Figure 1. Stainless steel synthesis equipment: a) technical drawing; b) interior of the jar; c) opened jar prepared for sample loading; d) closed jar; e) two jars in sample holder prepared for mounting on the mill.

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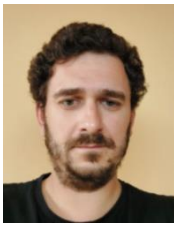

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