Supporting Information

An insight into the process and mechanism of mechanically activated reaction for synthesizing AlH_3 nano-composite

Congwen Duan, Lianxi Hu,* Yu Sun, Haiping Zhou and Huan Yu
School of Materials Science and Engineering, Harbin Institute of Technology, Harbin, 150001, China
E-mail: 12B909049@hit.edu.cn

Proposed reagent as identified by XRD

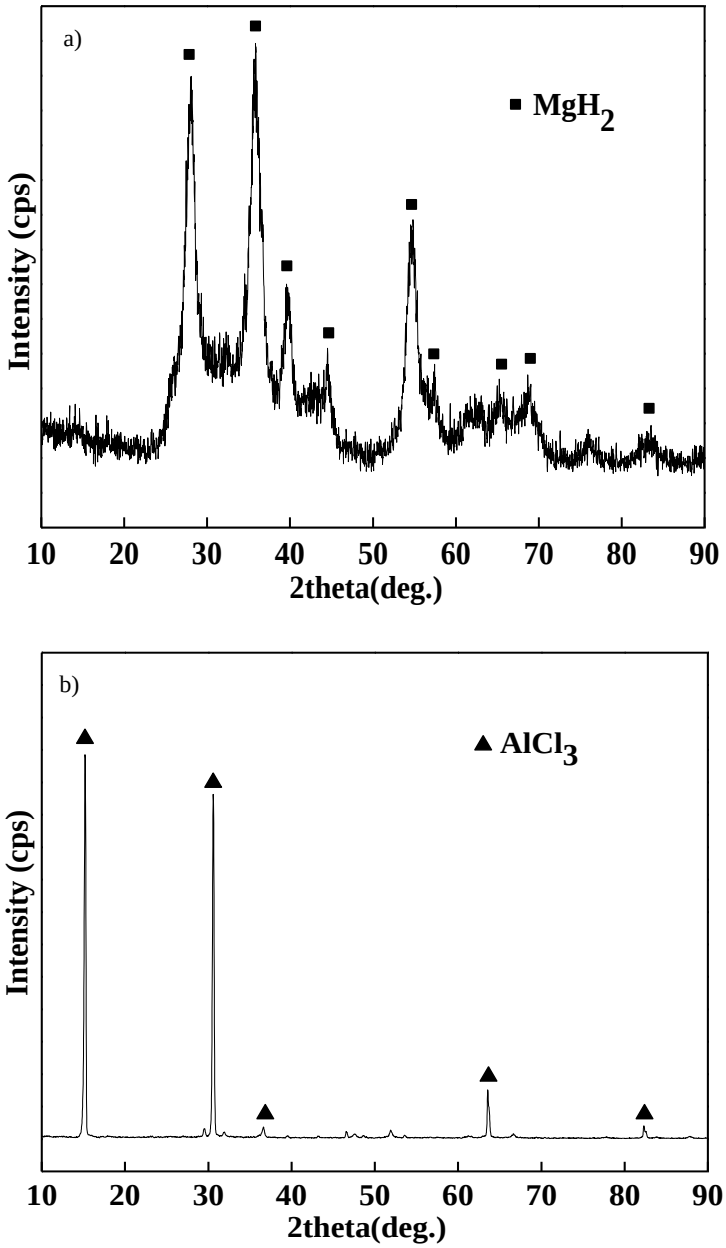

Fig. S1 XRD patterns of a) nanocrystalline MgH_2 phase, b) $AlCl_3$ phase,

It can be seen from Fig. S1a that the nanocrystalline MgH_2 was obtained by milling Mg for 20 h. Based on the Scherrer equation Calculation, the average crystallite size of product is estimated to be 10 nm.

Procedure

In general, 2.32 g of MgH_2 and 7.87 g of $AlCl_3$ were mixed together and sealed in the ball milling canister (Fig. S1), and then the milling experiments was preformed at 400 rpm for various milling times. The starting materials were characterized by using XRD analysis on a Philips 1050 diffractometer with 2θ range from 10° to 90°. The microstructure and morphology as well as the process of phase transition during mechanochemical reaction were characterized by SEM, TEM and NMR (Nuclear Magnetic Resonance) analysis. The measurements of as-milled powders were carried out on Quanta 200 FEG and JEOL JEM2011 apparatus. During SEM measurement, the powders were pressed into a carbon tape coating with thin film of gold. Before TEM measurements, powders were suspended in ethanol and then loaded onto the carbon support films with 200 mesh copper grids. NMR measurement was carried out by using a Bruker Advance NMR instruments, the samples were packed into ZrO_2 rotor and spun at 20KHz to identify resonance. All handling was performed inside of the argon-filled glove box to prevent the composite expose to air before being sealed into TEM column. In order to prevent composite from oxidizing, it should be minimized exposure time during transfer sample from glovebox to microscope.

SEM observation of as-milled $AlH_3/MgCl_2$ nanocomposite

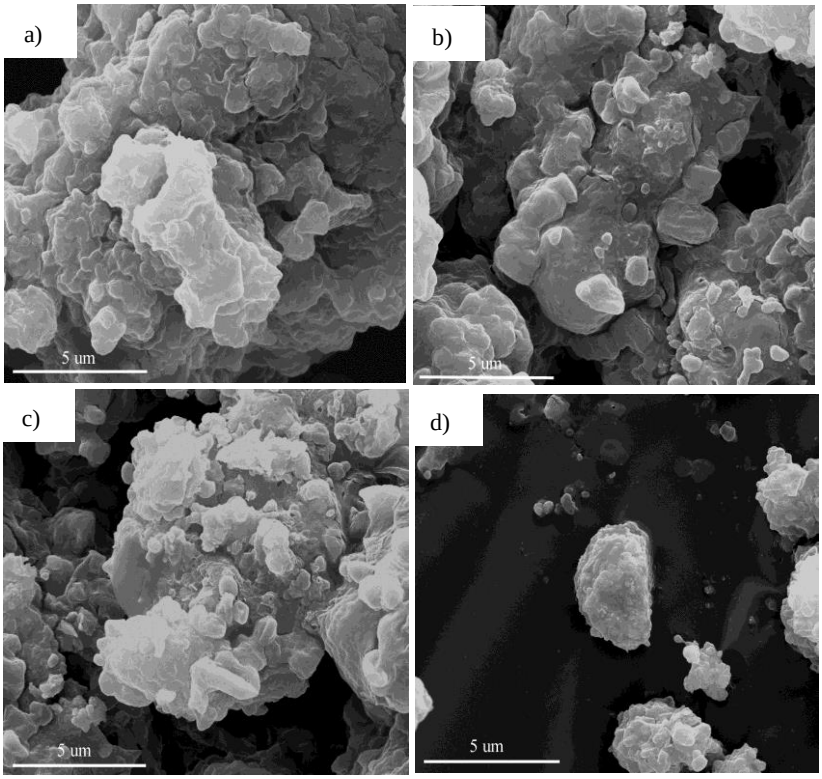

Fig. S2 SEM micrographs of MgH_2 and $AlCl_3$ milled for various times: a)4 h; b)8 h; c)12 h and d)16 h.

Fig. S2 shows the SEM images of as-milled sample milled for different times. It should be noted that different morphological characteristics of the powers are observed at different milling stages, which may be responsible for the extent of solid state reaction. As shown in Fig. S2a, after milling for 4 h, the as-milled powders revealed characteristic large agglomerates. The phenomenon of agglomeration seen from Fig. S2a indicates that much higher frequency of contact and rapid increment of connected interfaces occurred between the two reagents. It can be seen from Fig. S2b that when milled for 8 h, the particles of as-received resultant were irregular in shape with an average size of 1 μm. Along with two primary reagents attached to each other,

displacing and transforming into products, much finer particles were formed continuously on the contact area of reagents (see Fig. S2c). When the time of mechanical activation reaction went up to 16 h, cluster-like structures were observed in the obtained powders containing several finer particles (see Fig. S2d). Compared with the above results in Fig. S2c, it is obvious that the resultant shows a tendency to agglomerate, which may be attributed to the collision and coalescence of the numerous fine particles in the last stage of reaction.

XRD identification of as-milled $AlH_3/MgCl_2$ nanocomposite

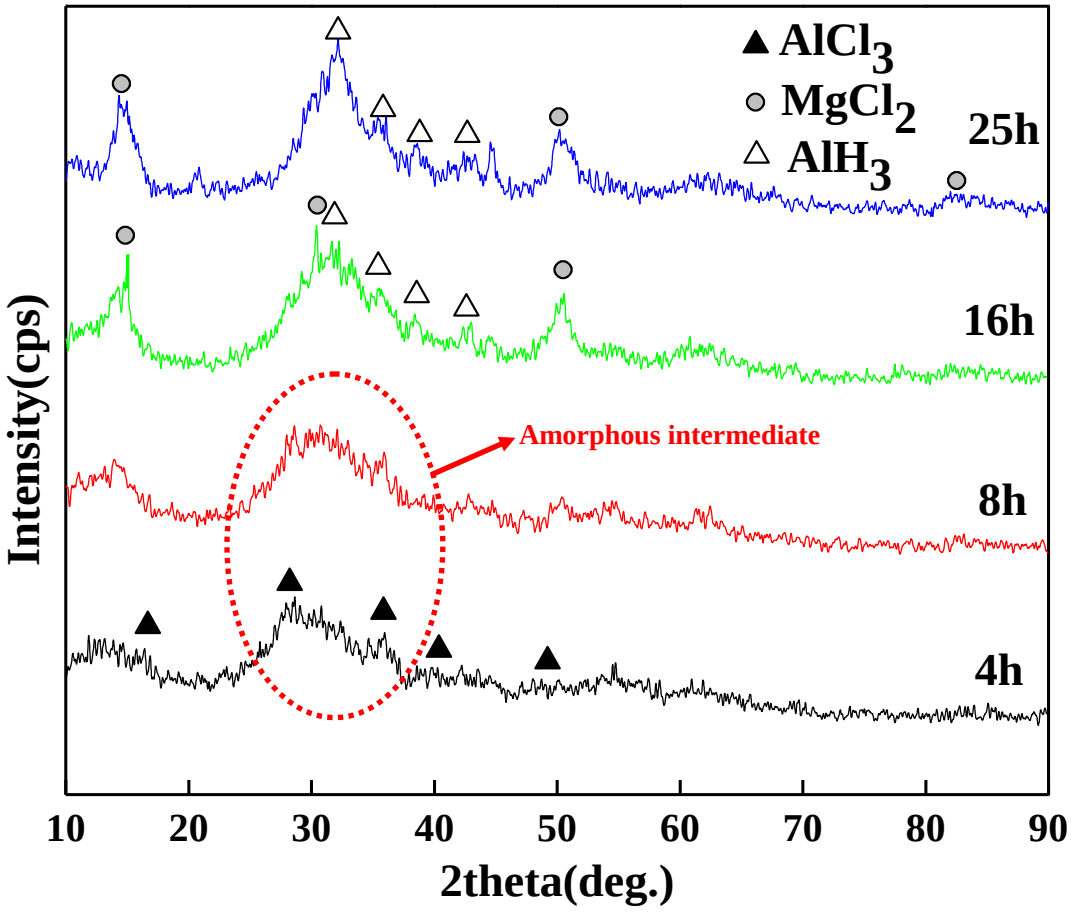

Fig. S3 XRD patterns of the MgH_2 and $AlCl_3$ mixtures with a BPR of 60:1 for different time.

It is suggested from Fig. S3 that a substantial change in the $MgH_2/AlCl_3$ mixtures for

the samples reacted for 4 and 8 h, as compared to the starting materials, and the broadening of the peak between 30° and 40° was significant, indicating that an amorphous intermediate was formed.

NMR characterization of the amorphous intermediate during the milling

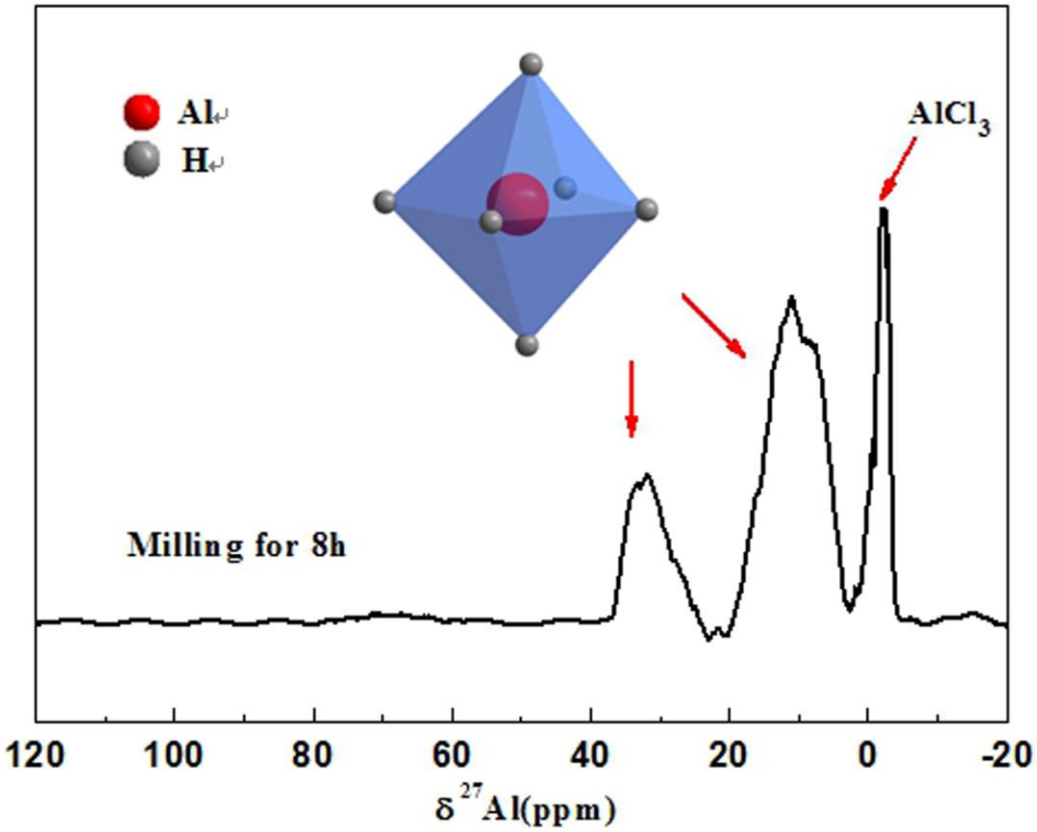

Fig. S4 Solid-state 27Al NMR spectra of as-milled powders after ball-milling for 8 h with a BPR of 60.