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New catalytic complexes for metal hydride systems

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Abstract

Catalysis is one of the critical factors in the improvement of hydrogen sorption kinetics in metal hydride systems. Effective catalysts, although usually added in small amounts, enable not only the practical performance of a hydride, but also provide an effective synthesis path for compounds that are otherwise inaccessible.

In the search for efficient and inexpensive catalysts for hydrogen sorption reactions, a new type of catalytic compounds was developed. These catalytic complexes demonstrated remarkable potential in a variety of systems, including sodium alanates and magnesium, as well as in hydrogen generation through hydrolysis. These new complexes demonstrated their unique molecular configuration (shown by FT-IR spectroscopy and X-ray diffraction) combined with nano-scale particle size.

Keywords: Hydrogen storage materials; Catalysis; Mechano-chemical synthesis

1. Introduction

Reactions involving hydrogen transfer, although generally common in chemistry, usually depend on the use of catalysts. The catalysts enhance reactions which are kinetically difficult (although thermodynamically favorable), and as a result they increase the reaction rate, decrease the activation energy and lower the effective temperature of the reaction. All of these factors are important in the development of advanced materials for hydrogen storage, where efficient catalyst can enable systems normally inaccessible. Many examples of catalysts can be found in the literature on metal hydrides, including noble metals such as platinum or palladium [1,2], transition metals [3], “fluorinated hydrides” [4], halides (particularly titanium chlorides for sodium alanates) [5–8], oxides, nitrides and carbides [9–11], as well as more complex compounds such as alkoxides [6,7]. Although the experimental data often demonstrate extraordinary performance of catalyzed hydrides, not much is known about the detailed mechanism of catalysis. It this paper, we propose a new approach to the interpretation of the catalysis mechanism and we introduce a new generation of catalysts, based on the concept of specific hydrogen bonding, as explained below.

In general, a catalyst has to enable dissociation of the dihydrogen molecules, resulting in the formation of mobile hydrogen species capable of entering and penetrating a solid matrix to form a hydride. The initial dihydrogen molecule is intrinsically balanced (with paired electrons) and therefore relatively stable. While homolytic dissociation breaks the dihydrogen molecule into separate hydrogen atoms, this state is extremely unstable and the only sustainable state for atomic hydrogen is in the ionic form, with either paired or absent electrons. As a result, hydrogen has a uniquely dual nature, being able to alternately form two types of ions: H^+ (positively charged ions without electrons, i.e. protonic form) or H^- (negatively charged ions, i.e. hydridic form) having an additional electron engaged to form an electron pair. For example, when atomic hydrogen reacts with oxygen, it forms a protonic bond, with the unpaired electron being transferred to the oxygen. On the other hand, in the presence of electropositive elements, such as alkali metals, hydrogen forms a hydridic bond and takes on an electronegative character. Generally hydrogen exhibits a hydridic coordination in hydrides, specifically in the stoichiometric (or

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non-interstitial) hydride types. Moreover, the degree of hydridization, which is enforced by the different electropositive character of the matrix elements, can be related to the stability of the hydrides. In particular, the standard redox potential in binary hydrides could be to some extent correlated with their decomposition temperature [12]. It should be noted that the delocalized hydridic coordination of hydrogen in hydrides does not necessarily contradict the postulated protonic mechanism of hydrogen diffusion, which can be explained by electrons being provided locally by the matrix.

This unique duality of hydrogen behavior leads to a question (being the base for the new catalysts concept): under specific conditions, can hydrogen adopt some type of ambivalent or polarized state in certain atomic configurations, which could play a key role in the catalysis mechanism? Hypothetically, such a situation would require formation of an atomic complex, simultaneously combining the protonic and hydridic types of bonding. In this concept, hydrogen needs to be bonded to a metal through a hydridic bond, where the electron pair is shifted toward hydrogen. However, the presence of a strongly electronegative element (such as oxygen, chlorine or carbon) on the other side of the molecular complex makes hydrogen have a tendency to adopt the electropositive character and to form a protonic bond with the electronegative element. This hypothetical connection (with hydrogen in a polarized or ambivalent state) between electropositive metals and electronegative elements through hydrogen, is the base of our new catalyst coordination. It is implied to differ in nature from both conventional and non-conventional hydrogen bonds in which the bonding is assumed to be electrostatic in nature as described in refs. [13,14]. We postulate that in order to achieve the essential “ambivalence” of the hydrogen state (anticipated to act as a catalytic site), electrostatic interference alone is insufficient and the configuration needs to involve electron sharing, similarly to the newly developed dihydrogen bonds (η^2–H_2) [15]. In this context, however, the present coordination clearly differs from these dihydrogen complexes, which represent three-center two-electron connection between a transition metal and an “intact dihydrogen molecule”.

Our understanding of the possible role of the postulated type of catalyst is based on the fact that the major function of a catalyst in the formation of hydrides is to stimulate and enable ionization of the dissociating hydrogen. In other words, the catalyst has to be able to transform stable diatomic hydrogen into the desired ionic configuration. On the other hand, in the desorption process hydrogen has to be “neutralized,” thus leading to the recombination into dihydrogen molecules. Therefore, the critical function of the catalyst is the ability to locally manipulate the charge. It is conceivable that atomic coordination involving the postulated ambivalent state of hydrogen is capable of such action and could also explain some of the previous results related to catalysis of hydrogenation reactions.

2. Experimental methods

The concept of the new catalysts requires forming an atomic complex containing both a hydride-forming metal and an electronegative element (such as oxygen, nitrogen or carbon) bridged by hydrogen. We have synthesized a large number of such molecular coordinations by using a variety of hydride forming metals (for example, titanium, zirconium, vanadium, niobium or magnesium), which were ball milled together with a source of hydrogen and the electronegative element, such as an oxide, hydroxide, carbon or carbide, etc. A very effective method involves the use of water or simple alcohols as the source of both the hydrogen and the electronegative element. Also, metal hydrides can be used instead of pure metals. Detailed procedures and many specific examples of such experiments are described in ref. [16] explaining particulars of the synthesis, composition and crystallographic structure of a series of new catalysts. In a typical experiment, the metallic element such as, for example, titanium or titanium hydride is ball-milled in the stainless steel vial of a high-energy ball mill (SPEX CentriPrep 8000 M Mixer/Mill) together with the electronegative element source: either water, methanol, an oxide, carbon, carbide or hydroxide. The molar ratio of titanium to the electronegative element is usually less than 1:1 and the loading is done in a glove box with protective argon atmosphere with less than 1 ppm of water and less than 1 ppm of oxygen. After the high-energy milling process (e.g., for 9 h), the material turns into deep-black, very fine powder, without any presence of the liquid phase, if such is used. In this process, the components are not allowed to react directly, which would otherwise result in the conventional formation of an oxide or carbide, which presence is an indication of the improper conditions of the process. Thus, produced powders were characterized by using X-ray diffraction (multi-sample BRUKER D8 Discover diffractometer with Cu Kα radiation) infrared spectrometry (FT-IR) with diffuse reflectance option (ABB, FTLA 2000-104), and scanning electron microscope (SEM) – Jeol 515. The catalytic powders (5–10 wt.%) were used to catalyze hydrogenation of various hydrogen storage systems (such as sodium alanate, lithium alanate, magnesium and titanium) and their catalytic ability was evaluated in a computerized gas titration system.

3. Results and discussion

In order to substantiate the postulated nature of the new catalytic coordinations, it was crucial to confirm that the produced powders did not exhibit conventional bonding between the metal and the electronegative element (such as in the oxides or carbides). Indeed, for the catalysts involving oxygen, no oxide-type coordinations were seen in both X-ray diffraction and IR spectra. In particular, when water or methanol was used in the reaction, the IR spectra of the resulting powders did not reveal any presence of the fundamental IR bands of the respective liquids. Instead, an indication of the presence

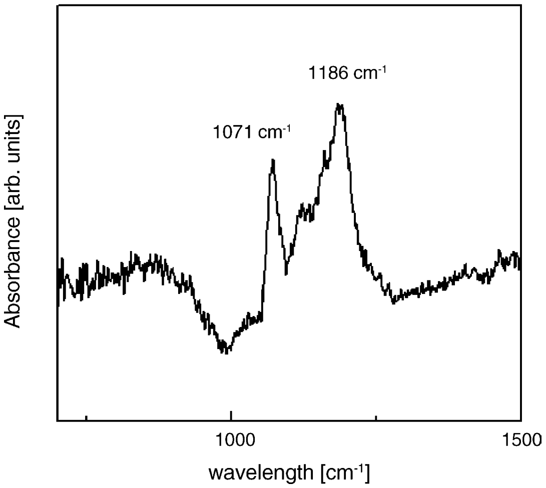

Fig. 1. Infrared spectrum of the new catalyst containing titanium, measured in the diffuse reflectance mode.

of the metal–hydrogen coordination was observed in the X-ray diffraction and moreover, some unique vibrational bands were produced. For example, in the case of the composition consisting of titanium, the resulting black powder exhibited an infrared spectrum that could neither have been attributed to any of the starting components, nor to the conventionally produced reaction products. This distinct and unique spectrum, as shown in Fig. 1, represents a "fingerprint" of the molecular structure of this catalyst, which might provide an explanation for the exceptional catalytic properties of this material. Another important feature of an effective catalyst is the size and shape of the catalyst particles. As shown in the scanning electron microscope (SEM) micrograph in Fig. 2, the catalyst is a solid, homogeneous powder, with average grain size of less than one micron.

Evaluation of the catalytic ability of this new group of compounds was done using various hydrogen storage materials. Catalyzed synthesis of sodium alanate, $NaAlH_4$, was an important target, in order to overcome the shortcomings (high cost and low purity) of commercially available $NaAlH_4$. The mixtures of the components (Al with NaH) were refined and catalyzed in a ball mill, followed by the subsequent exposure to hydrogen in the gas titration system. As shown in Fig. 3, almost 90% of the absorption reaction was completed within 30 min after the *first* exposure to hydrogen. In subsequent cycles, the kinetics of the hydrogenation and dehydrogenation improved further, without any deterioration of hydrogen sorption capacity. The practical, reversible capacity in the hydrogenation/dehydrogenation cycling was achieved between 3 and 3.2 wt.% for the first reaction, and 4.5–4.9 wt.% for both reactions. Fig. 4 shows examples of the dehydrogenation kinetics, where two reactions have been cycled at higher temperatures (finally reaching 4.5 wt.% – not shown in the figure for clarity). During the low-temperature cycling (i.e. below and around 100 °C), the reversible capacity of at least 3 wt.% was achieved. In order to characterize various stages of the hydrogenation cycles and to confirm the achieved capacities, the samples used for cycling (9–10 g) were taken out from the

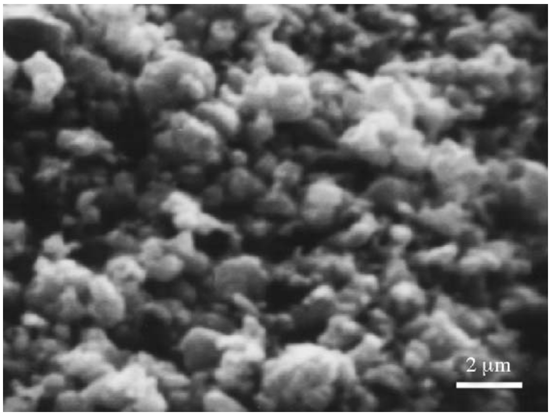

Fig. 2. SEM micrograph of the catalyst showing the average grain size of less than 1 μm.

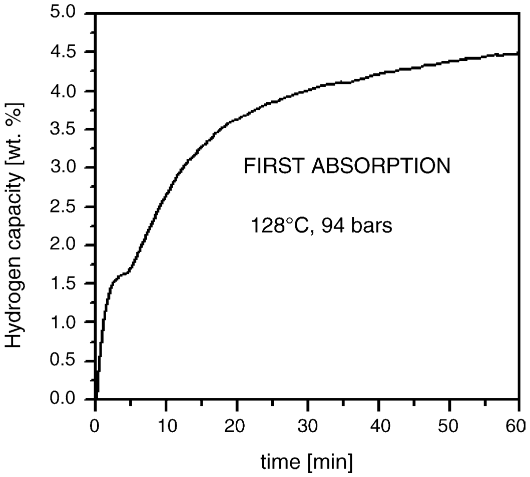

Fig. 3. Catalytic synthesis of sodium alanate $NaAlH_4$ from NaH and Al during first exposure to hydrogen.

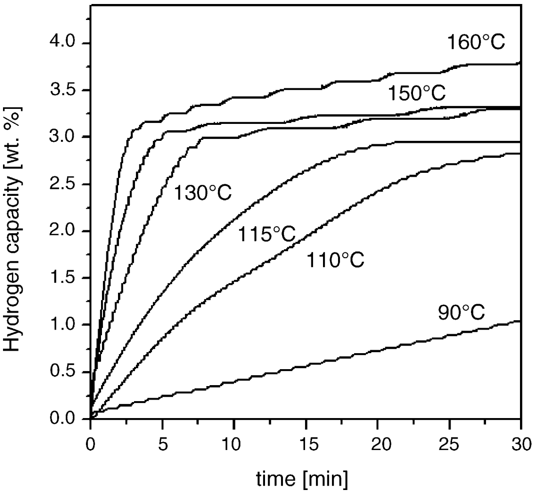

Fig. 4. Initial desorption rates at various temperatures for the catalyzed sodium alanate.

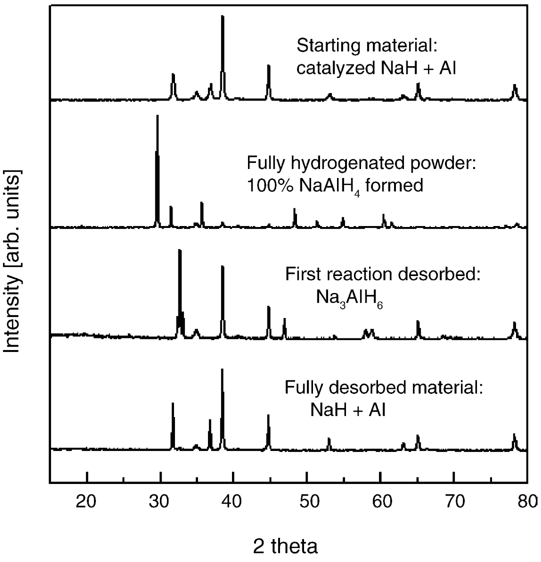

Fig. 5. X-ray diffraction patterns illustrating various stages of hydrogenation of the catalyzed mixture of NaH and Al.

titration system in different states, namely fully charged with hydrogen (where the formation of $NaAlH_4$ was expected), partially desorbed (to form Na_3AlH_6), and fully desorbed. Each X-ray diffraction pattern represented a "statistic" sample of each batch, in order to avoid possible effects of inhomogeneous hydrogenation. Fig. 5 shows X-ray diffraction patterns for every stage, which confirmed either full formation of $NaAlH_4$ or Na_3AlH_6, or the completely desorbed state, which was equivalent to the starting material. The only additional phase present in all these patterns is represented by a small diffraction peak attributable to the catalyst.

The efficiency of the new catalysts was also evaluated with lithium alanate. $LiAlH_4$ contains a large amount of hydrogen (5.3 wt.% in the first reaction (analogously to $NaAlH_4$) and an additional 2.65 wt.% in the high-temperature reaction). However, the decomposition is normally very slow and occurs only above 160–180 °C for the first reaction, and well above 200 °C for the second. As shown in Fig. 6, the non-catalyzed sample (ball milled in the same way as the catalyzed $LiAlH_4$) did not show any significant hydrogen release, while the catalyzed $LiAlH_4$ exhibited fast dehydrogenation at 75 °C. Almost 5 wt.% was generated in this process with kinetics much better than that for $NaAlH_4$ at similar temperatures.

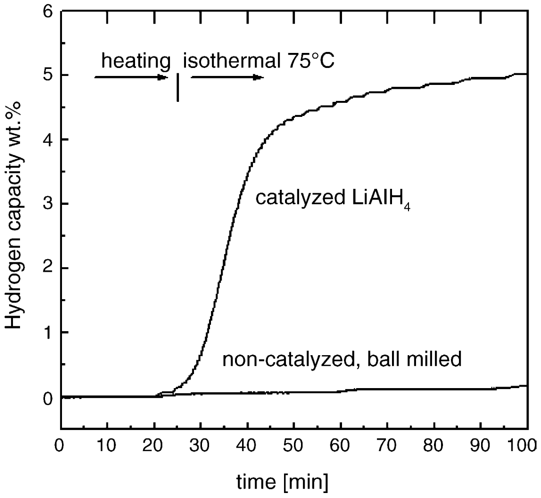

Fig. 6. Decomposition of the catalyzed $LiAlH_4$.

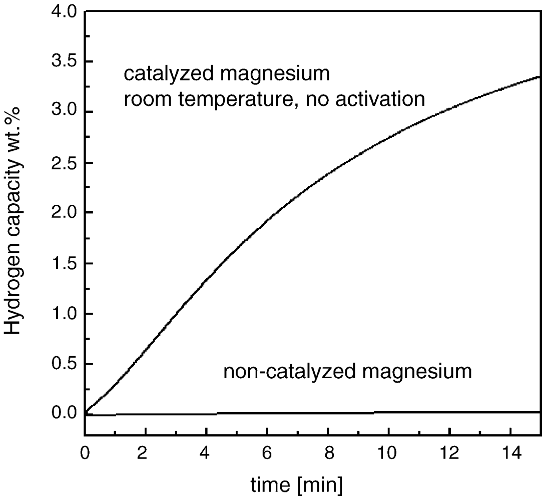

Fig. 7. Formation of magnesium hydride MgH_2 at room temperature without activation – hydrogen capacity of 6.5 wt.% was achieved.

Catalytic ability of the new catalysts was also evaluated in hydrogenation of magnesium to form magnesium hydride MgH_2. Without catalysis, magnesium hydride is very difficult to form and, even at 350 and 400 °C, the reaction is slow and hard to complete. In our experiments, magnesium powder was intermixed by a brief ball milling with one of the new catalytic compounds and the catalyzed sample was exposed to hydrogen at room temperature under hydrogen pressure of 10 bars, without any preheating or activation. Fig. 7 shows the

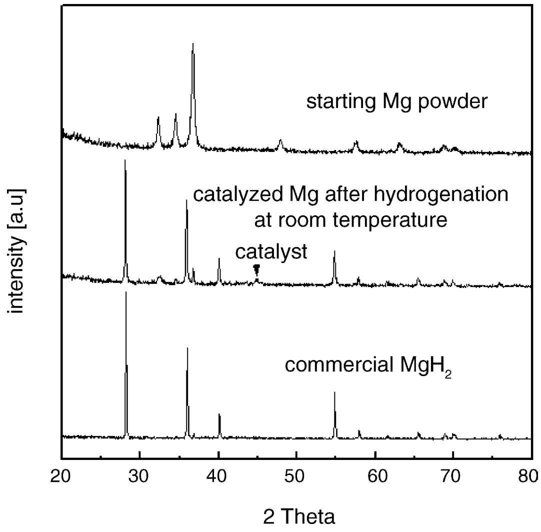

Fig. 8. X-ray diffraction patterns of catalyzed magnesium after hydrogenation at room temperature without activation.

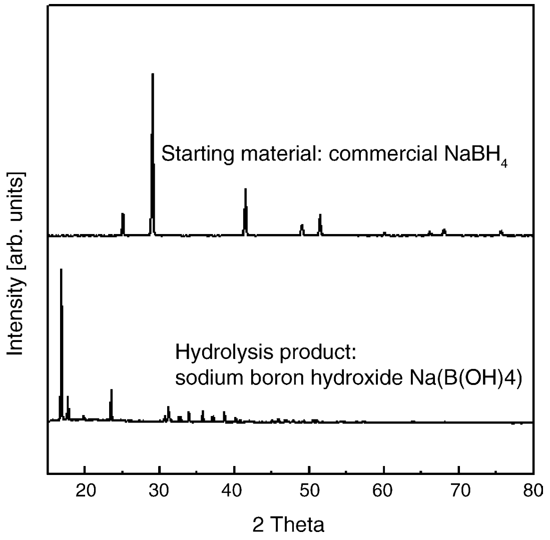

Fig. 9. X-ray diffraction patterns of sodium borohydride before and after hydrolysis.

immediate hydrogen uptake of the magnesium sample, which finally reached more then 6.5 wt.% capacity (not shown in the figure). After hydrogenation, the material exhibited an X-ray diffraction pattern characteristic for MgH_2, as shown in Fig. 8.

Another remarkable finding was the fact that the catalytic ability of the new compounds is not limited to gas phase reactions, but is outstanding in reactions of hydrides with water (hydrolysis). Experiments were performed on systems which are known to be relatively resistant to hydrolysis, such as sodium borohydride ($NaBH_4$) and magnesium hydride (MgH_2). Sodium borohydride dissolves in water forming a transparent solution, and magnesium hydride forms a suspension, but normally no significant generation of hydrogen is observed. In both cases, however, the addition of the new type of catalyst caused vigorous hydrogen generation. Fig. 9 shows a diffraction pattern of the initial sodium borohydride powder and of the solid residue formed after the hydrolysis was finished. It corresponds to the structure of a complex hydroxide of sodium and boron, which is the expected hydrolysis product. Fig. 10 shows a series of diffraction patterns illustrating hydrolysis of magnesium hydride. The first two spectra represent commercial MgH_2 before and after the hydrolysis, without any noticeable change of the powder. The next diffraction pattern shows the structure of the catalyzed magnesium hydride, which after hydrolysis fully transformed into magnesium hydroxide.

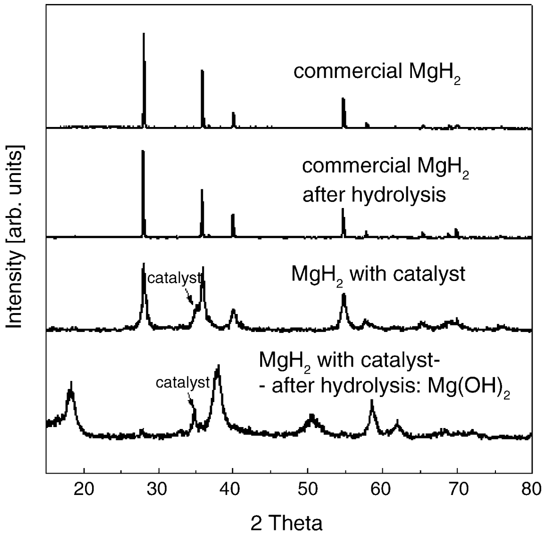

Fig. 10. Comparison of hydrolysis of non-catalyzed commercial magnesium hydride with catalyzed MgH_2, which fully transformed into magnesium hydroxide.

4. Conclusions

The new family of catalytic compounds has an exceptional capability of enabling hydrogen transfer in a variety of hydrogenation/dehydrogenation reactions, giving dramatically increased kinetics, performance at lower temperatures and elimination of the need for activation. A variety of systems have been tested, including sodium and lithium alanates, which were able to decompose well below 100 °C. Room temperature formation of magnesium and titanium hydrides was achieved without any activation. In addition, the research demonstrated catalytically enabled hydrolysis of sodium borohydrides and magnesium hydride with full conversion.

Acknowledgements

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