Hydrogen Storage

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Facilitated Hydrogen Storage in $NaAlH_4$ Supported on Carbon Nanofibers**

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Hydrogen is regarded as a suitable energy carrier for sustainable energy schemes. However, the reversible storage of hydrogen is still a major challenge, especially for mobile applications. Several storage media have been considered, for example, clathrate structures,[1] metal–organic frameworks,[2] and lithium nitride/amide[3,4] as well as physisorption on carbon or zeolites,[5–7] and alanates.[8] Sodium alanate ($NaAlH_4$) is promising because of its high reversible hydrogen storage capacity and optimal thermodynamic stability for reversible hydrogen storage at medium temperatures. Nevertheless, kinetic barriers restrict hydrogen desorption rates. Furthermore, reloading of undoped $NaAlH_4$ is also slow and not possible under practical conditions.[9,10] It has been found that Ti additives improve the kinetics of hydrogen absorption and desorption, but high pressures ($P > 100$ bar) and long times are still needed to reload depleted sodium alanate.[10–13] Further improvement of the kinetics requires new strategies and methods. A possible strategy is to decrease the particle size to the nanometer range, for which it is known that physicochemical properties of such particles may deviate considerably from the bulk properties.[13–17] By using nanosized sodium alanate, the phase segregation to micrometer-sized NaH and Al during hydrogen extraction from these materials will be prevented,[18,19] which might lead to enhanced rates of hydrogen desorption and absorption.

Therefore we prepared, for the proof of the principle, nanosized $NaAlH_4$ particles supported on a surface-oxidized carbon nanofiber support (CNF_{ox}) and investigated their hydrogen desorption and absorption properties in relation to the structural properties of the materials. The $NaAlH_4$ (9 wt%) supported on carbon nanofibers was obtained by impregnation and drying techniques (see the Experimental Section for details) and is referred to here as $NaAlH_4/CNF_{ox}$. A physical mixture of bulk $NaAlH_4$ and CNF_{ox} of identical gross composition was included in the study as a reference sample.

Figure 1 displays the X-ray diffraction (XRD) patterns of CNF, $NaAlH_4/CNF_{ox}$, and the physical mixture prior to hydrogen extraction. The diffractograms of CNF and $NaAlH_4/CNF_{ox}$ are identical. In contrast, the XRD pattern of the physical mixture showed sharp intense diffraction peaks that could be attributed to $NaAlH_4$ and intense broad peaks from the CNF. Thus, the crystallinity of the $NaAlH_4$ changed when impregnated on the support, and the $NaAlH_4$ was most probably present in a highly dispersed and/or amorphous phase, for example, as a thin film or as small particles. After desorption of the hydrogen, typically above 250 °C, the diffractogram of desorbed $NaAlH_4/CNF_{ox}$ only showed the presence of CNF diffraction peaks while the desorbed physical mixture showed intense narrow peaks of crystalline domains of Al and NaH (Figure 1). This observation indicates that in the case of the supported sample the NaH and Al were also present in a highly dispersed or amorphous phase after desorption.

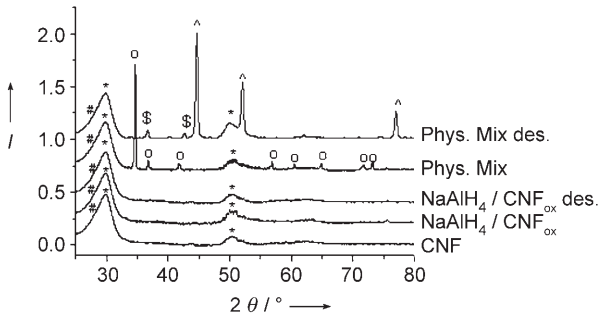

Figure 1. XRD pattern of Phys Mix, $NaAlH_4/CNF_{ox}$ and CNF, measured under a perspex cup. # = perspex, ⁎ = CNF, ○ = $NaAlH_4$, ^ = Al, and $ = NaH. Phys. Mix = physical mixture, des. = after desorption.

To investigate the details of the NaH and Al phases a desorbed sample of $NaAlH_4/CNF_{ox}$ was passivated with O_2 and studied by transmission electron microscopy (TEM). Figure 2 shows a representative bright-field TEM micrograph and scanning transmission electron microscopy energy dis-

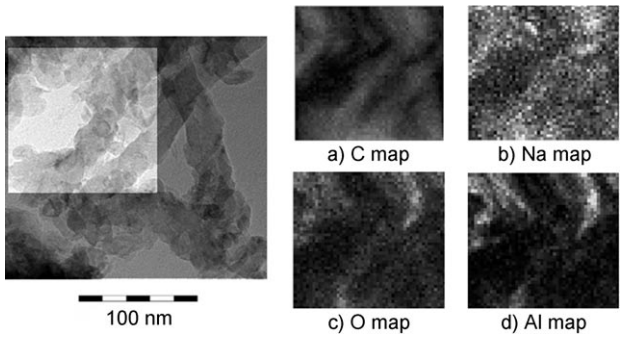

Figure 2. Left: TEM micrograph of "$NaAlH_4/CNF_{ox}$" after complete desorption and O_2 passivation. Right: EDX maps of C, Na, O, and Al of the highlighted region.

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persive analysis by X-rays (STEM-EDX) elemental maps of the highlighted region. The C map in Figure 2a followed the structure of the CNF. It can be seen in Figure 2b that the Na map coincided quite well with the C map, thus indicating that Na was highly dispersed on the fibers. In contrast, the Al was present in distinct areas on the support, which shows that the Al had segregated into nanometer-sized domains (Figure 2d). These observations differ from those obtained with unsupported alanates, where it is known that Na and Al segregate into micrometer-sized domains after desorption.[18,19] It can therefore be concluded that the phase segregation has been limited to the nanometer range in the desorbed $NaAlH_4/CNF_{ox}$. From the size of the Al domains (5–20 nm) observed in Figure 2d, one may expect a detectable XRD pattern. The absence of such a pattern (Figure 1) indicates, in our opinion, that either the Al was amorphous or the average crystallite size was much smaller.

The hydrogen desorption profiles of $NaAlH_4$ samples have been measured by temperature-programmed desorption (TPD). Hydrogen was desorbed by heating a sample to 160 °C at 2 °C min^{-1}, that is, below the melting point of $NaAlH_4$ (180 °C), thereby minimizing possible sintering. The H_2 desorption curves of $NaAlH_4/CNF_{ox}$ and the physical mixture are shown in Figure 3. Quantification of the H_2 released

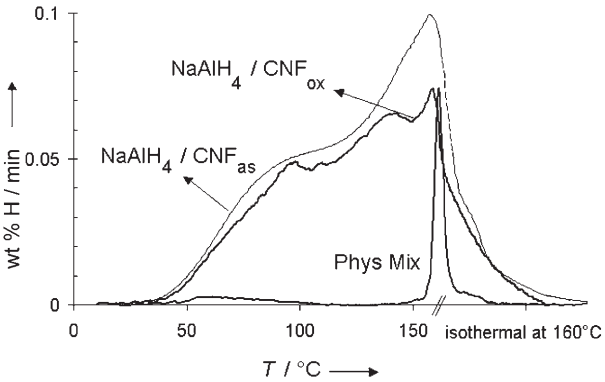

Figure 3. First desorption curve of $NaAlH_4/CNF_{ox}$, $NaAlH_4/CNF_{as}$, and the physical mixture. Heating rate 2 °C min^{-1} to 160 °C.

revealed that 2.9 wt % H_2 was desorbed from $NaAlH_4/CNF_{ox}$ (normalized to the amount of $NaAlH_4$), while only 0.15 wt % H_2 was desorbed from the physical mixture under identical conditions. Moreover, the $NaAlH_4/CNF_{ox}$ released H_2 starting from 40 °C, whereas the physical mixture started from 150 °C. This result clearly illustrates that the desorption kinetics have been significantly improved by using nanosized $NaAlH_4$.

The total hydrogen capacity for $NaAlH_4/CNF_{ox}$ was determined to be 3.6 wt % H_2 (normalized to the amount of $NaAlH_4$) by a temperature-programmed desorption to 300 °C. Since the theoretical hydrogen content is 5.6 wt %, it was concluded that 2 wt % H_2 was lost during the synthesis. To limit the hydrogen loss, $NaAlH_4$ was deposited on non-oxidized CNF (called CNF_{as}). It was found for $NaAlH_4/CNF_{as}$ that the hydrogen desorption capacity was 3.7 wt % H_2 up to 160 °C and 4.8 wt % H_2 for temperatures up to 300 °C. The hydrogen desorption profile is shown in Figure 3 and showed similar features as $NaAlH_4/CNF_{ox}$.

After the desorption step at 160 °C, the $NaAlH_4/CNF_{ox}$ was reloaded for 48 h at $T = 115$ °C and $P_{H_2} = 90$ bar, that is, under typical reloading conditions. The desorption curve (see the Supporting Information) reveals that 0.74 wt % H_2 had been reabsorbed at temperatures lower than 160 °C, which is 26 % of the originally desorbed H_2. Apparently, nanosized $NaAlH_4/CNF_{ox}$ can store hydrogen in a reversible manner under relatively mild conditions without the need for a catalyst, which to the best of our knowledge has never been observed for bulk, undoped alanates.[10–12]

The reversibility in this nanosized $NaAlH_4$ is tentatively attributed to a physical limitation of the phase segregation, which occurs when hydrogen is desorbed. In bulk $NaAlH_4$ phase segregation results in micrometer-sized Al and NaH domains,[18,19] whereas in nanosized $NaAlH_4$ the NaH and Al domains are limited to the nanometer range. Consequently, restoring the $NaAlH_4$ structure in the latter system is facilitated as a result of a decreased solid-state diffusion path length.

In summary, nanosized $NaAlH_4$ displayed improved hydrogen absorption and desorption characteristics compared to bulk alanates. The hydrogen desorption temperature decreased considerably and significant amounts of hydrogen could be desorbed at $T \leq 160$ °C with nanosized $NaAlH_4$. Moreover, reloading of the material was easier compared to bulk material, that is, hydrogen storage became partly reversible. This reversibility was facilitated most likely by the physical limitation of phase segregation when nanosized $NaAlH_4$ was desorbed. The approach, namely, deposition of nanosized clusters on a support material, opens up the possibility to study particle-size effects on kinetic, thermodynamic, and optical properties of complex metal hydrides in general. Nanosized alanates comprise a promising direction for developing a material that meets the requirements needed for the reversible storage of hydrogen.

Experimental Section

All syntheses were carried out by using Schlenk techniques. Handling and storage of the samples was carried out in a glovebox in an inert atmosphere. $NaAlH_4$ (Sigma–Aldrich; 90 % purity) was purified by dissolving it in dried THF and removing the insoluble species by filtration. Crystallization by evaporation of the THF under vacuum led to the isolation of $NaAlH_4$ as a white powder.

The CNF support materials were synthesized by using 5 wt % Ni/SiO_2 growth catalyst with syngas at 550 °C for 12 h as described elsewhere.[20] The growth catalyst (SiO_2 and non-encapsulated Ni) was removed by heating the sample at reflux in 1 M KOH, and in concentrated HNO_3 (CNF_{ox}) or concentrated HCl (CNF_{as}), respectively. Prior to the deposition of $NaAlH_4$, the supports were dried at 200 °C in N_2. Deposition was carried out by incipient wetness impregnation of a solution of $NaAlH_4$ in THF. For CNF_{ox}, the sample was dried in a vacuum to 10 mbar, and around 9 wt % of $NaAlH_4$ was deposited on the CNF_{ox}. For CNF_{as}, the sample was dried at −40 °C in a vacuum and the residual THF was evaporated at 0 °C.

Temperature-programmed desorption (TPD) measurements were performed on an AutoChem II 2920 in an Ar flow of 25 mL min^{-1}. The hydrogen concentration was measured using a calibrated thermal conductivity detector. The hydriding capacity was

measured using a Sieverts' apparatus purchased from the Hydro-Quebec Company at the Shell Research and Technology Centre. Powder X-ray diffraction (XRD) patterns were obtained at room temperature in an inert atmosphere from $2\theta = 10$–$100°$ with a Philips D-8 setup using $Co_{K\alpha}$ radiation. Transfer of the samples from the glovebox to the instrument was done in a special airtight sample holder. HR-TEM and STEM images were obtained on a Tecnai 20 microscope operating at 200 kV and equipped with an EDX and high-angle annular dark field (HAADF) detector.

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[1] H. Lee, J. Lee, D. Y. Kim, J. Park, Y. T. Seo, H. Zeng, I. Moudrakovski, C. I. Ratcliffe, J. A. Ripmeester, *Nature* **2005**, *434*, 743–746.
[2] J. L. C. Rowsell, O. M. Yaghi, *Angew. Chem.* **2005**, *117*, 4748–4758; *Angew. Chem. Int. Ed.* **2005**, *44*, 4670–4679.
[3] P. Chen, Z. T. Xiong, J. Z. Luo, J. Y. Lin, K. L. Tan, *Nature* **2002**, *420*, 302–304.
[4] K. Miwa, N. Ohba, S. Towata, Y. Nakamori, S. Orimo, *Phys. Rev. B* **2005**, 71, 195109.
[5] A. Zecchina, S. Borgida, J. G. Vitillo, G. Ricchiardi, C. Lamberti, G. Spoto, M. Bjørgen, K. P. Lillerud, *J. Am. Chem. Soc.* **2005**, *127*, 6361–6366.
[6] M. G. Nijkamp, J. E. M. J. Raaymakers, A. J. van Dillen, K. P. de Jong, *Appl. Phys. A* **2001**, 72, 619–623.
[7] J. Weitkamp, M. Fritz, S. Ernst, *Int. J. Hydrogen Energy* **1995**, *20*, 967–970.
[8] L. Schlapbach, A. Zuttel, *Nature* **2001**, *414*, 353–358.
[9] Sodium alanate decomposes upon heating according to the following steps: $NaAlH_4 \leftrightarrow \frac{1}{3}Na_3AlH_6 + \frac{2}{3}Al + H_2$ and $Na_3AlH_6 \leftrightarrow 3\,NaH + Al + 1\frac{1}{2}H_2$. By applying elevated hydrogen pressures $NaAlH_4$ is restored through the reverse reactions.
[10] B. Bogdanovic, M. Schwickardi, *J. Alloys Compd.* **1997**, *253*–254, 1–9.
[11] C. M. Jensen, R. Zidan, N. Mariels, A. Hee, C. Hagen, *Int. J. Hydrogen Energy* **1999**, *24*, 461–465.
[12] D. Sun, S. S. Srinivasan, T. Kiyobayashi, N. Kuriyama, C. M. Jensen, *J. Phys. Chem. B* **2003**, *107*, 10176–10179.
[13] F. Schüth, B. Bogdanivic, A. Taguchi (MPI Mülheim, Germany), patent application WO2005014469.
[14] X. He, D. M. Antonelli, *Angew. Chem.* **2002**, *114*, 222–238; *Angew. Chem. Int. Ed.* **2002**, *41*, 214–229.
[15] J. D. Aiken, R. G. Finke, *J. Mol. Catal. A* **1999**, *145*, 1–44.
[16] A. Gutowska, L. Li, Y. Shin, C. M. Wang, X. S. Li, J. C. Linehan, R. S. Smith, B. D. Kay, B. Schmid, W. Shaw, M. Gutowski, T. Autrey, *Angew. Chem.* **2005**, *117*, 3644–3648; *Angew. Chem. Int. Ed.* **2005**, *44*, 3578–3582.
[17] R. W. P. Wagemans, J. H. van Lenthe, P. E. de Jongh, A. J. van Dillen, K. P. de Jong, *J. Am. Chem. Soc.* **2005**, *127*, 16675–16680.
[18] B. Bogdanovic, R. A. Brand, A. Marjanovic, M. Schwickardi, J. Tolle, *J. Alloys Compd.* **2000**, *302*, 36–58.
[19] M. Felderhoff, K. Klementiev, W. Grunert, B. Spliethoff, B. Tesche, J. M. B. von Colbe, B. Bogdanovic, M. Hartel, A. Pommerin, F. Schüth, C. Weidenthaler, *Phys. Chem. Chem. Phys.* **2004**, *6*, 4369–4374.
[20] M. L. Toebes, E. M. P. van Heeswijk, J. H. Bitter, A. J. van Dillen, K. P. de Jong, *Carbon* **2004**, *42*, 307–315.

