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The $TiCl_3$ catalyst in $NaAlH_4$ for hydrogen storage induces grain refinement and impacts on hydrogen vacancy formation

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Abstract

$TiCl_3$ acts as an efficient catalyst for $NaAlH_4$ (sodium alanate), altering its hydrogen sorption kinetics and reversibility considerably. In order to clarify its role, we performed in situ neutron diffraction experiments on protonated catalysed and uncatalysed $NaAlH_4$. The phase transformations were monitored in the first two reaction steps during hydrogen release and in the second step during reloading. Our study for the first time provides clear indications that both Ti_xAl_{1-x} and NaCl formed act as grain refiner for Al and NaH, respectively, preventing particle growth. Particle sizes generally stay small upon desorption and reloading of $TiCl_3$ catalysed $NaAlH_4$, while significant particle growth is observed for uncatalysed $NaAlH_4$. The small crystallite sizes and observed hydrogen vacancy formation greatly facilitate the mass transfer during loading and unloading. This study underlines the importance of grain refining for achieving reversibility and faster kinetics of the hydrogen sorption processes, with a crucial double role played by the catalyst.

Keywords: Neutron diffraction; Nanocrystalline materials; Hydrogen storage; Phase transformations; Grain refining

1. Introduction

During the last decade, there has been growing interest in the development of lightweight metal hydrides capable of reversible hydrogen storage at low and medium temperatures. In a future sustainable energy economy, hydrogen may serve as a clean energy carrier, reducing (and eventually eliminating) carbon dioxide and other greenhouse emissions. A main challenge is to achieve safe and reliable hydrogen storage technologies that meet operating conditions, performance and cost requirements [1]. From a practical point of view, hydrogen should be stored with high hydrogen content at near-room temperature and at (or around) the standard operation pressure of 1 bar. Catalyst-doped $NaAlH_4$ (sodium alanate) is considered to be a promising hydrogen storage material because of its relatively large reversible hydrogen capacity (theoretically: 5.6 wt.%; practically: ~4.5 wt.%) and moderately low operating temperature (150 °C) [1–7]. The high hydrogen capacity of $NaAlH_4$ can be attained in two-step decomposition upon heating the material, involving the intermediate phase Na_3AlH_6 (sodium aluminium hexahydride), NaH (sodium hydride) and aluminium metal [2–7]:

$$NaAlH_4 \rightleftarrows 1/3Na_3AlH_6 + 2/3Al + H_2 \quad (1)$$

$$1/3Na_3AlH_6 \rightleftarrows NaH + 1/3Al + 1/2H_2 \quad (2)$$

Bogdanovic et al. showed that catalysing the reactions by Ti nanoparticles lowers the sorption temperatures and the reactions become largely reversible [2]. Their first, groundbreaking study [3] showed that $NaAlH_4$ samples doped with Ti-compounds ($TiCl_3$ and $Ti(OBu)_4$) begin to decompose at pragmatic rates at temperatures of about 100 °C, well below the melting point of the compound at

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about 180 °C. Since this discovery, considerable work has been done on improving the catalytic effects and understanding the role of the catalyst in $NaAlH_4$ [2–11].

The significance of the role of catalyst is well known [2–11], but the mechanism by which Ti enhances the cycling kinetics of hydrogen and reversibility of reactions (1) and (2) is still a big issue in the hydrogen storage field [11,12]. In fact, even the location of the Ti atoms remains unclear. It is indicated that Ti dwells on the surface of the material enabling dissociation of hydrogen molecules, substitutes for Na possibly facilitating the decomposition reactions, attracts a large number of H atoms [13–15] or induces increased hydrogen vacancy formation [16,17]. A number of different theories about the possible local environment of Ti have been suggested [18,19], but while the valence state of Ti was proven to be $Ti^{(0)}$ [18,19], a clear experimental and theoretical consensus is still under development.

A further essential aspect is that the reversibility of reactions (2) and (1) requires long-range migration of metal species. Small crystallite sizes therefore may clearly facilitate the through-solid mass transfer of H, Al and Na atoms, in the subsequent hydrogen absorption reactions to yield Na_3AlH_6 and $NaAlH_4$.

The aim of the study presented here is to better understand the role of Ti and Cl as a catalyst in the kinetics of hydrogen cycling in catalysed $NaAlH_4$, and to investigate the importance of both catalyst and nanoscale particle sizes in achieving reversibility. Therefore, we performed in situ neutron diffraction measurements on protonated catalysed $NaAlH_4$ in a comparison with uncatalysed $NaAlH_4$, and studied the phase transformations along with the reactions occurring during the hydrogen release and D_2 reloading. We report the importance of grain refinement – the phenomenon of keeping crystallite sizes small – in the rehydrogenation process of catalysed $NaAlH_4$, and show that $TiCl_3$ plays a (previously unanticipated) crucial role in this process.

Finally, the hydrogen site occupation was monitored to provide new insights into hydrogen migration through the mixed phase structures. In particular, quantitative information on hydrogen-vacancy formation and hydrogen–deuterium exchange was deduced from the neutron scattering data. Pronounced hydrogen vacancy formation was observed which can play a crucial role in the diffusion of H and possibly also of Al and Na through the particles during uptake and release of H.

2. Experimental

A catalysed sample was prepared by milling powders of protonated $NaAlH_4$ (sodium alanate) and 2 mol% $TiCl_3$ (titanium chloride) purity 99.9999% in a Spex 8000 apparatus for 15 min. Both the $NaAlH_4$ and $TiCl_3$ were obtained from Aldrich. Neutron and X-ray diffraction on the alanate showed only $NaAlH_4$ diffraction peaks. We used a high energy milling which ensures that 15 min is sufficient for a good distribution of the catalyst. Alanate was ball milled with a ball to powder ratio of 10:1 (30 g of balls:3 g of alanate). As a reference, an uncatalysed $NaAlH_4$ sample was prepared in the same manner without addition of $TiCl_3$. The size of the $NaAlH_4$ particles after ball milling was $\sim$110 nm in both cases. For the in situ neutron diffraction measurements both samples were loaded into quartz tubes under argon atmosphere and subsequently connected to a gas-handling system.

The catalysed and uncatalysed samples were heated to pre-determined temperatures between 100 and 250 °C. A constant flow of hydrogen gas at a pressure of 1–2 bar was maintained during hydrogen desorption at 100 °C in the catalysed sample in order to work under realistic pressure conditions for future applications. In contrast, in the uncatalysed sample a sudden increase in the hydrogen release rate after onset of the first decomposition step did not allow the maintenance of a controlled hydrogen flow.

The samples were placed under deuterium (D_2) at pressure to investigate the reloading behavior. After the first dehydrogenation step a pressure of 10 bar at 100 °C was applied for the catalysed sample in order to observe if Na_3AlH_6 shows uptake of D by exchanging H and D or by filling vacancies in the structure. Upon subsequent full decomposition of Na_3AlH_6 into NaH, Al and H_2 after the second desorption step, the catalysed sample was reloaded again at 150 °C and 10 bar (equilibrium pressure being 5 bar). The full conversion of NaH, Al and D_2 into $Na_3Al(H,D)_6$ was followed by a second decomposition of $Na_3Al(H,D)_6$ into $Na(H,D)$ and Al at 150 °C. Reloading the uncatalysed sample was attempted solely after completion of the second decomposition step at 150 °C and at 10 bar, since $NaAlH_4$ melted occurred during the first decomposition step.

Every 10 min during these procedures described above a neutron diffraction pattern was acquired using the general materials diffractometer (GEM) at the ISIS facility at the Rutherford Appleton Laboratory [20], amounting to a total of 89 patterns for the catalysed and 30 patterns for the uncatalysed sample. GEM combines an extraordinary neutron count rate with a very large Q range and a good resolution facilitating detailed in situ measurements. Due to the high signal to noise ratios it was possible to work with fully protonated materials, although these give a high diffraction background due to incoherently scattered neutrons. There are 7290 neutron detectors grouped into seven banks, each with a different range of accessible d-spacing. All diffraction patterns were fitted using Rietveld refinement using the General Structure Analysis System and the Sequentz program [21]. The different detector banks were fitted simultaneously, while phase fractions, lattice parameters, hydrogen site occupancies, temperature factors and line widths were allowed to vary freely. The particle sizes were calculated directly using the broadening of the fitted profile.

Further, as a reference, protonated $NaAlH_4$ (sodium alanate) was ball milled with 2 mol% Ti (titanium) metal powder in a Spex 8000 apparatus for 120 min. This longer milling time was needed because the Ti-metal powder is less brittle than $TiCl_3$, and resulted in $NaAlH_4$ particle sizes of