

4. Boron-based materials for hydrogen storage (reversible by sorption, and chemical for production on-demand with a focus on scaling up)

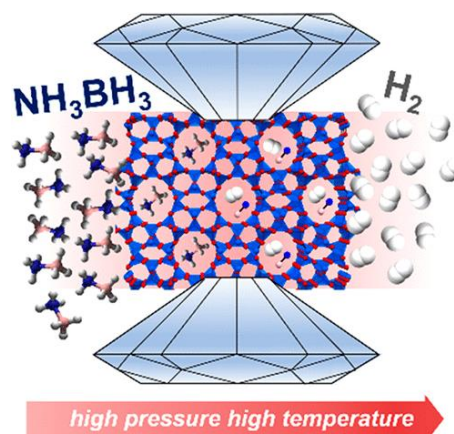
Anomalous Volume Changes in the Siliceous Zeolite Theta-1 TON due to Hydrogen Insertion under High-Pressure, High-Temperature Conditions

Journal of Physical Chemistry Letters 12 (2021) 5059-563

Collaboration: ICGM, Univ. Montpellier, CNRS, ENSCM, Montpellier-France ; ESRF, 38043 Grenoble-France ; Elettra Sincrotrone Trieste- Italy ; L2C, Univ. Montpellier, CNRS, Montpellier, France ; CNRS, IRCER, Univ. Limoges- France

Involved MCP researchers: Umit B. Demirci

High-pressure X-ray diffraction and Raman spectroscopy in a diamond anvil cell were used to study the insertion of the chemical hydrogen storage material, ammonia borane, in the one-dimensional pores of the zeolite theta-1 TON. Heating of this material up to 300 °C under pressures up to 5 GPa resulted in the release of a significant amount of hydrogen due to the conversion of ammonia borane confined in the channels of TON and outside the zeolite to polyaminoborane and then polyiminoborane chains. The filling of TON with hydrogen resulted in a much greater increase in unit cell volume than that corresponding to thermal expansion of normal compact inorganic solids. This process at high temperature is accompanied by a phase transition from the collapsed high-pressure Pbn21 form to the more symmetric Cmc21 phase with expanded pores. This material has a high capacity for hydrogen adsorption under high-temperature, high-pressure conditions.



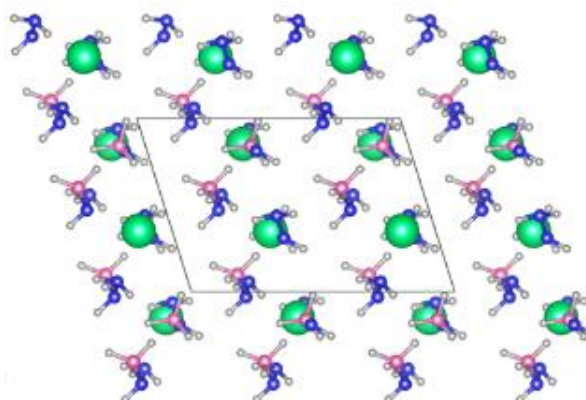
Calcium hydrazinidoborane: Synthesis, characterization, and promises for hydrogen storage

International Journal of Hydrogen Energy 45 (2020) 2022-2033

Collaboration: Institut Charles Gerhardt Montpellier, ICGM, Univ Montpellier, CNRS, ENSCM, Montpellier, France

Involved MCP researchers: Umit B. Demirci

Viewing calcium hydrazinidoborane $\text{Ca}(\text{N}_2\text{H}_3\text{BH}_3)_2$ (9.3 wt% H) as a potential hydrogen storage material, we long sought to synthesize it by solid-solid reaction of calcium hydride CaH_2 and hydrazine borane $\text{N}_2\text{H}_4\text{BH}_3$. However, it was elusive because of unsuitable experimental conditions. In situ synchrotron thermodiffraction helped us to identify the key role played by the temperature in the formation of the new phase. From 45°C, new diffraction peaks appear, and the DSC analysis shows an exothermic signal. Thermal activation is thus required to make solid-state



CaH_2 react with melted (liquid-state) $\text{N}_2\text{H}_4\text{BH}_3$. The XRD pattern can be indexed using a mixture of two phases: (i) unreacted CaH_2 as a minor phase (29 wt%) and (ii) the hitherto elusive $\text{Ca}(\text{N}_2\text{H}_3\text{BH}_3)_2$ (71 wt%). The as-formed $\text{Ca}(\text{N}_2\text{H}_3\text{BH}_3)_2$ crystallizes in a monoclinic 1c (No. 9) unit cell where the intermolecular interactions form chains (layers) along the a axis, resulting in intra-chain and inter-

chain Ca...Ca distances as short as 4.39 and 7.04 Å respectively. Beyond 90°C, $\text{Ca}(\text{N}_2\text{H}_3\text{BH}_3)_2$ decomposes, as evidenced by the diffraction peaks fading, an exothermic signal revealed by DSC, a weight loss (5.3 wt% at 200°C) observed by TGA, and a gas release (H_2 , and some N_2 , NH_3 , N_2H_4) monitored by MS. The as-formed thermolytic residue is amorphous and of complex polymeric composition. These results and the next challenges, are discussed herein.

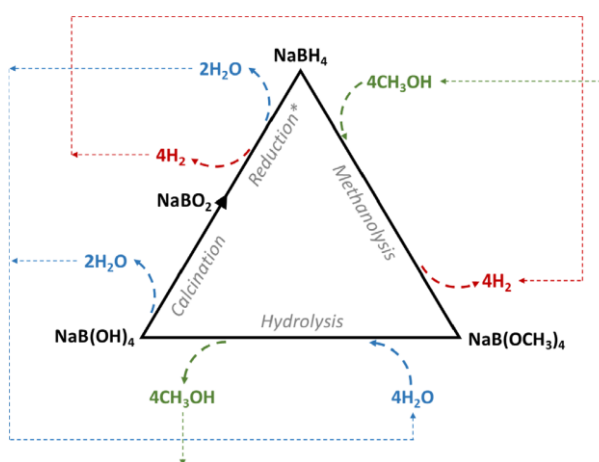
Closing the hydrogen cycle with the couple sodium borohydride-methanol, via the formation of sodium tetramethoxyborate and sodium metaborate

International Journal of Energy Research 44 (2020) 11405-11416.

Collaboration: Dept of Chemical Engineering, Yildiz Technical Univ., Istanbul, Turkey ; Science and Technology Application and Research Center, Yildiz Technical Univ., Istanbul, Turkey

Involved MCP researchers: Umit B. Demirci

Methanolysis of sodium borohydride (NaBH_4) is one of the methods efficient enough to release, on demand, the hydrogen stored in the hydride as well as in 4 equiv of methanol (CH_3OH). It is generally reported that, in methanolysis, sodium tetramethoxyborate ($\text{NaB}(\text{OCH}_3)_4$) forms as single component of the spent fuel. It is, however, necessary to clearly investigate some critical aspects related to it. We first focused on the methanolysis reaction where NaBH_4 was reacted with 2, 4, 8, 16, or 32 equiv of CH_3OH . With 2 equiv of CH_3OH , the conversion of NaBH_4 is not complete. With 4 to 32 equiv of CH_3OH , NaBH_4 is totally methanolized (conversion of 100%). The best conditions are those involving 4 equiv of CH_3OH as they offer the highest effective gravimetric hydrogen storage capacity with 4.8 wt%, an attractive H_2 generation rate with $331 \text{ mL}(\text{H}_2) \text{ min}^{-1}$ and the formation of $\text{NaB}(\text{OCH}_3)_4$ as single product as identified by X-ray diffraction, Fourier transform infrared spectroscopy, and nuclear magnetic resonance. We then focused on the transformation of this product $\text{NaB}(\text{OCH}_3)_4$ into sodium metaborate (NaBO_2), via the formation of sodium tetrahydroxyborate ($\text{NaB}(\text{OH})_4$). $\text{NaB}(\text{OCH}_3)_4$ is easily transformed in water, by hydrolysis, at 80 °C and for 90 minutes, into $\text{NaB}(\text{OH})_4$ and 4 equiv of CH_3OH . In doing so, the cycle with CH_3OH is closed. Subsequently, $\text{NaB}(\text{OH})_4$ is recovered and converted into NaBO_2 under heating at 500 °C. This reaction liberates 4 equiv of H_2O , which allows to close the cycle with water. Based on these achievements, we have finally proposed a triangular recycling scheme aiming at closing the cycle with the protic reactants of the aforementioned reactions. This scheme may be used as base for implementing a closed cycle with the couple NaBH_4 - CH_3OH .



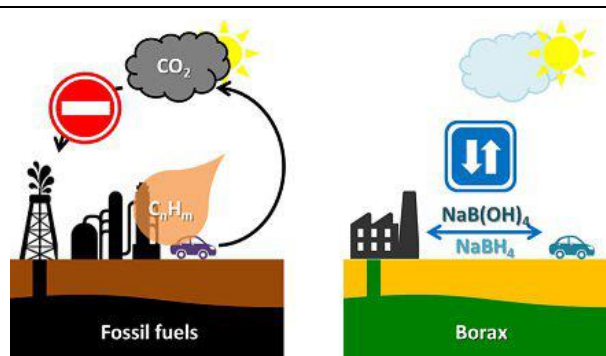
About the Technological Readiness of the H_2 Generation by Hydrolysis of B(-N)-H Compounds

Energy Technology 6 (2018) 470-486

Collaboration: /

Involved MCP researchers: Umit B. Demirci

At the beginning of the new millennium, hydrolysis of sodium borohydride (NaBH_4) was presented as a promising on-board technology to generate H_2 for light-duty vehicles. Years later, other B(-N)-H compounds (e.g., lithium borohydride (LiBH_4) and ammonia borane (NH_3BH_3)) emerged as attractive alternatives whereas NaBH_4 was struggling with several issues jeopardizing its implementation. Actually, efforts in the research and development of H_2 generation by hydrolysis of B(-N)-H compounds have been intensive since the advent of NaBH_4 almost 20 years ago. There may be a question with respect to this: What is the technological readiness of the promising hydrolytic B(-N)-H compounds? This Review aims at providing relevant elements in response to this question. In the first part, the most mature B(-N)-H compounds are discussed at length. In the second part, a survey of all other candidates is proposed. It is concluded that NaBH_4 is the best hydrolytic B(-N)-H compound for marketing on a broad scale, but there are still key challenges to address.



Nanosizing Ammonia Borane with Nickel: A Path toward the Direct Hydrogen Release and Uptake of B-N-H Systems

Adv. Sustainable Syst. 2 (2017) 1700122.

Collaboration: School of Chemical Engineering, The Univ. of New South Wales, Sydney, Australia
Involved MCP researchers: Umit B. Demirci

Ammonia borane (AB), with one of the highest hydrogen content (19.6 mass%), has attracted much attention as a potential hydrogen storage material. However, its complex and multistep thermal decomposition process has left the idea that AB can only be an irreversible hydrogen storage material. Herein, we demonstrate the potential of a novel nanosizing strategy in overcoming current drawbacks. By (a) successfully restricting the particle size of AB to the nanoscale (≈ 50 nm), and (b) discreetly encapsulating the synthesized nanosized AB particles within a nickel (Ni) matrix, AB showed unforeseen hydrogen reversibility along its decomposition path. Owing to the catalytic effect of Ni and the embedment of AB with the Ni matrix, this nanosizing approach reduced the hydrogen release temperature, suppressed the melting of AB and the production of volatiles by-products including diborane and borazine. But more remarkably, this approach enabled the reversible release and uptake of pure hydrogen at 200 °C and 6 MPa H_2 pressure, only. Reversibility is thought to occur through an iminoborane oligomer resulting from the initial decomposition of the nanosized AB/Ni matrix. This result demonstrates for the first time the possibility of tailoring.

