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Suppressing the formation of stable intermediates in hydride destabilization reactions[1]

CHANNING AHN, Caltech

Comprehensive computational screening efforts have identified numerous candidates for hydride destabilization reactions with reaction enthalpies that fall in the range of interest for engineering requirements (20 to 40 kJ/mol H_2). Less certain are the actual kinetic pathways of the solid–state reactions under consideration. Of particular interest are $LiBH_4$–based reactions. We have studied a number of destabilization reactions based on $LiBH_4$ and note that the $B_{12}H_{12}$ closo–borane is a commonly formed intermediate. Moreover, formation of $M_{2/n}B_{12}H_{12}$ phases as major intermediate species is observed in hydrogen desorption reaction of various $M(BH_4)_n$ systems before further conversion to either MB_n or $B+MH_n$. We have also examined a number of possible reactions that might destabilize $B_{12}H_{12}$ phases using reactions suggested in the recent literature but even under severe processing conditions, this closo–borane phase remains. Our inability to destabilize the closo–borane is particularly puzzling given that the initial work of Vajo on the $LiBH_4$–MgH_2 with dehydrogenation into several bar pressure showed complete reversibility. Our work however has generally been done under static vacuum. We have re-examined the reactions in the $LiBH_4$–MgH_2 and through the use of ^{11}B NMR, note that when dehydrogenated under 4 bar hydrogen pressure, no amorphous boron or $B_{12}H_{12}$ can be detected. When dehydrogenated into pressures below 1.5 bar hydrogen however, the closo–borane structure is formed. We will discuss these results and consider other possible reaction pathways that dictate the way in which these solid–state reaction experiments are conducted.

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