Hydrogenation of Magnesium Nickel Boride for Reversible Hydrogen Storage

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SUPPORTING INFORMATION PARAGRAPH.

(1) Additional Experimental Details

a. XRD

X-ray data were obtained with a Philips PW3040/60 X’Pert Pro diffractometer using Cu K\textsubscript{α} radiation with a combination of an X-ray mirror and a 2-crystal Ge(220) 4-bounce monochrometer. Samples were
mounted into 1mm glass capillary tubes in an Ar glove box and sealed prior to data acquisition. A broad feature seen the X-ray diffraction patterns at 15–60° two theta originates from the glass wall of the capillary tubes.

b. NMR

Solid-state NMR experiments were performed using a Bruker Avance 500 MHz spectrometer with a wide bore 11.7 T magnet and employing a boron-free Bruker 4 mm CPMAS probe. The spectral frequency was 160.50 MHz for the $^{11}$B nuclei. NMR shifts are reported in parts per million (ppm) when externally referenced to BF$_3$•O(CH$_2$CH$_3$)$_2$ for the $^{11}$B spectra. The powder samples in the present work were packed into a 4 mm ZrO$_2$ rotor and were sealed with a kel-F cap. Sample handling was performed in an argon filled glove box and the sample was spun under dry nitrogen gas as needed. Samples were often diluted with dehydrated quartz glass powder in order to improve sample spinning and probe tuning. The one dimensional (1D) $^{11}$B MAS NMR spectra were acquired after a 0.5 µs single pulse ($<\pi/12$).

c. FTIR

Infrared spectra were collected using a Nicolet 6700 FTIR spectrometer equipped with a N$_2$ chamber at room temperature. Ground sample was pressed into KBr pellets in an Ar glove box, then transferred in a sealed plastic bag to the chamber to minimize exposure to the air. Spectra were acquired at 4 cm$^{-1}$ resolution with data encoded at every 2 cm$^{-1}$ and 32 scans at room temperature.
(2) SIFig. 1 XRD spectra of MgB$_2$ + Ni mixtures heated to 975 °C with overall compositions of: (a) MgB$_2$ + 0.5Ni, (b) MgB$_2$ + 0.75Ni, (c) MgB$_2$ + 1.0Ni, (d) MgB$_2$ + 2.0Ni, (e) MgB$_2$ + 2.5Ni, and (f) MgB$_2$ + 3.0Ni. The unmarked peaks correspond to those for MgNi$_{2.5}$B$_2$, pattern number 04-009-9248 in the ICDD database.
Fig. 2 $^{11}$B MAS NMR spectra of MgNi$_x$B$_2$ as prepared with overall compositions of: (a) MgB$_2$ + 0.5Ni, (b) MgB$_2$ + 0.75Ni, (c) MgB$_2$ + 1.0Ni, (d) MgB$_2$ + 2.0Ni, (e) MgB$_2$ + 2.5Ni, and (f) MgB$_2$ + 3.0Ni. Spinning side bands are marked with asterisks.
(4) SIFig. 3. FTIR spectra of MgNi$_{2.5}$B$_2$ + 2LiH + 4MgH$_2$ mixture after hydrogenation at: (a) 250 °C, (b) 275 °C.
(5) SIFig. 4 $^{11}$B MAS NMR spectra for quantitative calibration: (a) MgNi$_{2.5}$B$_2$/4MgH$_2$/2LiH (as prepared mixture with a precisely known amount of MgB$_2$ added as a standard) and (b) MgNi$_{2.5}$B$_2$/4MgH$_2$/2LiH (after hydrogenation also with MgB$_2$ added as a standard). To use the added MgB$_2$ standard, five precisely known mixtures of MgNi$_{2.5}$B$_2$ and MgB$_2$, and separately LiBH$_4$ and MgB$_2$ spanning compositions from 10%/90% to 90% (molar ratios) were measured to determine calibration factors relating the ratio of the areas of $^{11}$B NMR resonances to molar ratios. These calibration curves were found to be linear over the whole composition range. Using the calibration factor relating the area ratio of the MgNi$_{2.5}$B$_2$ and MgB$_2$ resonances to the molar ratios, we determined that the amount of boron in the ternary phase (spectra (b), 145 ppm resonance) decreased by 31% upon hydrogenation relative to the as prepared mixture (spectra (a)). Using both calibration factors, it was determined that after hydrogenation, 29% of the boron occurred in the LiBH$_4$ phase and 71% occurred in the MgNi$_{2.5}$B$_2$ phase. The agreement between the loss of boron from the ternary phase (31%) and the fraction of boron in the borohydride phase (29%) indicates quantitatively hydrogenation of the MgNi$_{2.5}$B$_2$ phase.
(6) SIFig. 5. XRD spectra of MgNi$_{2.5}$B$_2$/2LiH/4MgH$_2$ mixture: (a) after hydrogenation, and (b) after dehydrogenation. During dehydrogenation some of the MgH$_2$ formed also dehydrogenated forming Mg metal. Note that there is no indication of Mg$_2$Ni alloy. The absence of Mg$_2$Ni indicates that the Mg$_2$NiH$_4$ is not simply dehydrogenating but rather reacting with the LiBH$_4$. 
(7) SIFig. 6. FTIR spectra of (a) MgNi$_{2.5}$B$_2$/2LiH, (b) MgNi$_{2.5}$B$_2$/4MgH$_2$, and (c) MgNi$_{2.5}$B$_2$ after hydrogenation.