(Supplementary information)

The interesting and superior hydrogenation properties for the potassium-doped $LiNH_2$ and their ternary mixed-cationic amide

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Experiments

Lithium amide ($LiNH_2$) (95%, Aldrich) and H_2 (99.999%) were used for the following experiments. As additives, potassium hydride (KH) (99.5%, Aldrich) and potassium amide (KNH_2) synthesized from the KH and NH_3 were chosen. The additives were dispersed into the samples by the following mechanical ball-milling method. A weighed amount of $LiNH_2$, together with 30 steel balls (6 mm in diameter) and each additive, was put into a milling vessel made of steel of which the inner volume is about 50 cm^3, where the amount of additive was 5 mol% to 300 mg of $LiNH_2$. And then, the ball milling was performed under 0.1 MPa H_2 (>99.999%) atmosphere for 2 hours using a planetary ball mill apparatus (QM-3SP4). The ball-to-powder weight ratio was about 90:1. To minimize the temperature increment of the samples, the milling process was paused for 30 minutes every hour of milling. All the samples were handled in a glove box filled with purified Ar (>99.999%) to avoid an oxidation and hydration due to water. A weighed MNH_2 ($LiNH_2$, KNH_2, KNH_2-doped $LiNH_2$, KH-doped $LiNH_2$, and $KLi_3(NH_2)_4$) was treated under 0.5 MPa of H_2 flow at the designed temperatures with a heating rate of 5 ℃/minute to examine the reactivities. The reaction yield is calculated according to the equation $Y_{MH}=M_{MH}/M_{MNH_2}$, where Y_{MH}, M_{MH}, and M_{MNH_2} present the reaction yield, the mass of MH produced, and the initial mass of MNH_2, respectively. The sample masses before and after the experiments were measured to calculate M_{MH} and M_{MNH_2}. The structural characters of the produced composites were examined by X-ray diffraction (XRD) measurements.

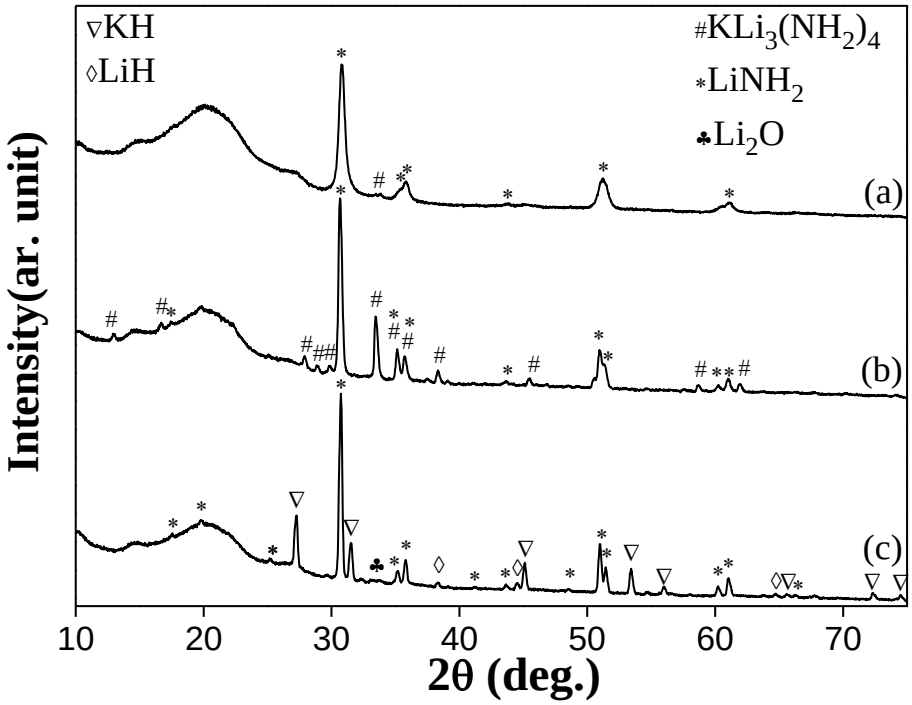

Fig. S1: XRD patterns of the 5 mol% KH-doped $LiNH_2$ after ball milling (a) and treatment under Ar (b) and H_2 (c) flow condition at 200 °C for 4 hours.

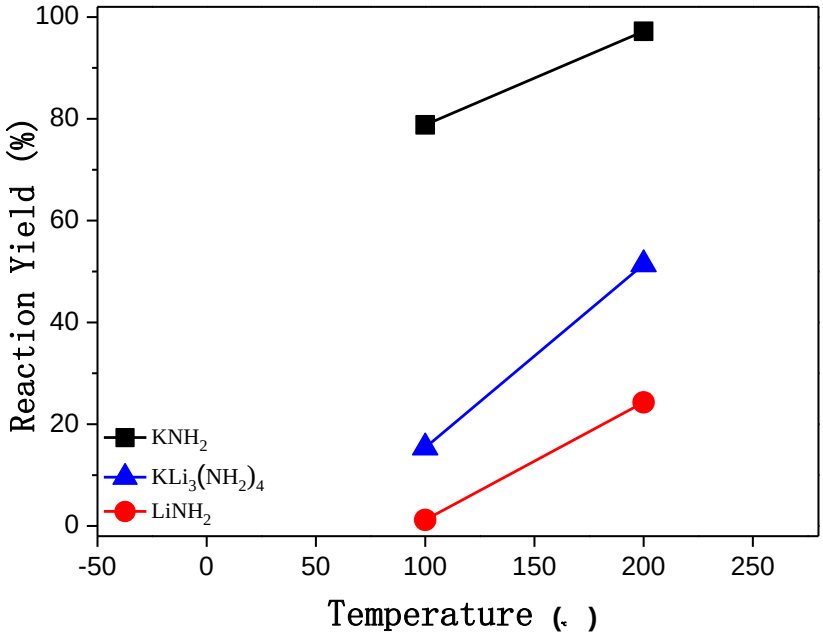

Fig. S2: Reaction yield of the reaction between MNH_2 (M = Li or K) and H_2 at different temperatures for 4 hours.

Reaction Equation S1: The hydrogenation mechanism of the KH-doped $LiNH_2$ system.

$$KH + 4LiNH_2 \xrightarrow{BM} KLi_3(NH_2)_4 + LiH$$

$$KLi_3(NH_2)_4 + H_2 \longrightarrow KH + 3LiNH_2 + NH_3$$

$$KH + 4LiNH_2 \longrightarrow KLi_3(NH_2)_4 + LiH$$

$$\vdots$$

$$1KH + 20LiNH_2 + 20H_2 \longrightarrow 1KH + 20LiH + 20NH_3$$