Supporting Information

New synthesis route for ternary transition metal amides as well as ultrafast amide-hydride hydrogen storage materials

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Experimental:

Mn (99.99%) and Zn (99.9%) were purchased from Sigma-Aldrich and Alfa-Aesar, respectively. K cubes with 99.5 % of purity purchased from Sigma-Aldrich as suspension in mineral oil. The K cubes were separated from the mineral oil and washed with hexane after polishing the surface. NH_3 was purchased from Air Liquide (Germany) with a purity of 99.98%. Monoclinic $K_2[Zn(NH_2)_4]$ (space group $P2_1/c$) was obtained in the cold temperature zone of an autoclave from zinc powder and potassium amide (molar metal ratio 1:2) under ammonothermal conditions (720 K furnace temperature, 259 MPa).[1]

For the mechanochemical synthesis of $K_2[M(NH_2)_4]$, Mn or Zn were mixed with K in a molar ratio of 1:2 in a pressure vial with 0.7 MPa of NH_3 ball milled for 12 h with a rotation rate of 150 rpm using a Fritsch Pulverisette 6 classic line planetary mill, with a ball to powder ratio ca. 40:1. The composite system $K_2[Zn(NH_2)_4]$-8LiH was ball milled 12 h at 250 rpm using a Fritsch Pulverisette 6 classic line planetary mill, with a ball to powder ratio of ca. 40:1 in a high pressure vial with 50 bar of hydrogen pressure. All powders handling and milling were performed in an MBraun argon glovebox with H_2O and O_2 levels below 10 ppm to prevent contamination.

X-ray diffraction (XRD) tests were carried out with a Bruker D8 Discover X-ray diffractometer, using Cu radiation (λ=1.54184 Å) with a current of 1000 μA and a voltage of 50 kV. The powder was spread onto a commercial sample holder and sealed in the glove box. The scanning range of 2 theta from 10 to 80 degree with 11 steps of 110 min. High resolution X-ray diffraction (XRD) experiments were performed at the PETRA III Synchrotron facility at Desy, Germany, beamline P.02.1. The wavelength was fixed λ = 0.20745 Å and a plate image detector (2048*2048 pixel, each of size 200*200 μm^2) was used to acquire the patterns, with a sample-to-detector distance of about 1400 mm. The powder was introduced in a sapphire capillary tube (about 1 mm diameter) and sealed. The 2-dimensional images were then integrated using FIT2D software.[2-4] The quantitative analysis were performed using MAUD software implementing with the Rietveld approach.[5-8]

Thermogravimetric analysis (TG), differential thermal analysis (DTA) as well as mass spectrometry (MS) measurements were carried out using a Netzsch STA 409 C and Hiden Analytical HAL 201 Mass-Spectrometer combined system, in 50 mL/min argon flow. The samples were investigated in the range of 30-500 °C with a heating rate of 5 °C /min. De/re-hydrogenation tests were

performed using a Sieverts-type apparatus (Hera, Quebec, Canada). The material was heated up to the final temperature of 400 and 300 °C under hydrogen pressure of 0 and 50 bar, respectively, using a heating rate of 3 °C/min.

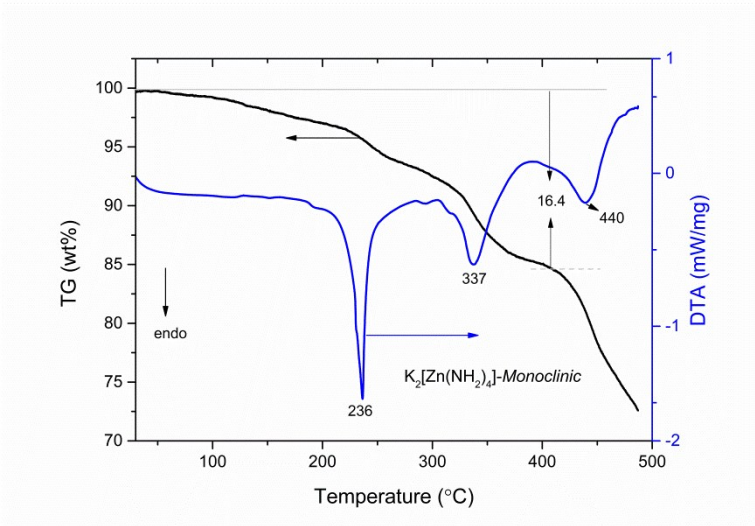

Fig. S1 TG-DTA curves of the monoclinic $K_2[Zn(NH_2)_4]$ heating from 30 °C to 500 °C in Argon with a ramping rate of 5 °C/min.

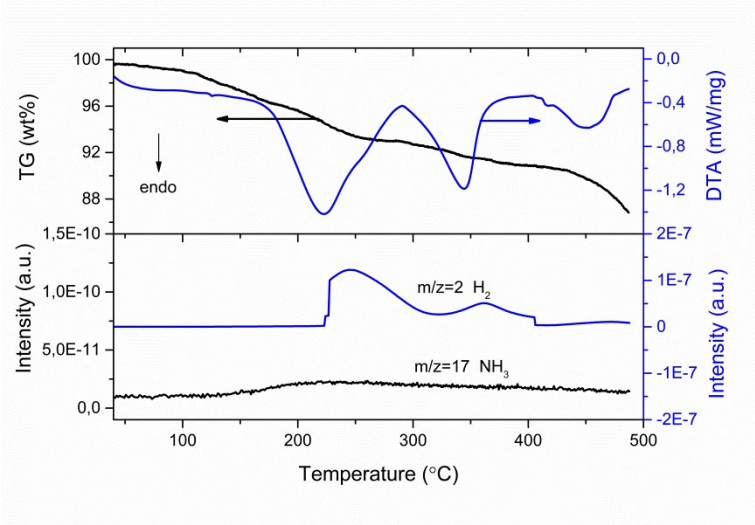

Fig. S2 TG-DTA-MS curves of the as ball milled $K_2[Mn(NH_2)_4]$-8LiH sample, heating from 30 °C to 500 °C in Argon with a ramping rate of 5 °C/min.

Table 1. Selected crystal structure parameters for $K_2[Mn(NH_2)_4]$ and $K_2[Zn(NH_2)_4]$ synthesized by mechanochemical reaction and ammonothermal synthesis, respectively.

Name	Structure data						Reference
	a (Å)	*b (Å)*	*b (Å)*	*α (°)*	*β (°)*	*γ (°)*	
$K_2[Mn(NH_2)_4]$	7.54(1)	7.00(1)	13.56(2)		105.94(9)		[9]
$K_2[Mn(NH_2)_4]$	7.300(1)	6.878(1)	13.319(2)		105.828(9)		This work*
$K_2[Zn(NH_2)_4]$	6.731(1)	7.433(1)	8.018(1)	72.128(7)	84.548(6)	63.883(6)	This work*
$K_2[Zn(NH_2)_4]$	6.730(1)	7.438(1)	8.019(2)	72.03(2)	84.45(2)	63.82(1)	[10]

* Rietveld's refinement results based on high resolution XRD (PETRA III, Desy, Germany).

Reference

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