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Effect of Nb_2O_5 content on hydrogen reaction kinetics of Mg

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Abstract

The effect of Nb_2O_5 concentration on the kinetics of the magnesium hydrogen sorption reaction at 300 °C and 250 °C is investigated. Absorption and desorption kinetics of nanocrystalline magnesium catalyzed with 0.05, 0.1, 0.2, 0.5, and 1 mole% Nb_2O_5 are determined at 300 and 250 °C. Fastest kinetics are obtained using 0.5 mole% Nb_2O_5. At 300 °C, absorption and desorption of 7 wt.% of hydrogen are facilitated in 60 and 90 s, respectively. At 250 °C, more than 6 wt.% are absorbed in 60 s and desorbed again in 500 s. Respective reaction rates and activation enthalpies are calculated. The activation energy for desorption varies exponentially with Nb_2O_5 concentration and reaches a limit of 61 kJ/mole at 1 mole%. The rate-limiting step for a particular parameter set is deduced by fitting the experimentally obtained transformed phase fraction and time data with analytical kinetics rate expressions. The results show that there is a change in the rate-limiting step with catalyst content.

Keywords: Hydrogen absorbing materials; Metal hydrides; Gas–solid reactions; Kinetics

1. Introduction

Hydrogen is the ideal means of storage, transport and conversion of energy for a comprehensive clean-energy concept. Regarding the use of hydrogen as fuel for the zero-emission vehicle, the main problem is the storage of hydrogen. Metal hydrides offer a safe alternative to storage in compressed or liquid form. In addition, metal hydrides have the highest storage capacity by volume. Mg hydride has also a high storage capacity by weight and is therefore favored for mobile applications. However, light metal hydrides have not been considered competitive because of their rather sluggish sorption kinetics. Filling a tank could take several hours.

In recent years, significant progress has been made using nanocrystalline Mg produced by high energy milling [1–8] and adding suitable catalysts [9,10]. For technical application, sufficiently fast kinetics have been achieved at 300 °C [11]. Among the catalysts used in different studies, transition metal oxides show a high potential [9–11]. In addition, oxides are cheap, and amounts as low as 0.2 mole% already have a substantial effect, thus capacity is only slightly reduced.

In a previous paper [11], the superior catalytic effect of Nb_2O_5 was demonstrated and compared to other metal oxide catalysts. In the present study, the influence of Nb_2O_5 content on the hydrogen sorption kinetics of magnesium is investigated, at reaction temperatures of 250 and 300 °C. The final goal is to identify the optimum amount of catalyst, which is required to guarantee superior kinetics, while giving maximum reversible storage capacity. Different amounts ranging from 1 down to 0.05 mole% are investigated. The rate-limiting step for transformation kinetics is determined by fitting various analytical kinetic rate expressions to the obtained experimental data.

2. Experimental

The initial MgH_2 powder was purchased from Goldschmidt AG, with 95% purity, the rest being magnesium. Milling was carried out in a Fritsch P5 planetary ball mill and a ball to powder weight ratio of 400 g/40 g. In the first phase, this powder was milled for 20 h, yielding a homogeneous brownish colored magnesium hydride powder. Afterwards, 0.05, 0.1, 0.2, 0.5, and 1 mole% Nb_2O_5

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were added to the milled magnesium powder and the mixture was milled for additional 100 h. Kinetics were characterized at 250 or 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 [12]. All milling experiments, preparation and transfer for characterization has been done under argon atmosphere to exclude any contact of the powder with ambient air. The reaction rates were calculated using the time and hydrogen content values between 20 and 80% of the respective maximum capacity.

3. Results

Fig. 1 shows the first 60 s of absorption of magnesium with different Nb_2O_5 contents at 300 °C and 8.4 bar hydrogen pressure. Although differences are rather small, absorption kinetics is slightly better using higher Nb_2O_5 content. In general, about 7 wt.% of hydrogen is absorbed within 1 min.

Differences in the desorption kinetics are more pronounced (Fig. 2). In general, an increase of Nb_2O_5 content again has a positive effect on desorption kinetics. However, a saturation limit is reached for 0.5 mole% of Nb_2O_5, and kinetics does not accelerate further, if more catalyst is present. With 0.5 mole% Nb_2O_5, magnesium hydride desorbs the full 7 wt.% of hydrogen within 90 s. To our knowledge, this is the fastest desorption kinetics for magnesium hydride reported so far.

It is worth noting that low catalyst contents also have a significant effect on kinetics: e.g. with only 0.1 mole% Nb_2O_5, full desorption takes place in 240 s. Even using only 0.05 mole% of Nb_2O_5, full desorption is possible within 500 s.

Similar results are obtained at 250 °C (Figs. 3 and 4). Absorption kinetics is almost independent of the amount of

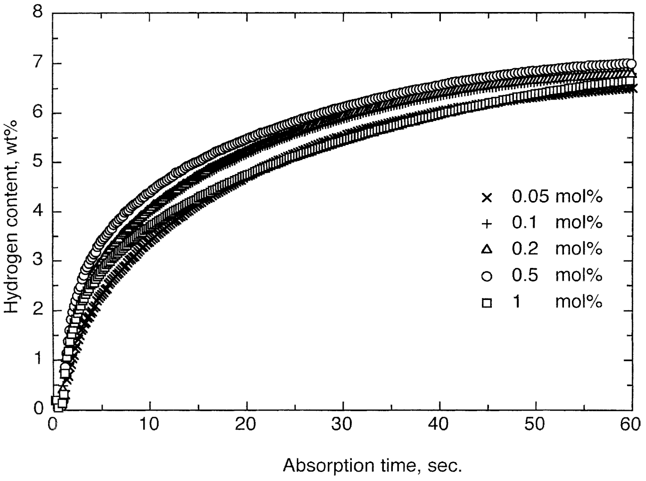

Fig. 1. Effect of Nb_2O_5 concentration on absorption kinetics of magnesium at a reaction temperature of 300 °C and a hydrogen pressure of 8.4 bar.

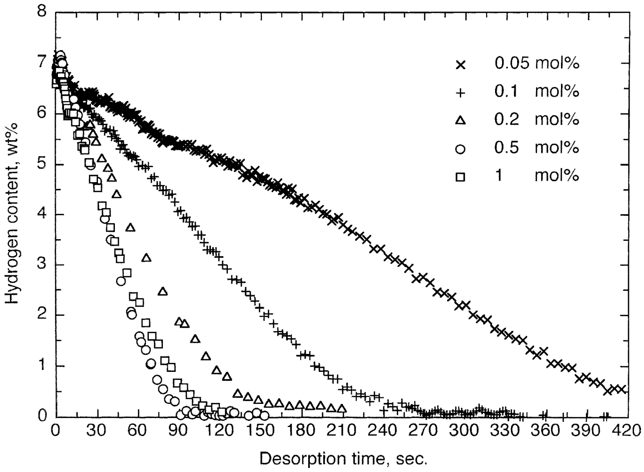

Fig. 2. Effect of Nb_2O_5 concentration on desorption kinetics of MgH_2 at a reaction temperature of 300 °C and under vacuum conditions.

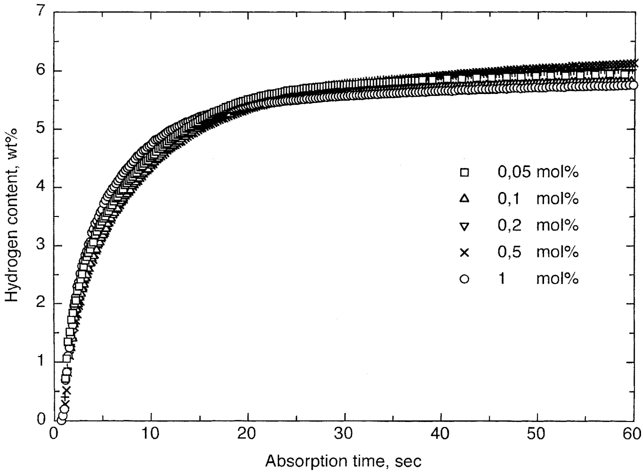

Fig. 3. Effect of Nb_2O_5 concentration on absorption kinetics of magnesium at a reaction temperature of 250 °C and a hydrogen pressure of 8.4 bar.

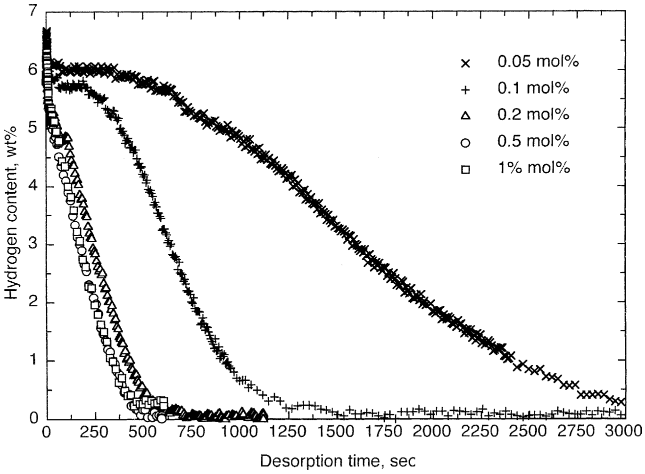

Fig. 4. Effect of Nb_2O_5 concentration on desorption kinetics of MgH_2 at a reaction temperature of 250 °C and under vacuum conditions.

Table 1
Reaction rates calculated between 20 and 80% of maximum capacity

Nb_2O_5 mole% (mole%)	Absorption rate at 250 °C (wt.%/s)	Absorption rate at 300 °C (wt.%/s)	Desorption rate at 250 °C (wt.%/s)	Desorption rate at 300 °C (wt.%/s)
0.05	0.23	0.146	0.00269	0.0157
0.1	0.3	0.152	0.00841	0.03132
0.2	0.3146	0.185	0.01154	0.05
0.5	0.38	0.205	0.0137	0.102

catalyst used, and even 0.05 mole% leads to fast absorption of about 6 wt.% of hydrogen within 1 min.

Desorption kinetics are again more critical and the optimum kinetics are achieved with catalyst contents of 0.5 or 1 mole%. Analogous to the results at 300 °C, the desorption curve for 0.2 mole% Nb_2O_5 is only slightly slower by about 20%. All reaction rates are listed in Table 1 for quantitative evaluation. Compared to other catalysts [13], Nb_2O_5 is superior also at 250 °C for both absorption and desorption.

4. Discussion

The results demonstrate that even small amounts of oxide catalysts result in a large improvement of the reaction kinetics.

The calculated kinetic rates in Table 1 show that the absorption rate at 250 °C is nearly two times faster than at 300 °C, independent of the catalyst content. This result can simply be explained by the higher thermodynamic driving force for the absorption reaction at lower temperatures at identical hydrogen pressures, according to the Van ‘t Hoff equation. This is a further proof that the kinetic barriers are efficiently reduced by Nb_2O_5 additions. Thus, the activation energy is lower and the barriers can be overcome also at lower temperatures. Consequently, the influence of the thermodynamic driving force increases and the reaction rate at 250 °C is faster than at 300 °C.

Compared to studies using pure metal catalysts [13], striking differences are observed with respect to the amount of catalyst required for equally fast kinetics. For full desorption within 250 s at 300 °C, 5 mole% of pure Nb is necessary, whereas only 0.1 mole% of Nb_2O_5 is sufficient to desorb even more hydrogen in the same time. At first glance, this already proves that the catalytic effect of the metals in a pure state is much weaker than in form of the respective oxide. However, the question may be posed, whether pure metallic Nb is catalytically active at all. Considering the high affinity of niobium to oxygen, it may be reasonable to conclude that at least a large part—if not all—of the reported catalytic effect of pure metals is due the presence of oxides in the samples. If one assumes, that the Nb used in other studies has technical purity, i.e. the material contains about 1 wt.% oxygen, an amount of 5 mole% Nb would include 0.0581 mole% of Nb_2O_5. In addition, if the catalytic effect of pure metals is studied, special care has to be taken not to expose the specimen to ambient air at any time, otherwise the formation of additional oxides can not be excluded. In this regard, it is also worth noting that not only oxides but also nitrides show a good catalytic effect [10], which may add to the observed catalytic effect, if commercially pure metals are used.

In one of our previous studies [10], we have already shown that V_2O_5 has a catalytic effect, while ultrapure V, processed in parallel under the same conditions under purified argon atmosphere, only shows a rather small influence. What is even more striking: if the MgH_2 milled with ultrapure metallic V is exposed to limited amounts of air, kinetics significantly improve [10]. Obviously, oxygen (or nitrogen) does indeed play a role in the catalysis of the sorption reaction.

In order to elucidate the mechanism of catalysis of transition metal oxides, tentative activation energies for the desorption reaction of magnesium catalyzed with different Nb_2O_5 contents are calculated using the kinetic rate constants at the two different temperatures (Fig. 5). Obviously, the activation energy varies exponentially with the Nb_2O_5 content and reaches a limit of 62 kJ/mole at 0.2 mole% Nb_2O_5. As will be discussed in the next paragraph, this can be explained by a change in the rate-limiting step of the desorption kinetics. The calculated value of 62 kJ/mole is in good agreement with the results for pure metallic Nb [13], where an activation energy of 64 kJ/mole was determined. This may be taken as a further indication that identical phases are present and identical processes take place.

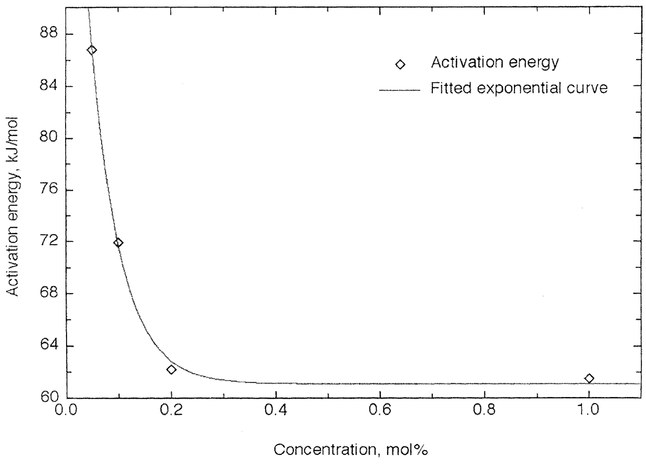

Fig. 5. Variation of the activation energy for the desorption reaction with Nb_2O_5 content.

Table 2
Rate limiting step in desorption reactions with various Nb_2O_5 concentrations

Used kinetic equation	Best fit found for reaction	Rate limiting step
$1-(1-\alpha)^{1/2} = kt$	At 250 °C and 0.2 mole% At 300 °C and 0.2 mole% At 250 °C and 0.5 mole% At 300 °C and 0.5 mole% At 250 °C and 1 mole% At 250 °C and 1 mole%	Interface controlled
$[-\ln(1-\alpha)]^{1/2} = kt$	–	–
$1-(2\alpha/3)-(1-\alpha)^{2/3} = kt$	–	–
$\alpha = kt$	At 300 °C and 0.05 mole% At 300 °C and 0.1 mole%	Surface controlled
$[-\ln(1-\alpha)]^{1/3} = kt$	At 250 °C and 0.05 mole% At 250 °C and 0.1 mole%	Three dimensional growth controlled

The reaction of metallic elements with hydrogen consists of five distinct steps, physisorption, chemisorption (recombination), surface penetration, diffusion, hydride formation (decomposition). 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. The kinetic curve at each step has a characteristic form, which can be formulated as equations relating the transformed phase fraction to time. Thus, it is possible to deduce the rate-limiting step of the kinetics, if a good fit of experimental data with a specific kinetic equation can be obtained. Using the above mentioned method, the rate limiting step of the reactions for different Nb_2O_5 contents are identified and the results are listed in Table 2. In detail, the results can be interpreted as follows:

1. At 250 °C and with catalyst contents lower than 0.2 mole%, the reaction is three dimensional growth controlled. This can be explained by the slower diffusion at this low temperature, as well as the slow hydrogen draining due to a lack of catalyst and longer diffusion paths.
2. At 250 °C and with catalyst contents above 0.2 mole%, the recombination rate is high enough and the kinetic rate-limiting step is changed to interface-controlled. As the Nb_2O_5 content increases, the catalytic effect reaches a limit at 1 mole%, see Figs. 3 and 5, because the recombination rate of hydrogen atoms is not the rate determining step anymore.
3. For a reaction temperature of 300 °C, with a catalyst content lower than 0.2 mole%, the kinetic is clearly surface controlled. Due to easier diffusion of hydrogen atoms at 300 °C, transport of hydrogen does not play an important role anymore. Now, the reaction rate is only determined by the slow gas–solid reaction due to the low catalyst content.
4. Again at 300 °C, if the catalyst content reaches values of 0.2 mole% or more, the recombination rate of hydrogen atoms increases up to a limit, where it is not rate-determining anymore and the reaction becomes interface controlled again.

At both temperatures investigated, i.e. at 250 and at 300 °C, the rate-limiting step changes for catalyst additions of around 0.2 mole%. However, at 250 °C, the rate-limiting process changes from ‘nucleation and growth’ to ‘interface-controlled’, while at 300 °C, rate-limiting process changes from ‘surface-contolled’ to ‘interface-controlled’. The change in the rate-limiting process at 0.2 mole% catalyst is in good agreement with the saturation in activation enthalpy (Fig. 5).

5. Conclusion

The effect of Nb_2O_5 catalyst concentration on the kinetics of hydrogen sorption reaction of nanocrystalline Mg is investigated at 250 and 300 °C. Fastest kinetics are obtained using 0.5 mole% Nb_2O_5. At 300 °C, absorption and desorption of 7 wt.% of hydrogen are facilitated in 60 and 90 s, respectively. At 250 °C, more than 6 wt.% is absorbed in 60 s and desorbed again in 500 s. Absorption kinetics are nearly independent of the catalyst content, even 0.05 mole% Nb_2O_5 yield the full hydrogen absorption of 7 wt.% within 60 s. Tentative activation energies for different catalyst contents were calculated, and it was found that the activation energy decreases exponentially with catalyst additions, reaching the lower saturation limit of 61 kJ/mole at 0.2 mole%. For this catalyst content, a change in the rate-limiting process was detected by fitting the experimentally transformed fraction and time data using analytical rate expressions.

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