Supplementary Material

For

Promotion of Hydrogen Release from Ammonia Borane with Magnesium Nitride

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Control experiments on determining the optimal AB:Mg_3N_2 phase ratio

In the initial screening experiments, we mechanically milled the xAB/Mg_3N_2 mixtures with varied molar ratios (x=4, 6, and 12) for 1 h and examined their decomposition behaviors by synchronous TG/DSC/MS analyses. The post-milled 12AB/Mg_3N_2 sample was observed to release H_2 from ~85 °C, accompanying with the evolution of a considerable amount of NH_3. The total weight loss from the sample amounts to ~20.7 wt% upon heating to 300 °C. When x=6 applied, the sample exhibited markedly lowered dehydrogenation temperature (~65 °C) and suppressed evolution of NH_3. Due to the low concentration of NH_3 impurity, the observed weight loss (~10.5 wt%) might reflect the hydrogen capacity of the 6AB/Mg_3N_2 sample. Upon reducing the AB:Mg_3N_2 molar ratio to x=4, the sample showed further slight improvement on the dehydrogenation temperature, but with a compromise of hydrogen capacity (~8.5 wt%). In an overall consideration of the hydrogen capacity, dehydrogenation temperature and NH_3 evolution, we selected the sample with the optimal phase ratio x=6 for further detailed studies.

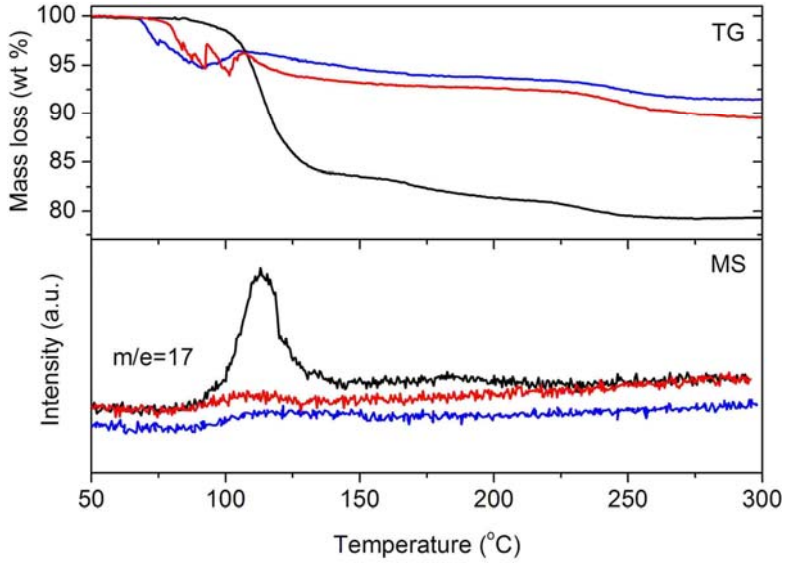

Fig. S1 TG (top)/MS (bottom, m/e=17, NH_3) profiles of the postmilled xAB/Mg_3N_2 samples with molar ratio x=12 (black), 6 (red), and 4 (blue). The samples were heated to 300 °C at a ramping rate of 2 °C min^{-1}.

Control experiments on determining the effect of the Fe contaminant

According to the elemental analysis results, mechanically milling the 6AB/Mg_3N_2 mixture using a high-energy SPEX8000 mill for 1h introduced ~5 wt% Fe contaminant. To check the effect of Fe contaminant on the dehydrogenation performance of AB and/or the 6AB/Mg_3N_2 sample, we conducted two control experiments, as detailed below.

In the first control experiment, we checked the effect of Fe on the dehydrogenation property of neat AB. To this end, we mechanically milled neat AB under identical conditions to that applied to the 6AB/Mg_3N_2 sample, which also introduced a considerable amount of Fe contaminant. Property examination found that the Fe-contaminated AB sample showed essentially unchanged decomposition behavior compared with neat AB, as seen in Fig. S2. This result indicates that the Fe contaminant exerts no appreciable effect on the dehydrogenation property of AB.

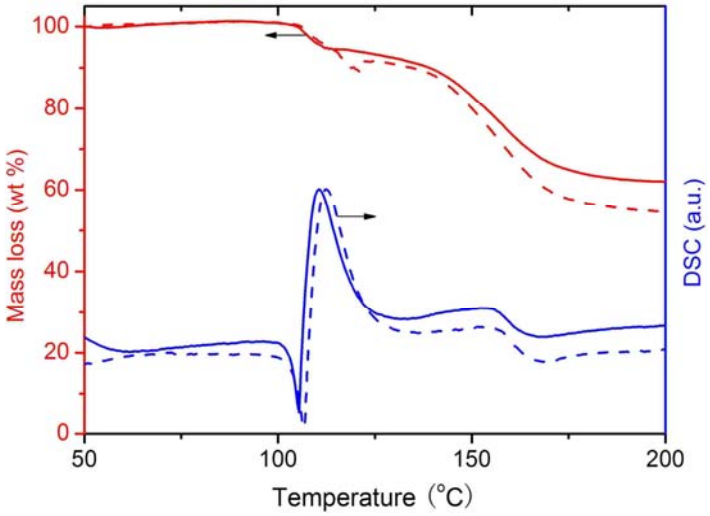

Fig. S2 TG/DSC profiles of AB (dashed line) and postmilled AB (solid line).

In the second control experiment, we examined the effect of Fe on the dehydrogenation property of the 6AB/Mg_3N_2 sample. For this goal, we intentionally added 5 wt% Fe powder to the 6AB/Mg_3N_2 mixture and then milled under identical conditions to that applied to the 6AB/Mg_3N_2 sample. Property examination found that the 5 wt% Fe-doped sample exhibited no appreciable improvement compared with the undoped sample, as seen in Fig. S3.

Based on the two control experiments, we concluded that the Fe contaminant is chemically inert to the dehydrogenation of the 6AB/Mg_3N_2 system.

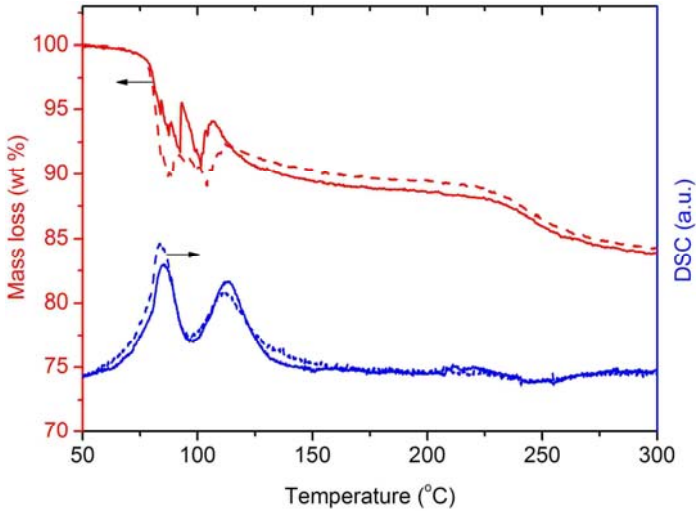

Fig. S3 TG/DSC profiles of the 6AB/Mg_3N_2 samples with (dashed line) or without (solid line) 5 wt% Fe dopant.

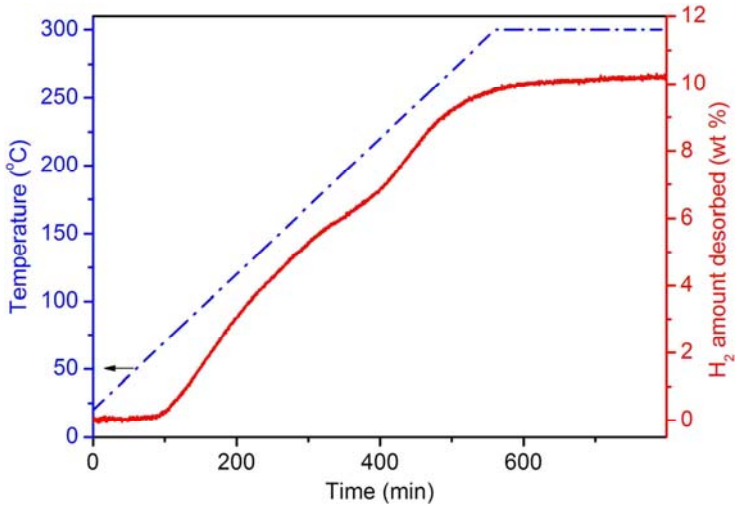

Fig. S4 Temperature-programmed desorption profile of the aged 6AB/Mg_3N_2 sample for 10 days at room temperature.