Technology Offer

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EMPA
Materials Science & Technology

Solvent free synthesis of borohydrides

Invention

The invention presents a new method for solvent-free synthesis of borohydrides at room temperature. Borohydrides are widely applied reagents for organic and inorganic synthesis. Due to their high gravimetric hydrogen density, they are very promising compounds for hydrogen storage in mobile applications. The synthesis is performed by milling of the corresponding metal hydrides in borane/hydrogen atmosphere.

Background

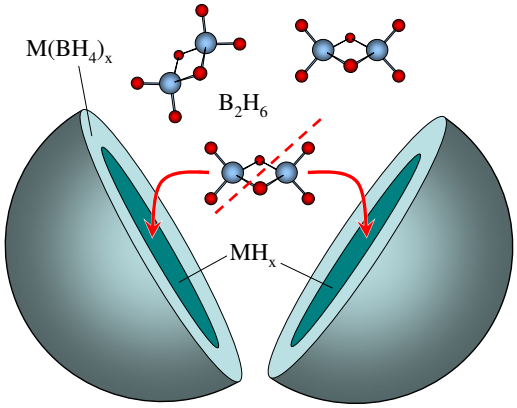
The synthesis of borohydrides is usually performed in wet chemical reactions with solvents such as ether or isopropyl amine making use of metathesis reactions with different halides or chlorides. In order to obtain a pure product the solvents and the salts forming as by-products have to be separated from the final product. This makes the synthesis process complex, time consuming and costly. Therefore, it is difficult to obtain pure borohydrides as end products. As a consequence many borohydrides are not yet commercially available or are very expensive.

Advantages

The new synthesis method presents a general way to prepare pure borohydrides solvent-free at room temperature. The aftertreatment of the final product becomes obsolete, which makes this process more effective and economic than other preparation methods. Additionally, the new synthesis method allows combining different metals for the borohydride formation. This might enable the synthesis of new, mixed borohydride systems with tunable sorption properties.

Applications

Borohydrides are applied in a wide range of different fields. In organic and inorganic chemistry they are used as reducing agents, starting compounds for the synthesis of organometallic derivatives, precursors for the production of borides and hydrides, as well as other inorganic materials and catalysts for hydrogenation, isomerisation, oligomerisation, and polymerization. Furthermore, borohydrides have high potential as future energy carrier due to their high volumetric and gravimetric hydrogen density.
The gravimetric energy density of $LiBH_4$ for example, exceeds the one of gasoline by a factor of three.



Schematic presentation of the solvent-free preparation route for borohydrides: B_2H_6 reacts with the metal hydride to the final borohydride, while the passivation layer forming on the surface is continuously broken by high energy milling. The reaction proceeds according to following equation:

$$MH_x + x/2\ B_2H_6 \rightarrow M(BH_4)_x$$

Ownership

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References

1. **Method to prepare metalborohydrides,** Friedrichs O., Borgschulte A., Remhof A., Züttel A., Patent Application CH01017/09.
2. **Hydrogen-storage materials for mobile applications,** Schlapbach, L. & Züttel, A.. Nature 414 (2001) 353-358.
3. **Convenient procedure for the conversion of sodium-borohydride into lithium-borohydride in simple ether solvents,** Brown HC, Choi YM, Narasimhan S. Inorg Chem 20 (1981)4454-4456.
4. **New developments in the chemistry of diborane and the borohydrides.**1. General summary, Schlesinger HI, Brown HC, Abraham B, Bond AC, Davidson N, Finholt AE, et al. J Am Chem Soc 1953;75(1):186.
5. **Titanium, zirconium, and hafnium tetrahydroborates as tailored CVD precursors for metal diboride thin-films,** J.A. Jensen, J.E. Gozum, D.M. Pollina, G.S. Girolami, J. Am. Chem. Soc. 110 (1988) 1643-1644.
6. **Transition-metal tetrahydroborate complexes as catalysts: 1. Non-empirical determination of static, dynamic, and chimical properties of the model compounds $NaBH_4$ and AlH_2BH_4,** V. Barone, G. Dolcetti, F. Lelj, N. Russo, Inorg. Chem. 20 (1981) 16871691.
7. **Book Review: Reductions by the Alumino- and Borohydrides in Organic Synthesis,** J. Seyden-Penne, Angew. Chem. Int. Edit. 31 (1992) 1534-1535.
8. **Structural and dynamic properties of tetrahydroborate complexes,** V.D. Makheav, Russ. Chem. Rev. 69 (2000) 727-746.
9. **Tetrahydroborates as new hydrogen storage materials,** A. Züttel, A. Borgschulte, S. Orimo, Scripta Mater. 56 (2007) 823-828.

Keywords

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