How intimate contact with nanoporous carbon benefits the reversible hydrogen desorption from NaH and $NaAlH_4$

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Supporting information

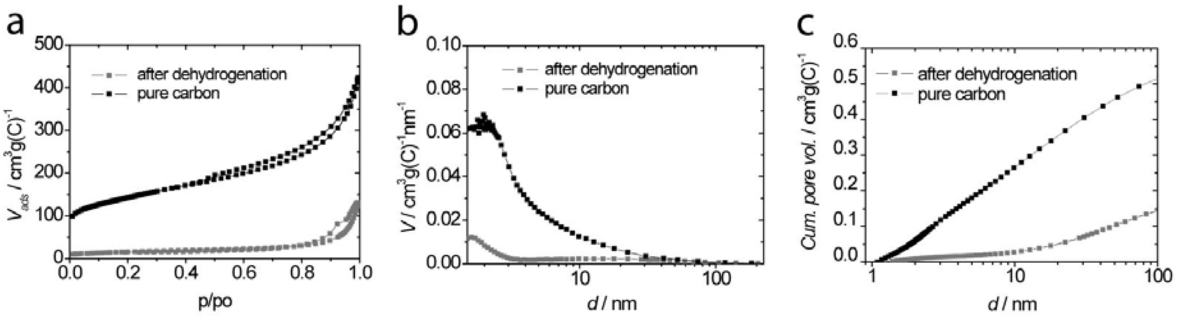

Figure S1. Results from nitrogen physisorption (77K) comparing pure carbon and 33NaH/C after dehydrogenation. (a) Isotherms, (b-c) pore size distributions and corresponding cumulative pore volumes (BJH, adsorption branch). The volume of Na added was 0.48 cm^3 $g(C)^{-1}$. In case of complete pore filling, this would correspond to filling of all pores with $d < 70$ nm.

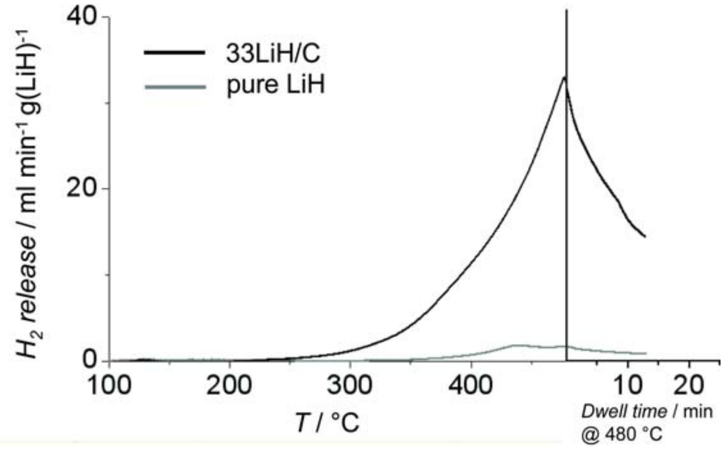

Figure S2. Thermal programmed desorption (TPD) of pure LiH and a 33wt% LiH/carbon mixture (33LiH/C) under Ar atmosphere (5 K min-1, 25 ml min-1). Around 50 % of the theoretical amount of hydrogen was released from 33LiH/C, 3% was found for pure LiH.

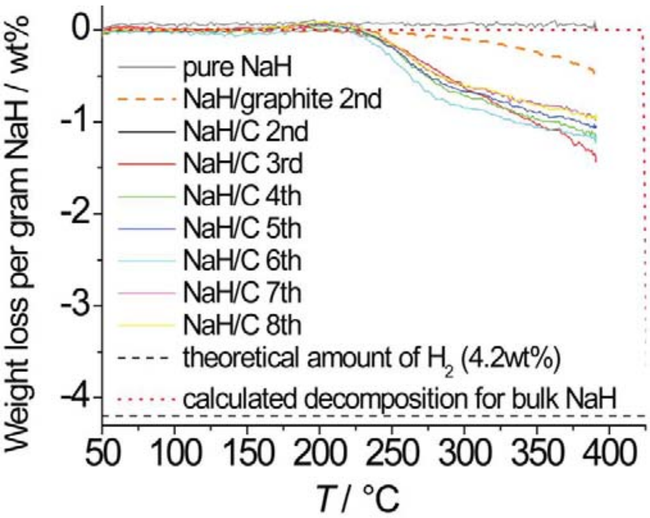

Figure S3. Dehydrogenation of 33NaH/C under 1 bar H_2 (5 K min^{-1}). The first dehydrogenation (not shown) was performed under Ar atmosphere at 330 ºC. Rehydrogenation was performed under 1 bar H_2 during cooling to 50 ºC.
Pure NaH is added for comparison and does not show any decomposition under these conditions.
The calculated decomposition of NaH under 1 bar H_2 is shown as red dots (the equilibrium pressure of NaH at 425 °C is 1 bar).
The sample containing graphite (33 NaH/graphite) exhibits a smaller weight loss, due to the lower degree of Na intercalation

Experimental details

HSAG-500 (Timcal) was used as carbon support and dried at 500 °C for 5 h under Ar flow before use. 90 wt% of the particles are smaller than 60 μm. Powders of NaH (Aldrich, 95%), $NaAlH_4$ (>90%) and LiH (95%, Aldrich) were used as purchased. Samples were prepared in a glove box by mixing carbon and metal hydride in a mortar for approx. 1 min. Powder X-ray diffraction (XRD) patterns were obtained under protective atmosphere with a Bruker AXS D8 Advance 120 machine (Co-$K_{\alpha 12}$ radiation). Crystallite sizes were determined using the Scherrer equation. Dehydrogenation was monitored by thermal programmed desorption under Ar flow (25 ml min^{-1}) using a Micromeritics AutoChem II equipped with a TCD detector. A magnetic suspension balance from Rubotherm was used for cycling under Ar (1.3 bar) and H_2 (1.0 bar) atmosphere. Rehydrogenation in the magnetic suspension balance was performed during cooling of the sample from the maximum desorption temperature to 50 °C (also under 1 bar H_2). Rehydrogenation at high pressures was conducted in an autoclave (Parr 4836 reactor). N_2 measurements were obtained at 77K using a Micromeritics ASAP 2020.