Electronic Supplementary Information (ESI)

Superior desorption properties of MgCl2-added ammonia borane compared to MgF2-added systems—Unexpected role of MgCl2 interacting with [NH3] units

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MATERIALS AND METHODS

All the chemical reagents including NH_3BH_3 (AB, 97% purity), anhydrous $MgCl_2$ and MgF_2 (98% purity) were purchased from Sigma Aldrich and used without purification. The AB powder was then mechanically milled with $MgCl_2$ or MgF_2 in a molar ratio of 2: 1 for 2 h under argon atmosphere by using a planetary mill at 400 rpm with a 40:1 ball to powder ratio. The post-milled samples were denoted as $MgCl_2$/2AB or MgF_2/2AB, respectively. For comparison, the pristine was also milled under the same conditions.

CHARACTERIZATION

The thermal decomposition behaviors were studied using synchronous thermogravimetry/mass spectroscopy (TG/MS, Netzsch STA 409 PC) with a ramping rate of 5°C•min^{-1} under a flowing Ar (99.999% purity) atmosphere. All the sample handlings were carried out in an Ar-filled glove box. To reveal the phase components and chemical bonding states, X-ray diffraction (XRD) and Raman spectroscopy were carried out on a Rigaku D/max 2500 with Cu K_a radiation, a RBD upgraded PHI-5000C ESCA system with Al K_a X-ray source and a Renishaw inVia Reflex Raman spectrometer excited by a 514 nm argon ion laser, respectively. Thein situ Raman measurements were carried out to examine the variations of chemical bonds under Ar atmosphere (99.999% purity) in temperatures ranging from room temperature to 250 °C at a ramping rate of 5 °C•min^{-1}. The ^{11}B solid-state nuclear magnetic resonance (NMR) spectra for the composites were recorded on a Bruker DSX-300 NMR spectrometer using a Doty CP-MAS probe with no probe background. All solid samples were placed in 4 mm ZrO_2 rotors and spun at 14 kHz. A 0.25 ms single-pulse excitation at an effective rf-field strength of 111 kHz were employed with repetition times of 1.5 s. All the measurements were performed in a flowing dry N_2 environment because of the H_2O/O_2 reactivity of the samples.

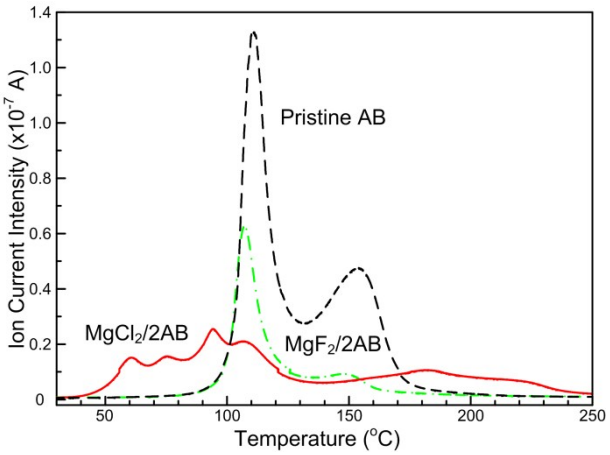

Fig. S1. Enlarged MS spectra of H_2 released from pristine AB and ball-milled MgX_2 (X= F, Cl)/AB (molar ratio, 1:2) samples.

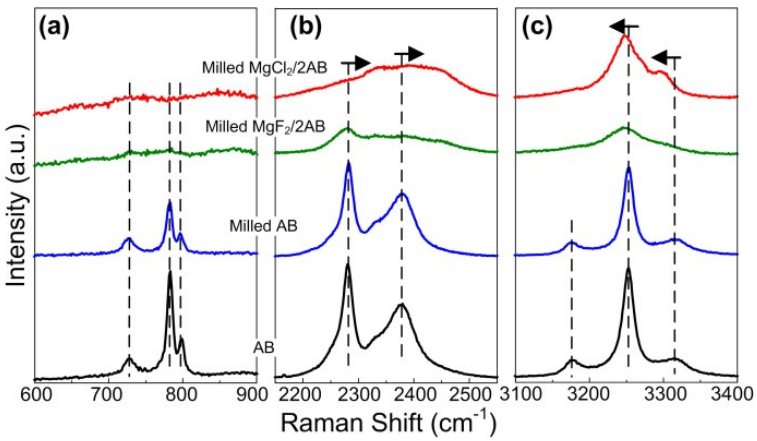

Fig. S2. Raman spectra for the pristine AB, post-milled AB and post-milled MgX_2/2AB (X = F, Cl): (a) B–N stretching modes, (b) B–H stretching modes and (c) N–H stretching modes.

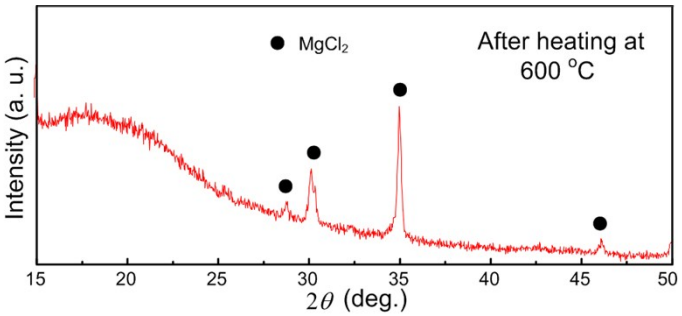

Fig. S3. XRD pattern for the post-milled $MgCl_2$/2AB after heating at 600 °C.