Catalytic Mechanism of Transition-Metal Compounds on Mg Hydrogen Sorption Reaction

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The catalytic mechanisms of transition-metal compounds during the hydrogen sorption reaction of magnesium-based hydrides were investigated through relevant experiments. Catalytic activity was found to be influenced by four distinct physico-thermodynamic properties of the transition-metal compound: a high number of structural defects, a low stability of the compound, which however has to be high enough to avoid complete reduction of the transition metal under operating conditions, a high valence state of the transition-metal ion within the compound, and a high affinity of the transition-metal ion to hydrogen. On the basis of these results, further optimization of the selection of catalysts for improving sorption properties of magnesium-based hydrides is possible. In addition, utilization of transition-metal compounds as catalysts for other hydrogen storage materials is considered.

1. Introduction

Although hydrogen is an ideal fuel for zero emission vehicles, there are still substantial technological challenges, which hinder its use as a fuel for normal applications. One of the major tasks for a future hydrogen technology for mobile applications is the development of a safe, nonexpensive, and lightweight storage facility. Several methods for storing hydrogen have been proposed and tested but none of them fulfills all the necessary requirements. Among the most promising methods, hydrogen storage in lightweight metals or compounds is being considered. The solid-state bonding of hydrogen in metals provides several advantages: the density of hydrogen is high, which is ideal for transportation, there is no risk of leakage or explosion, and finally, the hydrogen retained in this method has high purity, which is essential for its utilization in fuel cells.

Magnesium hydride exhibits a high gravimetric density of hydrogen up to 7.6 wt %. Therefore, magnesium and magnesium-based alloys have been proposed for hydrogen storage. However, kinetic problems cause a very slow reaction rate for absorption and desorption of hydrogen, in particular for magnesium. To solve these problems, two methods have been employed: a decrease of crystallite size of magnesium to nanoscale through high-energy ball milling and the use of suitable catalysts. In our previous work, we tested several catalysts and demonstrated that transition-metal oxides in particular have a significant catalytic effect on the sorption kinetics (Figure 1, refs 1 and 2). Although the catalytic effect has been clearly demonstrated, the microscopic mechanisms of the oxide catalysts are still not understood. Knowledge about the catalytic mechanism will highlight the necessary conditions for a good catalyst, may help to design better catalysts, and—likely most important—will indicate whether a similar catalytic behavior can also be expected for other hydride systems.

Therefore, we have undertaken a systematic study to investigate the mechanism of the catalytic behavior of nonmetallic and metallic transition-metal catalysts. In the present work, the
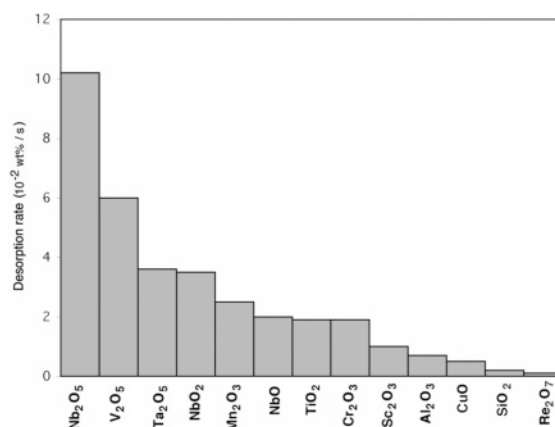

Figure 1. Various transition-metal oxides and their catalytic effect on the hydrogen desorption reaction rate of magnesium hydride at 300 °C.[1,2] Reaction rates were calculated between 20% and 80% of the respective maximum capacity.

experimental results of a magnesium−hydrogen reaction catalyzed with 13 different catalysts will be presented, with a particular focus on transition-metal compounds. On the basis of the results of a systematic variation of catalysts, we propose a correlation between the physicochemical properties of the catalyst and its catalytic activity. With this approach, four distinct factors for an effective catalytic behavior have been determined.

2. Experimental Section

The initial MgH_2 powder was purchased from Goldschmidt AG, with 95% purity (the rest being Mg) and was blended with different amounts of catalyst. Milling was carried out in a Fritsch P5 planetary ball mill with a ball-to-powder weight ratio of 10:1 g. Kinetics were characterized by titration experiments at 300 °C under 8.4 bar hydrogen or vacuum during absorption and desorption, respectively, using a volumetric Sieverts apparatus designed by Hydro Quebec/HERA Hydrogen Storage Systems.[3] It should be noted that, due to a slight hysteresis of the pressure membrane at the bridge balance point, the desorption curve can show an artificial plateau, which is particularly pronounced for

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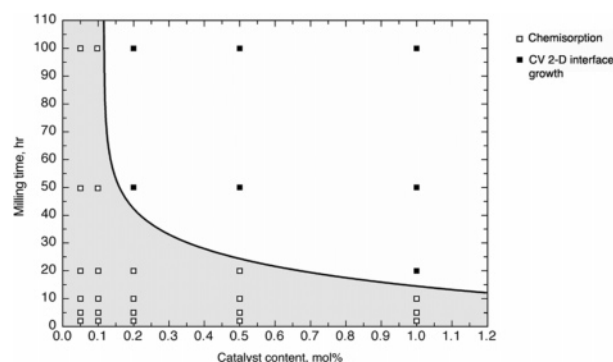† E-mail: Thomas.Klassen@gkss.de; Rüdiger.Bormann@gkss.de.

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Figure 2. Kinetic rate-limiting step for desorption as a function of milling time and Nb_2O_5 concentration (the two areas of different rate-limiting steps are separated by a tentative line). The measurements were performed at 300 °C.
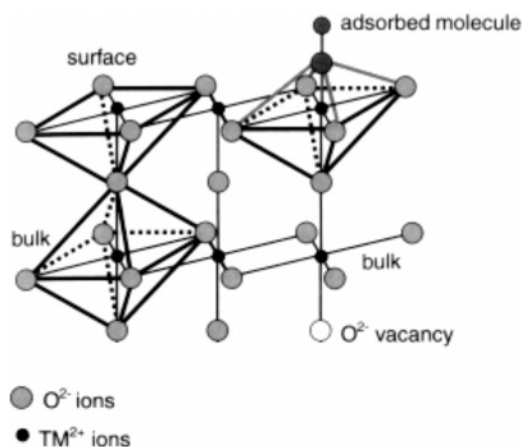

Figure 3. Illustration of the differences in symmetry of the crystal field experienced by bulk and surface transition-metal ions. Bulk ions are octahedrally surrounded by six O^{2-} ions. At the clean (100) surface (left), one O^{2-} ion of the octahedron is assumed to be missing and the surface transition-metal ions are pyramidally surrounded by five O^{2-} ions only, leading to a C_{4v} symmetric crystal field. Bulk transition-metal ions located next to an O^{2-} vacancy are exposed to a very similar crystal field.[5]

slow desorption rates. The reaction rates were calculated using the time and hydrogen content values between 20% and 80% of the respective maximum capacity. Specimen handling, milling experiments, and transfer for characterization have been done under purified argon atmosphere (O_2 and H_2O under 10 ppm each) to avoid the influence of atmospheric impurities which can substantially deteriorate the sorption kinetics of magnesium.

3. Results and Discussion

3.1. Kinetic Analysis of the Sorption Behavior. The reaction of hydrogen with metals and alloys consists of several distinct steps. For example, in the case of absorption, one requires physisorption, chemisorption (dissociation), surface penetration, diffusion, and hydride formation by nucleation and growth. As demonstrated, for example, by alkaline alanates, the latter step may also involve complex phase reactions. The slowest step determines the overall kinetic rate, and the experimentally measured kinetics represents the kinetics of the slowest part in each phase of the reaction.

Consequently, the experimentally determined kinetic curves for absorption and desorption have characteristic forms, which can be analyzed by applying different kinetic models. Accordingly, the rate-limiting step of the kinetics can be inferred, if a good fit of experimental data with a specific kinetic equation can be obtained. By the use of this method, the rate-limiting steps of the sorption reactions for different Nb_2O_5 contents and different milling times were identified.[4]

The results can be summarized as follows: Absorption kinetics of magnesium catalyzed with Nb_2O_5 are mainly determined by the diffusion of hydrogen through the hydride phase, formed at the outer shell of the magnesium particle. On the other hand, desorption kinetics of hydrogen is controllled either by chemisorption (recombination of hydrogen atoms) or by the velocity of the magnesium/magnesium hydride interface during phase transformation. The different mechanisms depend on the amount of Nb_2O_5 catalyst and on the milling time, as shown in Figure 2 (for further details, see ref 4). The results clearly demonstrate the distinct effectiveness of Nb_2O_5 catalysts in facilitating the chemisorption behavior.

As for magnesium-based hydrides, desorption kinetics are most crucial with respect to technological requirements. We will mainly focus in this paper on the catalytic mechanism of transition-metal compounds during desorption, for example, their influence on the recombination of hydrogen atoms to hydrogen molecules.

3.2. Factors for Transition-Metal Compounds to Improve the Catalytic Behavior during Desorption. A key to the understanding the catalytic effect of transition-metal oxides is

the electronic structure of the transition-metal ions. Thus, factors changing the electronic structure of the metal ions will change their catalytic properties. Four potential factors are discussed in the following sections, which are proposed as the main factors for transition-metal compounds to effectively catalyze the chemisorption behavior of magnesium-based hydrides.

3.2.1. Structural Defects. As reported by Fromme,[5] transition-metal ions on the surface and in the bulk of oxides may experience different crystal fields because of missing oxygen ions at the surface of these oxides. This causes a splitting of the electronic 3d state of these ions and can be responsible for the catalytic behavior of transition-metal oxides in adsorption of gas molecules. As an example, Figure 3 shows a generic crystal structure of a transition-metal oxide. In bulk, each transition-metal ion is surrounded by six oxygen ions, but at the surface, one oxygen ion is missing, which causes a change in the electronic structure of the metal ion, causing the high catalytic activity of the oxide catalyst.

To test the influence of catalyst defects on the desorption properties, specific milling experiments have been performed. Since high-energy ball milling is known to introduce a high number of crystal lattice defects into the material, it is interesting to study the efficiency of the catalyst with increasing milling time, that is, with increasing defect density. To separate the effect of microstructural refinement of the MgH_2, MgH_2 was first milled separately until it reached the ultimate minimum grain size. Subsequently, the catalyst was added and milling was resumed for the times indicated. As Figure 4 demonstrates, the desorption kinetics indeed improve continuously with milling time.

Therefore, we propose as the ***first factor*** that, for a transition-metal compound to be an effective catalyst, the compound should contain a high number of structural defects. On the basis of our experimental results, a favorable defect structure can be effectively achieved by prolonged high-energy ball milling.

3.2.2. Catalyst−Support Interaction. Usually in chemistry, pure metal catalysts are used in the form of thin films or clusters supported on ceramic substrates, mainly oxides. Although these supports were assumed to be catalytically inert, investigations have revealed that, depending on the support, the catalytic activity of the metal catalyst varies. The interface reaction
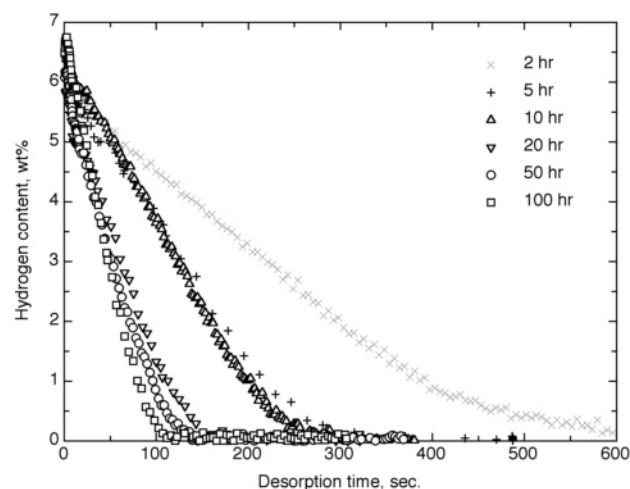
Figure 4. Effect of milling time on the desorption kinetics of magnesium hydride catalyzed with 1 mol % Nb_2O_5. The measurements were performed at 300 °C.
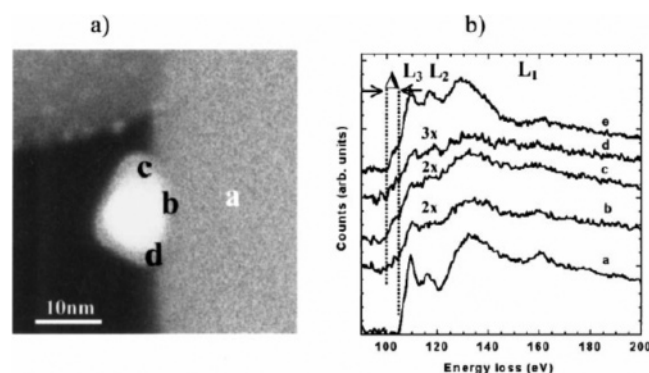

Figure 5. Pt/SiO_2 at 300 °C after 3 h of heating: (a) Z-contrast image showing the heated metal particle and locators for EEL spectra and (b) Si L-edges from the indicated positions (dwell time, $t = 0.3$ s). Spectrum e reflects a Si/SiO_2 model spectrum.[7]

between the metal catalyst and the oxide support and the morphological and electronic structure of the support can have a remarkable influence on the catalytic activity and selectivity of the supported transition-metal particles. This phenomenon of metal−support interaction was first emphasized by Schwab[6] and later confirmed by recent experimental results.[7,11]

As an example, Figure 5 shows a Z-contrast image and an electron energy loss spectrum (EELS) analysis of a Pt/SiO_2 system at 300 °C. As can be seen, the electronic structure of Si is different in the interface compared with the bulk of SiO_2, which can be attributed to the interaction of Pt atoms with the oxygen ions of the support at the interface. In turn, the electronic structure of Pt is modified also, which alters its catalytic activity. Hammer[8] has observed a similar positive metal−support interaction in the system MgO/Pd, where the interaction of Pd with MgO also leads to increased catalytic activity.

These results indicate that the electronic structure of transition metals in compounds can be altered by the interaction of magnesium support. For example, in the case of transition-metal oxides, magnesium may take one oxygen atom from the oxide structure, and this creates a defect, changing the electronic structure of the transition metal. Obviously, the stronger the magnesium−oxygen interaction compared with the transition-metal−oxygen interaction the more significant the change in electronic structure of the transition metal will be—in other words, we compare here the thermodynamic stability of MgO with the transition-metal oxide per oxygen atom.

As experimentally determined, all effective oxide catalysts are less stable than MgO (Table 1), and oxides comparably stable or even more stable (Sc_2O_3, Al_2O_3) than MgO are less active. On the basis of thermodynamics, a reduction of the transition-metal oxide by Mg is expected, forming a transition metal and MgO or a complex ternary oxide. However, this is generally not observed, which may be due to our experimental procedure, that is, milling at low temperatures which constrains the kinetics and the use of MgH_2 instead of pure Mg. The latter requires the decomposition of MgH_2, representing an additional barrier for magnesium-oxide formation. However, in cases where the transition-metal oxide is too unstable and the transition metal is reduced to its metallic state, any catalytic effect may diminish, in particular for early transition-metal compounds.

An example for a relatively unstable compound is Re_2O_7. The binding enthalpy of Re_2O_7 amounts to 180 kJ per O atom, it reacts immediately with magnesium during hydrogen desorption at 300 °C, and no catalytic effect is observed. Similarly, the catalytic effect of CuO decreases substantially with cycling at 300 °C. Consequently, efficiency of the catalyst increases only up to a certain limit with decreasing thermodynamic stability. If the critical compound stability is exceeded, the respective Mg compound is formed and the catalytic effect is decreased or even vanishes. This critical stability of the compound or oxide catalyst depends also on the operating conditions: For example, in the case of Nb_2O_5, which exhibits excellent sorption properties even after numerous sorption cycles at 300 °C, desorption kinetics are substantially reduced after annealing at 400 °C, due to the reaction of Nb_2O_5 with magnesium.[9]

These results are also in accordance with the observation that most of the pure transition metals of Table 1 do not show

TABLE 1: Thermodynamic Properties of the Oxide Catalysts and Experimental Desorption Rates

compound	TM hydride stability (kJ/mol H)	compound stability (kJ/mol O)	TM valence	desorption rate
Nb_2O_5	−43.5	−379	5	10.2
V_2O_5	−30.5	−310	5	6
Ta_2O_5	−32.6	−409	5	3.6
NbO_2	−43.5	−398	4	3.5
Mn_2O_3	−7.6	−319	3	2.5
NbO	−43.5	−405	2	2
TiO_2	−72	−472	4	1.9
Cr_2O_3	−8	−380	3	1.9
Sc_2O_3	−67	−636	3	1
Al_2O_3	−3.8	−558	3	0.7
CuO	−156	−156	2	0.5
SiO_2		−455	4	0.2
Re_2O_7		−180	7	0
MgO		−635		

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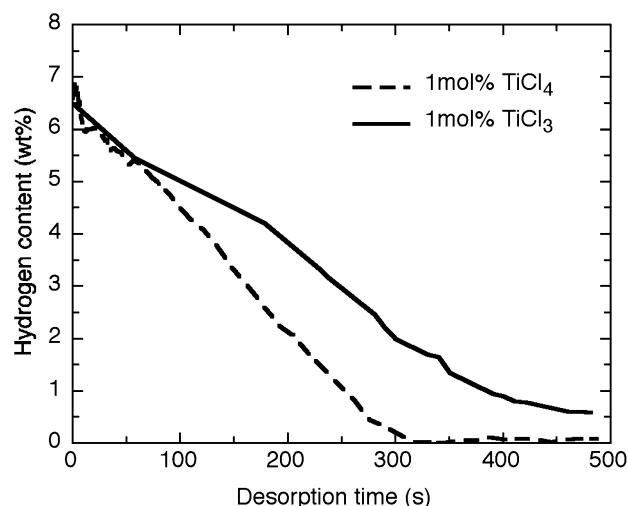
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Figure 6. Desorption kinetics of magnesium hydride catalyzed with 1 mol % $TiCl_3$ and $TiCl_4$. The measurements were performed at 300 °C.
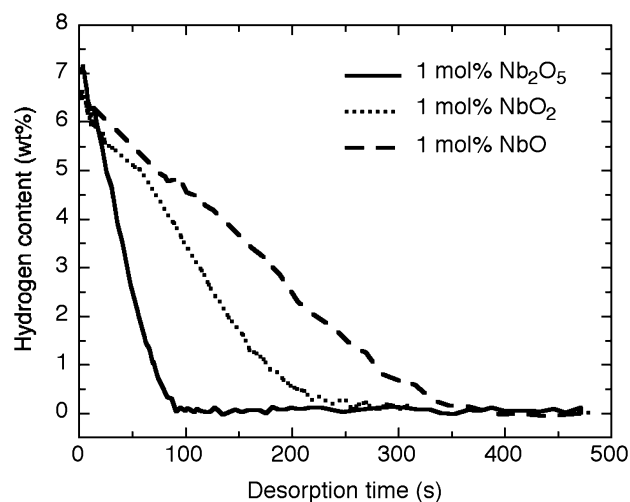

Figure 7. Desorption kinetics of magnesium hydride catalyzed with 1 mol % of three different niobium oxides which contain different valance states of niobium. The measurements were performed at 300 °C.

interesting catalytic behavior. For example, the effects of pure V and V_2O_5 were compared and only a marginal catalytic effect for pure V was found.[10] However, the catalytic behavior could be substantially enhanced by exposing the MgH_2−V composite to air for a short time. Clearly, these results demonstrate the important contribution of oxygen.

To test the proposed low-stability factor also for non-oxide transition-metal compounds, the desorption of magnesium hydride catalyzed with $TiCl_3$ and $TiCl_4$ is investigated. The enthalpies of formation of $TiCl_3$ and $TiCl_4$ are −240 and −201 kJ per Cl atom, respectively, that is, $TiCl_3$ is more stable than $TiCl_4$. Therefore, Mg atoms can more easily change the electronic structure of the Ti in $TiCl_4$ rather than $TiCl_3$. According to the low-stability factor, $TiCl_4$ should have a better catalytic effect compared with $TiCl_3$. As can be seen in Figure 6, this is indeed in agreement with our experimental results.

Therefore, we propose as the ***second factor*** for a transition metal compound to be an effective catalyst that the compound should have a low thermodynamic stability to allow a chemical interaction with the magnesium support. However, as many pure transition-metals are catalytically not very efficient, the chemical stability should be high enough to avoid a complete reduction of the transition-metal compound by magnesium or magnesium hydride. This constraint limits the desired decrease of compound stability. As a result, an optimum stability of the transition-metal compound exists for the given operating conditions meaning that less stable oxides have higher catalytic activity, comparing $TiCl_3$ and $TiCl_4$, for example. However, if the stability is too low—like Re_2O_7—the compound reacts completely with magnesium and its catalytic activity is diminished.

3.2.3. Valency of the Transition Metal in the Transition-Metal Compound. As previously published (and also shown in Figure 1),[1,2] the multivalency of the transition metal in the compound is critical for an efficient catalytic behavior. To separate the different effects, the catalytic efficiency of different niobium oxides, namely, NbO, NbO_2, and Nb_2O_5, was investigated. While the thermodynamic interaction of niobium with hydrogen is the same, and the stability per oxygen atom is almost identical, these three compounds differ mainly with respect to the oxidation state of niobium. As can be seen in Figure 7, the catalytic activity increases with the valence state of niobium. This can be explained by the ability of niobium in Nb_2O_5 to exchange more electrons for the catalytic reaction as compared with NbO_2 or NbO.
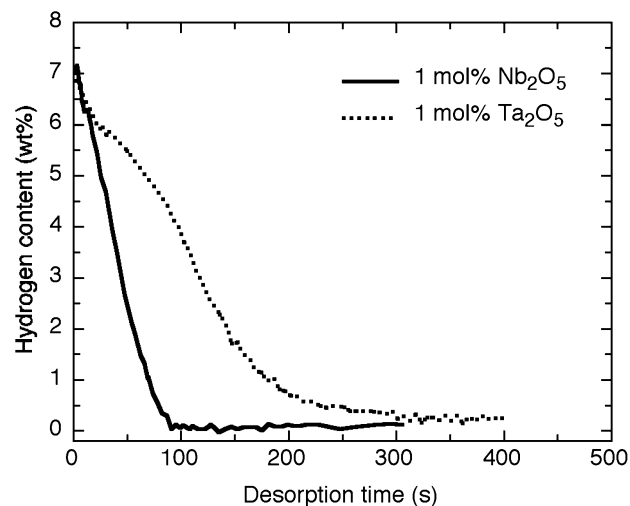
Figure 8. Desorption kinetics of magnesium hydride catalyzed with 1 mol % Ta_2O_5 and Nb_2O_5. The measurements were performed at 300 °C.

As the **third factor** for a transition-metal compound to be an effective catalyst, we therefore propose that the transition metal of the compound should have a high valence state.

3.2.4. Affinity of Hydrogen to the Transition Metal of the Catalyst Compound. The conclusion that hydrogen atoms interact with the transition-metal ions implies that stronger transition-metal−hydrogen reaction energies will improve the catalytic activity. To test this hypothesis, desorption kinetics of magnesium with Nb_2O_5 and Ta_2O_5 are investigated and the results of desorption experiments are compared in Figure 8. The reaction rate using Nb_2O_5 is significantly higher than that for Ta_2O_5. As the thermodynamic stability of both is almost equal and the valence state is identical, this difference is mainly attributed to the stronger interaction of niobium with hydrogen.

Therefore, we propose as the **fourth factor** for a transition-metal compound to be an effective catalyst that the transition metal of the compound should have high interaction energy with hydrogen.

3.3. Proposed Mechanism. On the basis of the above discussion, the following mechanisms are proposed for the transition-metal-based catalysts for the magnesium hydrogen reaction:

In the case of absorption, hydrogen molecules are dissociated (chemisorbed) mainly on the transition-metal ions of the catalysts, with the formation of a hydrogen–transition-metal bond. The ability of the transition-metal ions to have multiple valence states allows them to easily dissociate hydrogen molecules and pass hydrogen atoms to the near magnesium atoms, where a magnesium hydride is then formed. The transition-metal ion can then dissociate another hydrogen molecule from the gas phase. This process decelerates due to slow diffusion of hydrogen through magnesium hydride and is therefore usually not observed to be the rate-limiting step of absorption kinetics for catalyzed nanocrystalline magnesium. Nevertheless, an improved catalytic activity increases the gradient in the chemical potential of hydrogen within the hydride phase, which accelerates the diffusion of hydrogen and formation of the hydride phase. Therefore, the kinetics of absorption is also influenced by the appropriate choice of catalyst.

During desorption, magnesium hydrogen bonds are thermodynamically unstable, leading to dissociation of magnesium hydride. Since the diffusion of hydrogen through magnesium is relatively fast, hydrogen atoms reach the surface of particles rapidly. The transition-metal ions of the catalysts then form a bond with hydrogen atoms, these act as an intermediate state which allows easier recombination of hydrogen atoms toward the molecular state.

In general, the main catalytic role is played by the transition-metal ions of the catalysts and their ability to form hydrogen bonds with different stoichiometries, providing a fast route for the dissociation of hydrogen molecules or recombination of hydrogen atoms. Anions, like oxygen, carbon, and halogenides, tailor the electronic structure of the transition-metal ion; they are essential for the catalytic behavior. In addition, the interaction with the magnesium substrate and the defects of the catalyst's surface alter the electronic structure and influence the ability of the transition-metal ion to form hydrogen bonds.

Regarding their catalytic activity for other hydrides, similar improvements may be expected, if the rate-limiting reaction step is chemisorption of hydrogen. However, the interaction of the catalyst compound with the particular hydride will have to be evaluated individually, according to the second factor of this study.

4. Conclusions

The sorption behavior of magnesium-based hydrides can be improved by small amounts of suitable transition-metal compounds acting as catalysts. A substantial increase is particularly achieved for the desorption of hydrogen, which was one of the crucial constraints with respect to technical applications of lightweight metal hydrides. An analysis of desorption kinetics was able to determine the critical kinetic step of the reactions

in different temperatures and catalyst contents. As a result, it could be concluded that effective catalysts promote chemisorption, that is, the recombination of hydrogen atoms to form the hydrogen molecule.[4]

To investigate the mechanisms by which the transition-metal compounds act as effective catalysts for chemisorption of hydrogen, detailed and relevant experiments have been performed. Four distinct factors are proposed for the transition-metal compound to be an effective catalyst: a high number of structural defects, a low stability of the compound, which, however, has to be high enough to avoid complete reduction of the transition metal under operating conditions, a high valence state of the transition-metal ion within the compound, and a high affinity of the transition-metal ion to hydrogen.

As quantified in Table 1, the catalytic activity is substantially influenced by each of the four factors individually. It is also evident from experiments that when one factor is fulfilled, an even improved catalytic activity can be achieved by satisfying the other factors.

On the basis of the factors discussed in this paper, further optimization of catalysts for improving the sorption properties of magnesium-based hydrides in view of a technical application could be possible. In addition, it becomes obvious that whenever chemisorption is a crucial step for the sorption behavior of reversible hydrogen storage materials, small additions of transition-metal compounds satisfying the proposed factors above may improve the technical performance.

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