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# Catalytic activity of noble metals promoting hydrogen uptake

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**Abstract**

The engineering of pure and metal alloy catalysts for hydrogen absorption is needed to improve the kinetics of hydrogen-related devices. We introduce a new route to search for alloys that can yield superior catalytic behavior for hydrogen absorption, using an optical technique to measure the catalytic activity for hydrogen sorption of thin films. The catalytic activity of the noble metals Pd, Ni, Cu, Ag, Pt, and Au is studied as a function of hydrogen pressure and temperature. The rate-limiting step is identified by the pressure dependence and the normal isotope effect for hydrogen absorption. The measured rates and activation energies are correlated to such physical properties as activation barrier for dissociation and heat of solution. The observed compensation effect is explained in the framework of interplay between surface and bulk processes. From the experimentally derived model, a guiding principle for the search for catalysts promoting hydrogen absorption is drawn.

*Keywords:* Hydrogen storage; Kinetics; Hydrogenography; Noble metal catalysts; Heat of solution; Hydrogen dissociation

## 1. Introduction

Limited energy resources and increasing pollution associated with classical energy production have stimulated the search for cleaner, cheaper, and more efficient energy technologies. One promising technology involves hydrogen that can be used in fuel cells stored in metal hydrides and switchable mirrors for smart window coatings [1,2]. An important issue of these systems is hydrogen uptake kinetics.

Hydrogen absorption in metal hydrides involves two main steps [3]: dissociation of the hydrogen molecule and transport of the chemisorbed hydrogen toward the subsurface and adjacent diffusion in the bulk (see Fig. 1). According to diffusion data, hydrogen transport inside metals or metal hydrides (with the important exception of $MgH_2$ [4]) is fast enough to provide high hydrogen absorption and desorption rates at room temperature. However, in most systems only slow rates are observed, which is one clue that the *surface properties* of the metal grains determine their H sorption kinetics, that is, the dissociation of the hydrogen molecule [3,6].

Nonetheless, surface and bulk processes are not completely decoupled, because the number of free active sites for dissociation at the surface depends also on the concentration of hydrogen in the bulk [7,8].

Several empirical studies have advanced the possibility of enhancing hydrogen uptake kinetics by special additives (catalysts) to the metal hydride system. For instance, the kinetics of hydrogen sorption in Mg-based storage devices is greatly enhanced by such additives as transition metal oxides [9], and without a Ti catalyst, reversible hydrogen sorption is impossible in alanates [10]. Sensors [11] and hydrogen-switchable mirrors [2] use Pd as a catalytic cap layer, whereas Pt is usually used for hydrogen dissociation in fuel cell electrodes [12]; however, principal fundamental relations for the rational design of catalysts for hydrogen absorption remain under discussion.

In contrast to the enormous body of empirical knowledge and fundamental principles of catalysis and catalysts frequently used in chemistry [13–15], relatively little attention has been given to catalysis for the absorption of hydrogen. The general mechanism of catalysis implies that catalyst and reactant form an intermediate state, whose binding energy is smaller and the formation rate is faster compared with the noncatalyzed (final)

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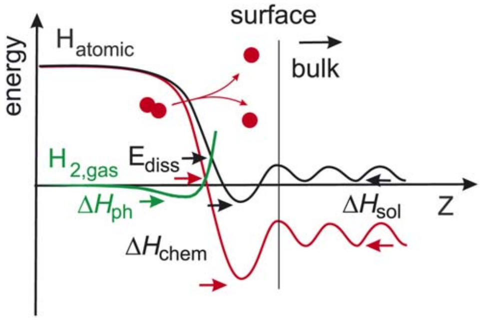

Fig. 1. Characteristic solid–gas interaction steps pictured by the dependence of the potential energy on distance $z$ from surface for two different metals with a positive (black line), and negative (red line) heat of solution $\Delta H_{\mathrm{sol}}$. Intuitively, there may exist a correlation between the heat of solution and the barrier height of dissociation, i.e., a high negative heat of solution corresponds to a small dissociation barrier $E_{\mathrm{diss}}$. This is indeed empirically found within a similar group of materials (Brønsted–Evans–Polanyi (BEP) relation).

reaction. It was already found in the 1930s that for electrocatalysis of hydrogen, there is an empirical relationship between the stability of the intermediate state and the rate of the reaction (here the chemisorption energy $\Delta H_{\mathrm{chem}}$ and exchange current $i_0$, respectively) [16]. The plot of the logarithmic rate versus the chemisorption energy usually leads to the so-called "volcano curve." This curve is characterized by a linear *increase* of the logarithmic rate with increasing chemisorption energy up to an optimum, after which the logarithmic rate *decreases* linearly. Similar behavior is found for many catalyzed reactions in chemistry [18]. The reason for this is that a chemical reaction at a surface has two main parts: the dissociation of the reacting molecules and the removal of the dissociation products. The rate of dissociation is determined by the activation barrier for dissociation, $E_{\mathrm{diss}}$, whereas the rate of product removal is given largely by the stability of the intermediates on the surface [13]. It has been found that the dissociation barrier and the interaction strength are often linearly correlated, through the Brønsted–Evans–Polanyi (BEP) relation [13,15,19]. The search for a catalyst with intermediate interaction strength, also known as the Sabatier principle [17], leads directly to a volcano curve with maximum rate at intermediate bonding enthalpy [16].

Transferring this principle, a good catalyst for hydrogen absorption is characterized by a low dissociation barrier and weak bonding of the intermediates. But what are these intermediates and what determines their interaction strength with hydrogen and the height of the dissociation barrier? Because the chemisorption enthalpy $\Delta H_{\mathrm{chem}}$ is normally the strongest interaction (compare Fig. 1), we would expect it to be the rate-determining parameter for hydrogen uptake, and thus a linear relation between uptake rate $\ln R$ and $\Delta H_{\mathrm{chem}}$ in the first half of the volcano curve is deduced. Consequently, a promising catalyst promoting hydrogen uptake would be formed by materials with the appropriate surface properties [13,14].

To prove this hypothesis experimentally, we measured the catalytic activity of several noble metals and their alloys. We found a linear relation, not between $\ln R$ and chemisorption enthalpy, but rather between $\ln R$ and the *heat of solution* of hydrogen in the catalyst ($\Delta H_{\mathrm{sol}}$). Surprisingly, a *bulk* property seems to be rate-limiting, which seemingly implies that the critical intermediate state is hydrogen absorbed in the catalyst. Still other experimental results hint toward a more surface-controlled hydrogen uptake [6–8,20–22]. Apparently, the aforementioned considerations oversimplify the involved mechanisms; hence the need for a fundamental experimental investigation of catalysts promoting hydrogen uptake.

For this, we use an optical method to determine the effect of catalysts on the kinetics of hydrogen sorption. The method uses an indicator layer, whose hydrogen uptake can be optically monitored [22,23]. The metallic indicator layer has a high affinity for hydrogen but is not able to absorb it directly due to its nonactive oxide top layer. This thin oxide layer does transport hydrogen to the optically active indicator layer, once the molecular hydrogen is dissociated [3] by a catalyst (e.g., Pd clusters [6]). Various catalysts are deposited on the indicator layer and their catalytic effect is studied as a function of composition, temperature, and hydrogen pressure. The measured rates and activation energies are correlated with such physical properties as heat of solution and chemisorption enthalpy. We present a simple model for the catalyzed hydrogen uptake that incorporates both dissociation and absorption steps. From this analysis of the experimental results, we conclude that for high catalytic activity, we need materials that combine a small dissociation barrier $E_{\mathrm{diss}}$ with a small and negative heat of solution without exceeding the heat of formation/solution of the hydride.

## 2. Experimental

Polycrystalline Y, Au, Pt, Pd, Ni, Cu, and Ag are grown using DC/RF sputter sources on glass substrates. The argon pressure during sputtering is $10^{-2}$ mbar, and the background pressure is $<10^{-7}$ mbar. The indicator layer yttrium is surface-oxidized by exposing it to air for 2 min. The surface composition of the gradient film is determined by Auger electron spectroscopy.

Yttrium film is used as indicator for the H concentration, because yttrium displays large optical changes on hydrogen incorporation, or hydrogenography [2,22,23]. Pure yttrium and $YH_x$ with $x \leqslant 0.21$ ($\alpha$ phase) are shiny metals. The dihydride $YH_2$ ($\beta$ phase) is also metallic, but has a weak transparency at a photon energy of around 1.9 eV. $YH_3$ ($\gamma$ phase) is a large-gap semiconductor with a band gap of 2.68 eV [24]. This metal–insulator transition is followed as a function of time. The time evolution of the optical changes of such yttrium samples is monitored with a CCD camera using a macro-objective. The sample is exposed to hydrogen in a loading cell with optical windows that can withstand temperatures up to 300 °C in a hydrogen atmosphere at pressures up to 10 bar. The signal of the CCD camera is read out by a personal computer. The time evolution of the RGB signals during hydrogen absorption/desorption for each pixel is analyzed by means of the dedicated image processing software eescan. More detailed descriptions of this process are available elsewhere [21,22]. The time evolution of the optical changes of such yttrium samples is monitored with a CCD camera using a macro-objective. The sample is exposed to hydrogen in a loading cell with single-crystalline sapphire windows that can withstand temperatures up to 300 °C in hydrogen atmosphere at pressures up to 10 bar. The loading cell is placed in an oven to perform measurements at temperatures between room temperature and 300 °C. The camera and light source are placed outside the oven. The optical setup to measure catalytic activity is described more precisely elsewhere [22].

The time between the opening of the $H_2$ valve and the first maximum (corresponding to the infrared transparency window of the dihydride $YH_2$) is known as the switching time, $\tau$, of the film. We consider the switching time only within the $\alpha$ and $\beta$ phases, because the position of a maximum is better defined than the saturation level at the metal–insulator transition within the $\gamma$ phase ($YH_{3-\delta}$). Additional reasons are thermodynamic considerations (see below). The switching time is a measure for the average hydrogen uptake rate, $R$, of the yttrium film. Moreover, the hydrogen absorption kinetics can mathematically be modeled by assuming a Lambert–Beer-like law, a linear law for the change of the optical absorption, $Kd$, with hydrogen concentration, $x$, and a constant hydrogen flux, $\dot{x}$, into the yttrium [21,22]. Both the reciprocal value of $\tau$ and the logarithmic change of transmission can be taken as measures for the hydrogen uptake rate and thus also as measures of the catalytic activity of the cap layer. The analogousness of both methods has been proven previously [21], demonstrating also that the hydrogen uptake rate is indeed constant. In this paper we use $R \equiv 1/\tau$. The experimental error of such a (relative) rate measurement is $\Delta R/R \simeq 0.1$, due to uncertainties of the layer thickness and the error of optical measurements. The experimental error from these rate-determined apparent energies is approximately $\Delta E_{AA} \simeq 0.02$ eV.

The mechanism of catalysis implies that catalyst and reactant form an intermediate state with (i) a lower binding energy and (ii) a faster formation rate faster than that of the non-catalyzed (final) reaction. Condition (i) sets a first barrier for catalysis of hydrogen absorption; the heat of hydride formation of the catalyst must be less negative than that of the final hydride. By empirical measurements of the uptake rates of various catalysts, we quantify condition (ii) and therefore gain knowledge about the rate-limiting step and hence about the hydrogen absorption process itself. For that purpose, we work with the stable yttrium dihydride as the final hydride and the less stable hydrides of transition/noble metals as catalysts, thereby fulfilling the binding energy condition. The prerequisite for condition (ii) is given by artificially deactivating the yttrium by surface oxidation. Yttrium will take up hydrogen only via diffusion through its passivating oxide skin, once the hydrogen is dissociated by a catalyst [3,6]. This allows us to determine the relative hydrogen uptake rates of various catalysts deposited on the yttrium. The kinetics depends strongly on the surface modification, particularly the cap layer thickness [6,22,25]. However, after a steep increase in the rate with increasing thickness, the uptake rate changes only slightly. This saturation value is usually reached at thicknesses of about 10 nm and is interpreted as the "intrinsic" catalytic activity of a catalyst [6]. Accordingly, we use this cap layer thickness for measurement. Furthermore, effects impurity and oxidation effects also may need to be taken into account [3]. Oxidation as a possible explanation for the reduction of the catalytic effect of Ni was investigated previously [21]. Fortunately, only complete oxidation of Ni clearly reduces its catalytic effect. An accordingly small effect is expected for all metals with a heat of oxidation more positive than that of hydrogen ($\Delta H_{water} = -282\ kJ/mol_O$). This is the case for the elements investigated in the present study.

## 3. Results

In what follows, we present our results of experiments aimed at measuring trends in the hydrogen uptake rate catalyzed by various metals, determining the underlying rate-limiting steps, and quantifying their barrier heights.

### 3.1. Empirical Volcano curve

To gain first experimental insight into the origin of the uptake process, Fig. 2 shows the hydrogen uptake rate $R$ at 420 K and hydrogen pressure of 2 bar of an 130-nm-thick yttrium indicator layer catalyzed by several noble and transition metals. The catalytic effect decreases in the order Pd, Ni, Pt, Cu, Au, Ag. The rate, $R$, is plotted logarithmically against the heat of hydrogen solution, $\Delta H_{sol}$ (from [28]), and the heat of chemisorption, $\Delta H_{chem}$ (from [26]), of the corresponding catalysts. We find both a nearly linear relation between $\ln R$ and $\Delta H_{sol}$ and $\Delta H_{chem}$, respectively. The heat of chemisorption and solution are linearly correlated [35], so that a correlation of the heat of solution with any parameter will also be reflected in a correlation of the heat of chemisorption with that parameter. Fortunately, the correlation between heat of solution and heat of chemisorption has some exceptions; hydrogen binds stronger in the bulk to Pd than in the bulk to Ni and binds stronger on the surface of Ni than on Pd. However, Pd is the better catalyst, which underlines the better correlation of the catalytic activity with the heat of solution than the heat of chemisorp-

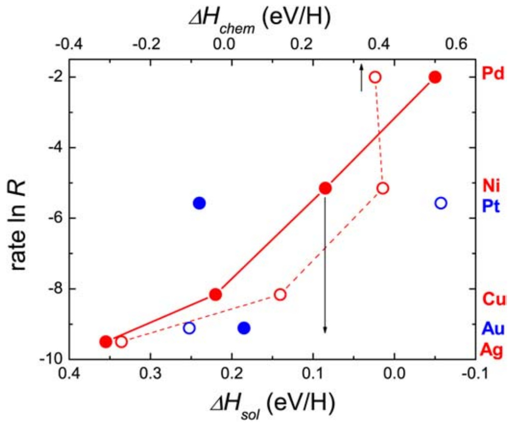

Fig. 2. Hydrogen uptake rate $R$ of a 130 nm thick yttrium film at 420 K and 2 bar hydrogen. The film is covered with the noble metals Pd, Ni, Cu, and Ag (red points) and Au, Pt (blue points) with a thickness of 10 nm. The logarithmic uptake rate $\ln R$ is compared to the heat of hydrogen solution $-\Delta H_{sol}$ (full circles) and to the heat of chemisorption $-\Delta H_{chem}$ (empty circles). A nearly linear relation is found between $\ln R$ and $\Delta H_{sol}$ with the exception of Pt and Au (the lines are a guide to the eyes). The color code used for the two classes of materials is preserved in subsequent figures.

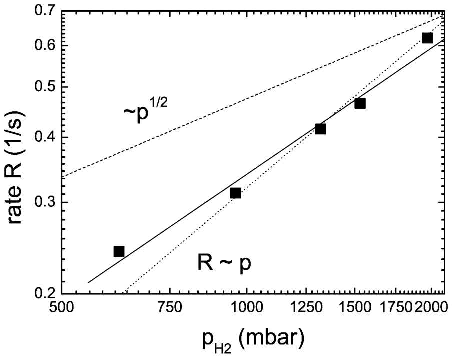

Fig. 3. Hydrogen absorption rate $R$ of Pd-capped yttrium film as a function of applied hydrogen pressure. The yttrium thickness is 150 nm, the Pd thickness is 10 nm. The experimental data (square) varies nearly linearly as expected for a dissociation limited process. For comparison we have also drawn the $p$ (dotted) and $\sqrt{p}$ (dashed) curves expected for a surface and diffusion limited process, respectively. The fitted slope (straight line) is $r \simeq 0.81 \pm 0.06$.

tion. The correlation is best for the 3d and 4d elements (plotted in red), with the 5d elements (Au, Pt, plotted in blue) deviating slightly. This is not too surprising, because the 5d elements do not obey the BEP rule either [13,15,19]. The better correlation of catalytic activity with the heat of solution is surprising; dependence on surface properties (i.e., a better correlation with the heat of chemisorption) might intuitively be expected (surface dissociation as the rate-limiting step).

Fig. 2 suggests that a high negative heat of solution is required for a high absorption rate. This is a first clue that Fig. 2 can be interpreted as the first half of the volcano curve for catalyzed hydrogen absorption, with hydrogen dissolved in the catalyst as the intermediate state.

### 3.2. Rate-limiting step

The rate-limiting step can be experimentally determined by probing the pressure dependence of the uptake rate. According to earlier work [7,27], the rate $R$ is proportional to $p - p_Y$, if dissociation is the rate-limiting step and diffusion processes are neglected. The plateau pressure $p_Y$ is around $10^{-9}$ Pa at room temperature [23] and thus can be set as zero. Consequently, the uptake rate is proportional to the applied pressure, which is frequently found in metal hydride systems [7]. To prove this for the investigated system, we plot the pressure dependence in a log–log plot (Fig. 3).

The additional lines refer to the kinetics that would be obtained for process purely limited by diffusion ($\propto \sqrt{p}$, dashed line) and purely surface limited ($\propto p$, dotted line). The linear fit reveals a slope slightly $<1$ (slope $r \simeq 0.81$). From this experiment, we can conclude that the hydrogen uptake is limited mainly by the surface reaction, but other effects influence the rate, too.

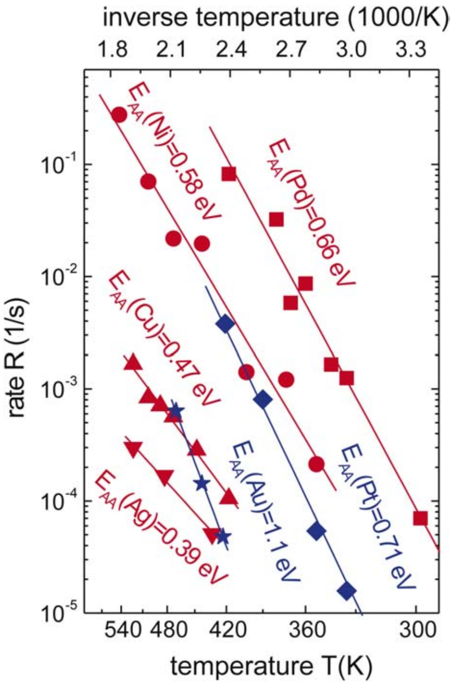

Fig. 4. Arrhenius plot of the hydrogen uptake rate of 130 nm yttrium films capped with the noble metals Pd, Ni, Cu, and Ag (red points) and Au, Pt (blue points) at constant pressure (2 bar). For each material the apparent activation energy as calculated from the slope of a linear estimation is given.

Whenever dynamical processes dominate the interaction, isotope effects can occur. These effects have been reported for H-binding energy, the dynamics of trapping and sticking, and diffusion [3,28]. An interesting phenomenon is the reverse-isotope effect observed in Pd. In this metal, the heavy deuterium (D) diffuses faster ($D_D^{Pd} = 5.61 \times 10^{-8}\ \mathrm{cm^2\,s^{-1}}$) than the hydrogen ($D_D^{Pd} = 3.76 \times 10^{-8}\ \mathrm{cm^2\,s^{-1}}$), whereas in Ni the effect is reversed and rather small, $D_H^{Ni} = 7.87 \times 10^{-11}\ \mathrm{cm^2\,s^{-1}}$, $D_D^{Ni} = 7.28 \times 10^{-11}\ \mathrm{cm^2\,s^{-1}}$ (all values for room temperature, as published previously [28]). When performing our experiments with $D_2$ and $H_2$, we find that at given temperature range

$$\left(\frac{R_{H_2}}{R_{D_2}}\right)^{Pd}_{T=300,\ldots,400\ \mathrm{K}} = 1.48 \pm 0.34$$

and

$$\left(\frac{R_{H_2}}{R_{D_2}}\right)^{Ni}_{T=360,\ldots,440\ \mathrm{K}} = 1.60 \pm 0.26.$$

The observed normal isotope effect both for Pd and Ni provides evidence that the diffusion inside the catalyst is not the rate-limiting step.

### 3.3. Determination of the activation energy

To determine the height of the activation barriers, we measured the hydrogen uptake rate at constant hydrogen pressure (2 bar) for various temperatures. The corresponding Arrhenius plots are shown in Fig. 4 for several transition metals. The values are well fitted with a linear function from which an apparent activation energy $E_{AA}$ is calculated:

$$R = R_0 e^{-E_{AA}/(kT)}. \tag{1}$$

We call the experimental activation energy $E_{AA}$ “apparent,” because it is not directly related to an actual microscopic activation barrier. This is nicely illustrated by the experimental

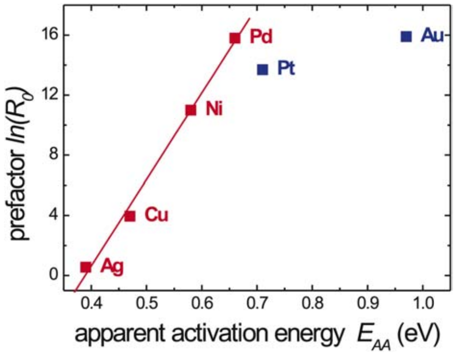

Fig. 5. Constable plot of the catalytic effect of noble metals Pd, Ni, Cu, and Ag. The prefactors $\ln R_0$ and apparent activation energies $E_{\mathrm{AA}}$ are calculated from the measurements shown in Fig. 4. The slope of the straight line is fitted to $m = 57\ \mathrm{eV}^{-1}$.

fact that high activation energy, which might intuitively be interpreted as a high activation barrier and hence a low rate, is found for systems with highest uptake rates (e.g., Pd). The latter can be indirectly demonstrated in a so-called "Constable plot" (Fig. 5), where the experimentally determined apparent activation energy is plotted as a function of the logarithm of the simultaneously calculated prefactor, $R_0$. The linear relation between $\ln R_0$ and $E_{\mathrm{AA}}$ is also known as the compensation effect (high activation energy corresponds to a high rate) [29]:

$$\ln R_0 = m E_{\mathrm{AA}} + c. \tag{2}$$

An explanation of the effect, which is generally observed in catalyzed reactions [18] as well as in bulk hydrides [30], is given in the next section.

## 4. Discussion

There is generally a good qualitative physical understanding of the various steps involved in hydrogen absorption and corresponding reaction mechanisms: physisorption, dissociation, chemisorption, subsurface penetration, subsurface occupation, bulk site occupation, and diffusion [3, pp. 33, 165; 31]. However, their relative importance for the hydrogen absorption process is still under discussion. The description so far treated the hydrogen uptake through the surface of a hydride-forming metal in the two-phase regime [3,27,31]. However, a catalyzed system consists of a hydride-forming metal (yttrium) covered by a metal catalyst. This scheme is illustrated in Fig. 6. Hydrogen is dissociated by the catalyst and subsequently diffuses through the catalyst, then through a thin oxide layer into the hydride. The corresponding energy potential surface is drawn. Energy minima represent stable states of hydrogen in matter (i.e., chemisorbed hydrogen, hydrogen dissolved in the catalyst, and the oxide and hydrogen in yttrium hydride). At these energy minima hydrogen is concentrated, resulting in locally enhanced hydrogen concentrations at surface and interface sites. The characteristics of the local hydrogen concentration are sketched in Fig. 6. First, we may assume that the two metals are in (quasi-) equilibrium, if we consider only dissociation as the rate-limiting step. Indeed, the measured isotope effect excludes a greater influence of the diffusion of hydrogen in the metal catalyst on the uptake rate. Similarly, one might argue that the (atomic) H diffusion in oxides is fast [3], and indeed no experimental evidence has been found for strong reduction of the hydrogen absorption through a thin oxide interface [34]. In equilibrium, the chemical potentials of the two layers are equal: $\mu_{\mathrm{H,cat}} = \mu_{\mathrm{H,Y}}$. Because the interface between catalyst and yttrium (the oxide) and also the diffusion inside the catalyst were not expected to be rate limiting, the chemical potential would remain nearly constant in nonequilibrium.

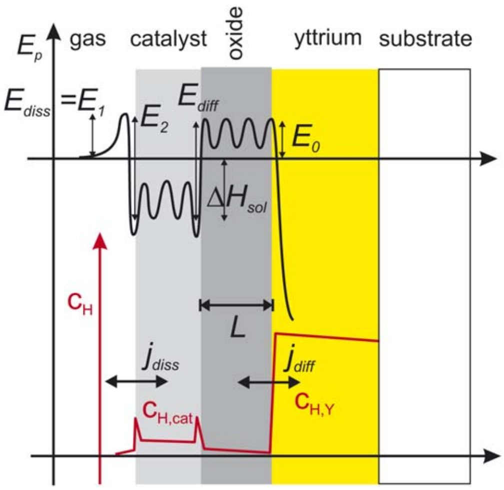

Fig. 6. (Top) Simplified potential-energy diagram for hydrogen activated by a catalyst placed on the oxide skin of a hydride forming metal. Hydrogen has to overcome the dissociation barrier at the surface ($E_1$), diffuses through the catalyst, the oxide interface, and finally through the hydride. See text for details. (Bottom) Concentration of hydrogen in the system.

But the interface does reduce the rate, particularly at high absorption rates. To account for these complications, we introduced a model considering two main steps: a surface barrier (barrier height, $E_1$) and an interface barrier (barrier height, $E_2$). We also consider only one intermediate state. Typically, the hydrogen concentration is locally enhanced at the surface due to adsorption. However, we assume that chemisorbed hydrogen is in quasi-equilibrium with bulk and thus set

$$\theta_{\mathrm{ch}} - \theta_0 \propto c_{\mathrm{H}}, \tag{3}$$

with $\theta_{\mathrm{H}}$ and $c_{\mathrm{H}}$ as the surface coverage by hydrogen and the hydrogen dissolved in the catalyst, respectively. $\theta_0$ includes details of the coverage dependence (e.g., number of required vacancies) and is neglected in subsequent equations. With this, the stability of the intermediate state is related to the heat of solution, not to the heat of chemisorption. This first-order approach is chosen to limit the number of parameters. The heat of chemisorption and solution are linearly correlated (compare Fig. 2; see also Ref. [35]), so that one common parameter might be sufficient to model the surface dependence. We take the heat of solution, because we find that it has a better correlation with catalytic activity (Fig. 2). Furthermore, we need this parameter to model the diffusion process. It is important to mention that this assumption may no longer be valid for extreme temperatures and/or very low pressures. The dissociation of one physisorbed hydrogen molecule ($H_2$(ph)) forms two chemisorbed hydrogen molecules (H(ch)),

$$H_2(\mathrm{ph}) + 2V \rightleftharpoons 2H(\mathrm{ch}) + V. \tag{4}$$

The number of physisorbed hydrogen is proportional to the applied pressure (known as the Henry isotherm). Here the theoretical minimum for dissociation is two vacancies per physisorbed hydrogen; however, previous investigators found experimentally [33] and theoretically [32] that dissociation is improbable for only two vacancies, and usually more free sites are involved. With equating coverage and concentration of hydrogen in the catalyst, the dissociation rate $j_{\mathrm{diss}}$ can be modeled by

$$j_{\mathrm{diss}} = Ap_{H_2} - Bc_H^2 \tag{5}$$

$$\text{with } A = a\mathrm{e}^{-E_1/kT},\ B = b\mathrm{e}^{-E_2/kT}. \tag{6}$$

The corresponding energies are defined in Fig. 6. The values $a$ and $b$ are temperature-independent parameters that correct the assumption of the impreciseness of Eq. (3). This also rules out coverage dependent changes (e.g., $\theta_0$) as we consider effective values for $a$, $b$, $E_1$, and $E_2$. Diffusion is assumed to occur only at the interface,

$$j_{\mathrm{diff}} = D\frac{\mathrm{d}c_H}{\mathrm{d}x} = c_H\frac{D}{L} = c_H\frac{D_0}{L}\mathrm{e}^{-E_{\mathrm{diff}}/kT}. \tag{7}$$

Here we neglect the possibility of diffusion in the reverse direction. This means physically that $p_{\mathrm{eq,Y}} = 0$, but describes well the situation with $YH_x$, which has a very low plateau pressure. Considerations of $p_{\mathrm{eq,Y}} \neq 0$, as illustrated in Fig. 6, will be published in a forthcoming paper. In steady state, $j_{\mathrm{diff}} = j_{\mathrm{diss}}$ and

$$Ap_{H_2} - Bc_H^2 = c_H\frac{D}{L}. \tag{8}$$

The rate, $R$, is proportional to the flux of particles injected into the indicator. Thus

$$R \propto c_H\frac{D}{L} \tag{9}$$

and

$$Bc_H^2 + \frac{D}{L}c_H - Ap_{H_2} = 0; \tag{10}$$

and we obtain

$$R \propto \frac{D^2}{2BL^2}\left(\sqrt{1 + 4\frac{ABL^2p_{H_2}}{D^2}} - 1\right). \tag{11}$$

At low pressures,

$$R \simeq \frac{D^2}{2BL^2}\left(\frac{1}{2}\frac{4ABL^2p_{H_2}}{D^2} + 1 - 1\right) = Ap_{H_2} \tag{12}$$

and the rate is proportional to the applied pressure $p_{H_2}$. In contrast, a small diffusion, $D^2 \ll ABL^2p_{H_2}$, leads to

$$R \propto \frac{D}{L}\sqrt{\frac{A}{B}}\sqrt{p_{H_2}}, \tag{13}$$

with the rate proportional to the square root of the applied pressure. The apparent activation energy is given by the following Eq. (1):

$$E_{AA} = kT^2\frac{\mathrm{d}\ln R}{\mathrm{d}T},$$

$$E_{AA} = 2E_{\mathrm{diff}} - E_2 + kT^2\frac{\mathrm{d}}{\mathrm{d}T}\ln\left(\sqrt{1 + 4\frac{ABL^2p_{H_2}}{D^2}} - 1\right). \tag{14}$$

With $\alpha = (4ABL^2p_{H_2})/D^2$, we obtain

$$E_{AA} = 2E_{\mathrm{diff}} - E_2 + (E_1 + E_2 - 2E_{\mathrm{diff}})\underbrace{\frac{\frac{1}{2}\alpha}{(1+\alpha) - \sqrt{1+\alpha}}}_{=r}. \tag{15}$$

The factor $r$ defines the regime of the system, that is, the change from a surface-limited to a diffusion-limited rate. It varies between $\frac{1}{2}$ for diffusion-limited rate ($D^2 \ll 4AL^2Bp_{H_2}$, i.e., $\alpha \to \infty$), and 1 for $\alpha = 0$ (i.e., a surface-limited rate). The corresponding apparent activation energies are then:

$$E_{AA}(\alpha = 0) = E_1,$$
$$E_{AA}(\alpha \to \infty) = \tfrac{1}{2}(E_1 - E_2) + E_{\mathrm{diff}}. \tag{16}$$

These values can also be evaluated directly from the estimates of the rates [Eqs. (12) and (13)]. Apart from the purely surface-limited case, the activation energy depends on the stability of the intermediate state in the catalyst, which enters $E_2$ and $E_{\mathrm{diff}}$ (see also Fig. 6).

In what follow, we apply this model on the present experimental results. The surface barrier, $E_1$, can be estimated by the dissociation barrier of the clean metals, $E_{\mathrm{diss}}$. It has been long realized that the dissociation energy and the interaction strength are often linearly correlated-for adsorption, in the BEP relation [13,15,19]. This relation is indeed found within a similar group of materials (red-colored triangles in the bottom graph). The correlation of the dissociation barrier height with the heat of hydrogen solution for Pd, Ni, Ag, and Cu (data for these elements plotted in red) reveals

$$E_1 \simeq E_{\mathrm{diss}} \simeq e_1\Delta H_{\mathrm{sol}}, \quad \text{with } e_1 = 3.0. \tag{17}$$

But this BEP relation is empirical, and thus exceptions must be expected (e.g., Au and Pt, always plotted in blue). Values for $E_{\mathrm{diss}}$ [15,36,37] and $\Delta H_{\mathrm{sol}}$ [28,38] are taken from the literature. Usually, hydrogen absorption takes place at relatively high pressures. Therefore, coverage of the surface by chemisorbed hydrogen is high, and, consequently, we have to consider an effective, probably higher dissociation energy. This has been proven for Pd surfaces in particular [32,33]. In a addition, we assume that $\Delta H_{\mathrm{phys}}$ is equal for all investigated metals and thus is neglected. With the BEP relation, Eq. (15) reveals some interesting consequences. All metal catalysts show a linear function of the uptake rate as a function of the heat of solution (Fig. 2) with the exceptions Au and Pt. The lower the heat of solution, the lower the dissociation energy and thus the higher the rate (holds both for the surface- and diffusion-limited regime). But this relation is not general; a high negative heat of solution also lowers the diffusion rate. Moreover, the measured activation energies do not fit the dissociation energies (Fig. 8).

The energy parameter for the back-reaction is $E_2 = E_1 - \Delta H_{\mathrm{sol}}$, the diffusion energy is $E_{\mathrm{diff}} = E_0 - \Delta H_{\mathrm{sol}}$ (see Fig. 6),

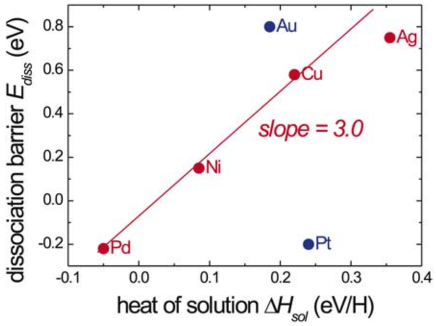

Fig. 7. Correlation between the heat of solution and the barrier height of dissociation, i.e., a high negative heat of solution corresponds to a small dissociation barrier $E_{\mathrm{diss}}$ (values from Refs. [15,36,37] and [28,38]). This is empirically found within a similar group of materials (red colored points). The blue colored points are exceptions from this rule, which is also known as the BEP-relation (red line), which gives $E_{\mathrm{AA}} \propto \Delta H_{\mathrm{sol}}$.

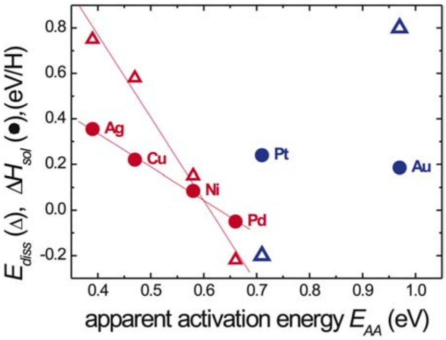

Fig. 8. Apparent activation energy $E_{\mathrm{AA}}$ as a function of the heat of solution $\Delta H_{\mathrm{sol}}$ (dots) and the activation barrier height for dissociation $E_{\mathrm{diss}}$ (triangulares).

and thus the apparent activation energy becomes

$$E_{\mathrm{AA}} = 2E_0 - 3\Delta H_{\mathrm{sol}} - r[2E_0 - \Delta H_{\mathrm{sol}}]. \tag{18}$$

Experimental measurements of $E_{\mathrm{AA}}$ revealed a linear function of the heat of solution $\Delta H_{\mathrm{sol}}$ (see Fig. 8),

$$E_{\mathrm{AA}} = e_a \Delta H_{\mathrm{sol}} + e_0, \quad \text{with } e_a \simeq -1.5. \tag{19}$$

Comparing the experimental apparent activation energies with Eq. (18) leads to the parameter $r \simeq 0.8$. Thus, the system is indeed in an intermediate state between the surface-controlled and diffusion-controlled regimes. Value $r$ might be interpreted as the "reaction order," which defines the concentration and pressure dependence for a chemical reaction [39,40].

This result can be generalized in the following way. We can calculate the pressure dependence by

$$\frac{\mathrm{d}\ln R}{\mathrm{d}p_{\mathrm{H}_2}} = \frac{\mathrm{d}\ln R}{\mathrm{d}\alpha}\frac{\mathrm{d}\alpha}{\mathrm{d}p_{\mathrm{H}_2}} = \frac{1}{p_{\mathrm{H}_2}}r. \tag{20}$$

Thus

$$r = \frac{\mathrm{d}\ln R}{\mathrm{d}\ln p}. \tag{21}$$

This means that the reaction order $r$ can also be determined by the pressure dependence of the absorption rate. The reaction rate $r$ obtained by the temperature dependence of the rate fits perfectly well to that derived by fitting the pressure dependence of rate (Fig. 3). At the same time, $r \simeq 1$ means that the absorption of hydrogen obeys nearly zero-order kinetics with respect to hydrogen concentration in the catalyst. In other words, the absorption rate is nearly constant, which is indeed observed (see Experimental section).

Another piece of evidence for the validity of this explanation is the measured isotope effect. We expect an isotope effect of the absorption rate due the pre-exponential factor for physisorption, if the surface reaction is rate-limiting: The pre-exponential factor $A_f$ depends on the hydrogen mass $m$, if thermodynamic equilibrium between free hydrogen gas and physisorbed hydrogen is assumed,

$$A_f \propto \frac{1}{m^{3/2}}. \tag{22}$$

This means that the rate of deuterium absorption should be lower than that of hydrogen by a factor of 2.83. Other factors (e.g., mass-dependent heat of solution, zero-point energies etc. [41]) could lower this ratio. The isotope effect through the oxide interface should be constant and $\propto \sqrt{2}$, if diffusion were rate-limiting [3]. We found a normal isotope effect both for Pd and Ni with $R_{\mathrm{H}_2}/R_{\mathrm{D}_2} > \sqrt{2}$, confirming that the intermediate lies between the surface and diffusion controlled regime.

Evidently, the transition from one regime to the other is continuous. Moreover, the underlying parameter $\alpha$ (i.e., the ratio of surface to diffusion rates) can be described as a function of the total rate, as the diffusion parameters are experimentally unchanged. A high rate corresponds to a diffusion-limited rate and thus a large $\alpha$ and thus $r \simeq \frac{1}{2}$). Accordingly, small rates represent the surface-limited regime. The important consequence is that $r$ depends on the absolute rate at which the system takes up hydrogen. Therefore, $\ln R_0$ is directly correlated to the regime in which the system is. That means that $E_{\mathrm{AA}}$ depends on the applied pressure and temperature and the specific diffusion process and is therefore not an intrinsic property of a catalyst. Experimental evidence for this is the Constable plot (Fig. 5), that is, $E_{\mathrm{AA}} = E_{\mathrm{AA}}(\ln R_0)$.

In fact, the compensation effect (i.e., that $E_{\mathrm{AA}} = E_{\mathrm{AA}}(\ln R_0)$) is a demonstration of the functioning of catalysis in general [18]. In heterogeneous catalysis for chemical reactions, the reaction rate depends on the dissociation of the reacting molecules *and* on the removal of the dissociation products [13,42]. Both processes compete with each other and the interplay is the origin of the compensation effect [18]. In our case, we also find that $E_{\mathrm{AA}}$ is a system-specific parameter and model it via the competition of two processes (dissociation and diffusion). For the mathematical description, we assumed an interface barrier to explain the varying chemical potentials. However, also without an interface, a "continuous" barrier due to diffusion inside the hydride will occur. Here, the mathematical description is more difficult (see, e.g., Ref. [43]). Nevertheless, the principle leading to a compensation effect remains valid and is therefore general in hydrogen absorption. The compensation effect has indeed been found in bulk hydrides [30], underlining the generality of our model.

How can we make use of the mathematical model to anticipate promising catalysts? Substituting $E_1 = E_{\mathrm{diss}}$ and $E_2 =$

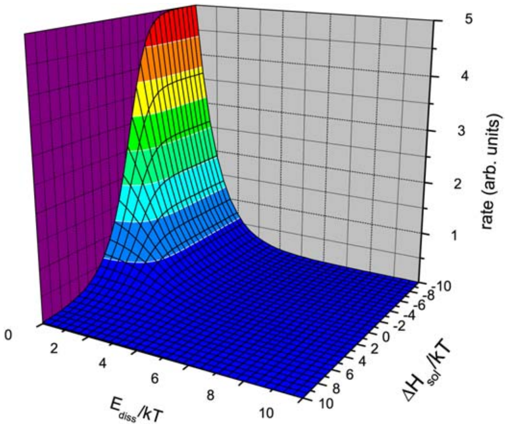

Fig. 9. Plot of Eq. (23) with the arbitrarily chosen value of the free parameter const. = 10. The figure makes immediately clear that for a high rate a small dissociation barrier $E_{\text{diss}}$ is favorable and that the heat of solution $\Delta H_{\text{sol}}$ should be small or negative.

$E_{\text{diss}} - \Delta H_{\text{sol}}$ in Eq. (11) and assuming $D$ to be constant, we obtain the following rate:

$$R \propto \mathrm{e}^{-\Delta H_{\text{sol}}/kT}\left(\sqrt{\mathrm{e}^{2E_{\text{diss}}/kT} + \text{const.}\mathrm{e}^{+\Delta H_{\text{sol}}/kT}} - \mathrm{e}^{E_{\text{diss}}/kT}\right). \tag{23}$$

This simplified rate equation, plotted in Fig. 9, shows that $R$ is a monotonically increasing function of $-\Delta H_{\text{sol}}$ and $-E_{\text{diss}}$. Evidently, good catalysts display a small dissociation barrier $E_{\text{diss}}$ together with a small and negative heat of solution $\Delta H_{\text{sol}}$. The importance of both parameters can also be demonstrated by the two limiting cases [Eqs. (12) and (13)]. In the purely surface-limited regime, the uptake rate $R$ is proportional to $\exp(-E_{\text{diss}}/kT)$. In the purely diffusion-limited regime, the uptake rate is $R \propto \exp(-\Delta H_{\text{sol}}/2kT)$. A real system will always lie in between. The two parameters are coupled only coincidentally for certain materials (with the BEP relation found empirically), allowing us to highlight the importance of the two conditions by experimental examples. The first condition (low $E_{\text{diss}}$) is demonstrated by the Pd–Pt couple (see Figs. 7 and 2). Hydrogen dissociation is nonactivated on both elements. Yet, due to the Pt's low solubility of hydrogen, its catalytic effect for hydrogen absorption is rather low, despite the fact that their apparent activation energies are nearly equal (see Fig. 8). In the Au–Cu couple, even though the solubility of hydrogen is higher in Au than in Cu, Cu is the better catalyst, because Au has a very high dissociation barrier (Fig. 7). Accordingly, gold has a higher activation energy than copper (Fig. 8).

For these noble/transition metals, $\Delta H_{\text{sol}}$ is the most important parameter most effectively depicted by a volcano curve (Fig. 2). This is true only if sufficient vacant chemisorption and physisorption sites are available on the surface. Accordingly, the catalytic effect will be eliminated if the number of available sites on the surface is drastically reduced by, for example, total oxidation of the metal. This means that the catalytic effect of oxides or similar compounds should display differing behaviors, because here the probability of finding a vacancy is the rate-limiting step for hydrogen absorption [44]. This was indeed found for the catalytic effect of Ni, which is strongly suppressed by the presence of (bulk) NiO [21]. Hence, for reactive materials, the coverage of the metals by contaminants has to be considered (poisoning). On the other hand, stable oxides like $Nb_2O_5$ may be considered as new materials, with their own intrinsic dissociation barrier and heat of hydrogen solution [9,45]. The advantage of the phenomenological model is that these compounds are equally treated as the measured noble metals, due to the use of effective parameters $a$, $b$, $E_1$, and $E_2$, which describe the interplay between a surface and a diffusion barrier. Even though the underlying physics will change (particularly the elementary steps), the model will remain applicable.

The principle presented here considers the promotion of hydrogen uptake. But this cannot be the only origin of the catalytic effect of, say, Ti catalyst catalyzing formation of the complex hydride $NaAlH_4$ [10,46,47]. Additional processes (e.g., phase formation, metal atom diffusion) need to be considered. Nonetheless, the active promotion of hydrogen dissociation remains mandatory.

## 5. Conclusions

Our novel optical technique allows measurement of catalytic activity for hydrogen sorption of thin films. We studied the catalytic activity of the noble metals Pd, Ni, Cu, Ag, Pt, and Au as a function of hydrogen pressure and temperature, and developed an analytic model to calculate the reaction order from experiment. The consistency of the isotope effect, the pressure and temperature dependence are posteriori evidences of the validity of our model. It confirms that the used dynamic equilibrium assumption is valid, confirming that the absorption of solved hydrogen obeys a nearly first-order kinetics with respect to the applied hydrogen pressure. In addition, we propose a principle for catalysts promoting hydrogen uptake: For a high catalytic activity, we have to search for materials, which combine a small dissociation barrier $E_{\text{diss}}$ with a small and negative heat of solution. This principle rationalize a number of known facts about catalysts for hydrogen absorption and points to new ways of improving them. In particular, we explain the observed compensation effect. It is a consequence of the change of the reaction order due to the varying relative importance of the diffusion and dissociation processes involved. The apparent activation energy depends on the applied pressure and temperature and the specific diffusion process and thus is not an intrinsic property of a catalyst. This should be taken into account when comparing activation energies obtained by different methods, particularly when comparing model catalysts at extreme temperatures and pressures with real-world systems.

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