Supporting Information

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

Hujun Cao,* Antonio Santoru,a Claudio Pistidda,a Theresia M.M. Richter,b Anna-Lisa Chaudhary,a Gökhan Gizer,a Rainer Niewa b Ping Chen,c Thomas Klassen a and Martin Dornheima

a. Institute of Materials Research, Materials Technology, Helmholtz-Zentrum Geesthacht, Max-Planck-Strasse 1, Geesthacht 21502, Germany. E-Mail: hujun.cao@hzg.de; Fax: +49 04152 /87-2625; Tel: +49 04152 /87-2643

b. Institute of Inorganic Chemistry, University of Stuttgart, Pfaffenwaldring 55, Stuttgart 70569, Germany

c. Dalian National Laboratory for Clean Energy Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, PR China.

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. NH₃ was purchased from Air Liquide (Germany) with a purity of 99.98%. Monoclinic K₂[Zn(NH₂)₄] (space group P2₁/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).

For the mechanochemical synthesis of K₂[M(NH₂)₄], Mn or Zn were mixed with K in a molar ratio of 1:2 in a pressure vial with 0.7 MPa of NH₃ 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 K₂[Zn(NH₂)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 H₂O and O₂ 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 µm²) 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. The quantitative analysis were performed using MAUD software implementing with the Rietveld approach.

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 $\text{K}_2[\text{Zn(NH}_2)_4]$ 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 $\text{K}_2[\text{Mn(NH}_2)_4] \cdot 8\text{LiH}$ 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.

<table>
<thead>
<tr>
<th>Name</th>
<th>a (Å)</th>
<th>b (Å)</th>
<th>c (Å)</th>
<th>α (°)</th>
<th>β (°)</th>
<th>γ (°)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>K$_2$[Mn(NH$_2$)$_4$]</td>
<td>7.54(1)</td>
<td>7.00(1)</td>
<td>13.56(2)</td>
<td>105.94(9)</td>
<td></td>
<td></td>
<td>9</td>
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<td>K$_2$[Mn(NH$_2$)$_4$]</td>
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<td>6.878(1)</td>
<td>13.319(2)</td>
<td>105.828(9)</td>
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<td>K$_2$[Zn(NH$_2$)$_4$]</td>
<td>6.731(1)</td>
<td>7.433(1)</td>
<td>8.018(1)</td>
<td>72.128(7)</td>
<td>84.548(6)</td>
<td>63.883(6)</td>
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<td>K$_2$[Zn(NH$_2$)$_4$]</td>
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<td>7.438(1)</td>
<td>8.019(2)</td>
<td>72.03(2)</td>
<td>84.45(2)</td>
<td>63.82(1)</td>
<td>10</td>
</tr>
</tbody>
</table>

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

Reference