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Hydrogen sorption mechanism of oxidized nickel clusters

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Using an optical technique to measure hydrogen sorption kinetics the catalytic activity of the NiO_x clusters is determined. The thus measured temperature dependence reveals an activation energy of 0.58 eV. The catalytic activity of NiO_x clusters is studied as a function of the oxygen concentration. The surface properties are analyzed by Auger-electron spectroscopy. It appears that the catalytic hydrogen sorption originates from the dissociative chemisorption of hydrogen on O:Ni, which is strongly suppressed by the presence of oxides. © 2004 American Institute of Physics.
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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 the hydrogen uptake kinetics. According to diffusion data, hydrogen transport inside metals or metal hydrides 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 hint among others that the surface properties of the metal grains determine their H sorption kinetics.³ Several empirical studies prove the possibility to enhance the kinetics by special additives ("catalysts") to the metal hydride system. Still, the exact role of the additive and the corresponding mechanisms remained unclear, which led to a controversial debate on the origin of the effect. In particular, the enhancement of the sorption kinetics in magnesium by adding transition-metal oxides is explained by a catalytic effect of the metal oxide surface,⁴ while other groups attribute the enhancement to a volume effect of the corresponding transition metal.⁵ The reason for this confusion is that nearly all hydride forming metals are usually covered with an oxide skin, if stored in air (for transition metals see Ref. 6, for rare earths see Ref. 7) or exposed to technical hydrogen with contaminants. This oxide layer impedes hydrogen absorption, if *all* dangling bonds of the surface are saturated.^{3,8,9} In fact, suboxide layers do not strongly influence the hydrogen sorption.⁸ However, it is not clear *a priori*, whether an oxide forms catalytically active suboxides during hydrogen exposure or not. For this, the particular energies of the involved elementary processes have to be measured.

In this letter, we demonstrate a unique 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.¹⁰ 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. On this layer various catalysts are deposited and their catalytic effect can be studied as a function of composition, thickness, temperature, and hydrogen pressure.

As a demonstration of this technique we investigate the catalytic effect of NiO_x clusters for hydrogen absorption. NiO_x is chosen as Ni and NiO are well-known catalysts for chemical synthesis.^{11–13} Their importance in the hydrogen uptake kinetics is reported for several intermetallic Ni compounds [e.g., LaNi_5 (3,14), Ni on Mg (15)], while it is still unknown, whether metallic Ni or oxidic NiO is catalytically active. We investigate the appropriate thermodynamic conditions for a fast sorption kinetics. We study the role of oxygen in the sorption process and show that the dissociative chemisorption of hydrogen on oxidized Ni clusters (O:Ni) is the rate determining step of the catalytic effect.

For these experiments polycrystalline Y, Ni, and NiO_x are grown using a dc sputtering system. The argon pressure is 10^{-2} mbar, the background pressure less than 10^{-7} mbar. The yttrium is surface oxidized by exposing to air for 2 min. The surface composition of the films is determined by Auger-electron spectroscopy (AES). Before analysis, the samples are transported in air and thus also metallic Ni clusters are surface oxidized. The optical set up to measure catalytic activity is described elsewhere.¹⁶ Yttrium films are used as indicator for the H concentration, as yttrium displays large optical changes upon hydrogen incorporation (see Refs. 2 and 10). Pure yttrium and yttrium with a hydrogen concentration $x_H \leq 0.21$ (α phase) are shiny metals. The dihydride YH_2 (β phase) is also metallic, but has a weak transparency at a photon energy around 1.9 eV (first maximum in Fig. 1).

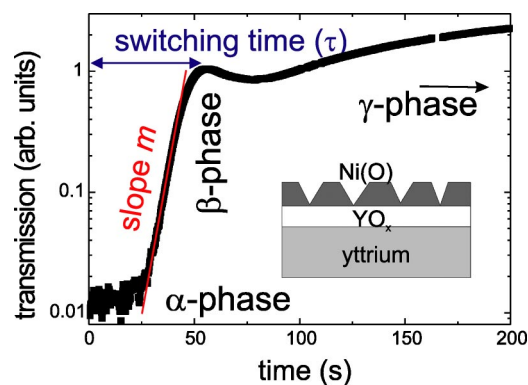


FIG. 1. Optical transmission of a 150-nm yttrium film capped with 5-nm Ni (sketched in the inset) during loading. The film is exposed to 2-bar hydrogen at 423 K at $t=0$. For $t < 2.5$ s the transmission lies in the noise level of the camera.

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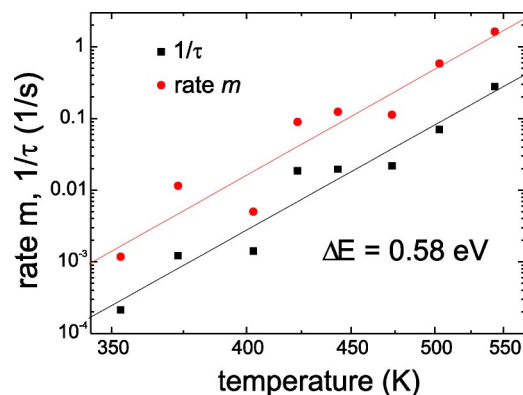


FIG. 2. Arrhenius plot of the reciprocal switching time $1/\tau$ and the slope m determined from temperature-dependent transmission measurements similar to that in Fig. 1.

YH_3 (γ phase) is an insulator with a band gap of 2.68 eV (Ref. 17) (maximum transmission in Fig. 1). This metal-insulator transition is observed in Fig. 1; it evidences the hydrogen uptake by yttrium and therefore the catalytic activity of the O:Ni cap layer. The time between the opening of the H_2 valve and the first maximum (corresponding to the infrared transparency window of the β phase) is defined as the switching time τ of the film. We consider only the switching within the α and β phases. Here, the dissociation pressure of YH_2 is lower than the used hydrogen pressure of 2 bar [$p_{\text{diss}} = 10^5$ Pa at 600 K (Ref. 18)]. The switching time is a measure for the average hydrogen uptake of the yttrium film. However, it does not inform us about the progression of the kinetics. There are no optical changes with hydrogen concentration within the α phase, while the transmission T increases exponentially with the formation of the β phase (see Fig. 1). This can mathematically be modeled by assuming a Lambert-Beer law, a linear law for the change of the absorption $k \cdot d$ with hydrogen concentration x_H and a constant hydrogen flux \dot{x}_H into the yttrium,

$$T = T_0 \cdot e^{-k(x) \cdot d}, \quad k(x) \propto -\dot{x}_H.$$

Indeed, the logarithmic transmission function in Fig. 1 is well fitted with a linear function within the mixed $\alpha + \beta$ state.

The switching process is strongly temperature dependent. For various temperatures, the corresponding slopes $m = d \ln T / dt$, i.e., the mass of the hydrogen flux $\dot{x}_H \propto m$, and the reciprocal switching times $1/\tau$ are plotted in an Arrhenius plot in Fig. 2. Both properties display an identical behavior, which proves a constant hydrogen flux from the beginning of hydrogen exposure, in particular during the α phase, which cannot be proven optically. The hydrogen flux, i.e., the catalytic activity of the cap layer, increases exponentially with temperature. The activation energy is 0.58 eV.

Since we are dealing with oxidized Ni clusters, the question arises of which role the thin oxide layer plays in the catalytic sorption process. The high activation energy could be due to the fact that the Ni surface is not purely metallic, but is covered with an oxide skin as deduced by AES measurements. Hence, we investigate the catalytic properties of Ni and NiO under the same conditions. A 5-nm NiO_x film with locally varying oxygen content was grown on top of a surface-oxidized 200-nm-thick yttrium film. The oxide gradient is realized by introducing 10^{-5} mbar oxygen through a tube towards one side of the 70-mm-long sample during Ni

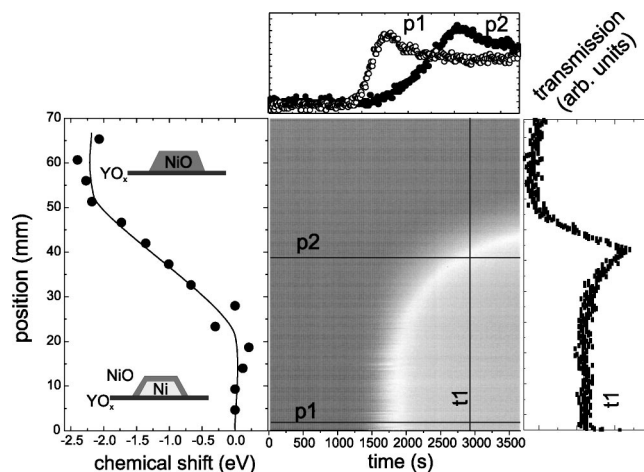


FIG. 3. Left: Chemical shift of the Ni LVV Auger line with respect to the O KLL line as a function of the location on a NiO_x gradient sample. The proposed structure of the NiO_x clusters is sketched. Right: Transmission of the corresponding sample (5-nm NiO_x on 150-nm surface oxidized yttrium) during hydrogen exposure at 2 bar, 403 K, as a function of location and time. Bright intensities display high transmission. Two representative linescans at fixed positions ($p1$, $p2$) and a linescan at fixed time ($t1$) are given for illustration.

sputtering at an argon pressure of 10^{-2} mbar. The determination of the oxygen concentration is very delicate since the clustered layer is too thin to use bulk methods [e.g., x-ray diffraction (XRD), Rutherford backscattering spectroscopy (RBS)]. Therefore, we use the chemical shift of the Ni LVV Auger line, which depends on the chemical state of Ni. The chemical shift of the Ni LVV line is measured with respect to the O KLL line. The chemical shift with respect to clean Ni is -5.4 eV for NiO .²¹ Since the sample is transported in air, the whole Ni layer is surface oxidized, while only the part grown near the oxygen outlet is fully oxidized. This is verified by the chemical shift shown in Fig. 3. A continuous shift of zero to -2.5 eV is measured. This is interpreted as the changing weights of two unresolved peaks of the chemical states (Ni, NiO), i.e., we are dealing with Ni clusters with a NiO skin to fully oxidized NiO clusters.

To correlate the amount of oxygen of the NiO_x clusters with their catalytic properties, the sample is exposed to 2 bar hydrogen at 403 K and simultaneously the transmission is recorded as a function of time and location. In Fig. 3, a vertical linescan through the grayscale image at a fixed position represents the optical transmission as a function of time at a given oxygen concentration. Thus, we are able to study the catalytic activity of the NiO_x clusters as a function of the oxygen content by measuring the time for the first appearance of substantial transmission (evolution of the dihydride phase, compare Fig. 1). Figure 3 clearly shows that an increase of the switching time (rise of the transmission) coincides with an increase of the estimated oxygen content, i.e., pure NiO clusters have a negligible catalytic effect. The fully oxidized NiO clusters only become catalytically active at higher temperatures, probably due to the formation of metallic Ni by the reduction of NiO by hydrogen.¹⁶

On clean Ni surfaces, the activation energy barrier for hydrogen to go from a surface site to a subsurface site is 0.74 eV.²⁰ The activation energy we observe for the hydrogen absorption process in $\text{Ni}/\text{YO}_x/\text{Y}$ equals 0.58 eV. This can be understood if we assume that only surface processes are involved, i.e., that hydrogen is adsorbed on Ni but not ab-

sorbed in bulk Ni. Indeed, we find that a coalesced Ni layer has a strongly reduced catalytic activity.¹⁶ Here, hydrogen has to diffuse through bulk Ni and has thus to overcome the much higher energy barrier from surface to subsurface sites of 0.74 eV. Therefore, a high catalytic activity is found for clusters, where hydrogen is adsorbed and delivered via surface diffusion towards the metal hydride (oxide). In fact, our measured barrier height of 0.58 eV coincides with the value 0.54 eV reported by Villarubia *et al.*¹⁹ for the energy barrier of the surface reduction process of oxidized Ni. They also found that the rate limiting step of the complex surface reduction process is the dissociative hydrogen adsorption on O:Ni (Refs. 19 and 22). Since the adsorption of hydrogen during the reduction process takes, preferentially, place on metallic Ni (Ref. 22), we conclude that the energy barrier for surface reduction also constitutes the energy barrier for hydrogen adsorption on O:Ni.

In conclusion, we have demonstrated the high catalytic activity of oxidized Ni clusters for hydrogen absorption. It originates from the dissociative chemisorption of hydrogen on metallic Ni, and is strongly suppressed by the presence of oxides. Still, a positive effect of oxygen impurities cannot be excluded, e.g., oxygen as a precursor on the Ni surface. NiO clusters do not show a substantial catalytic effect nor does bulk Ni. The last effect emphasizes the importance of nanocrystalline materials for hydrogen storage. Ni is only one possible catalyst. However, the optical indicator method is suitable for other promising materials, e.g., Nb₂O₅. Together with the proper surface analysis tools it provides us with a powerful method to improve old, and find new, catalysts for hydrogen sorption.

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