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Surface Reactivity of Nickel and Nickel Hydride Films as Catalysts in Parahydrogen Conversion

A. FRĄCKIEWICZ, M. POLESKI AND W. PALCZEWSKA

Department of Catalysis on Metals, Institute of Physical Chemistry, Polish Academy of Sciences, 01-224 Warszawa, Poland

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The kinetics of the parahydrogen conversion were studied on nickel and nickel hydride thin films as catalysts. The rate of conversion was measured by a conventional method from 1 to 30 Torr and from 165 to 195°K. The transformation of nickel into the hydride phase under the influence of atomic hydrogen was attested by observing the change of electrical resistance of the film. The transformation diminished 300-fold the rate of the *p–o* hydrogen conversion, due to a decrease in the preexponential factor of the Arrhenius equation. The results are in keeping with the poisoning effect of "hydride" hydrogen in nickel or palladium hydrides already reported in hydrogenation reactions. The effect is discussed in terms of the surface heterogeneity of the hydrided nickel film. Nickel crystallite patches which are not transformed into hydride are suggested to be responsible for the residual activity. The nickel hydride areas are catalytically inactive, which can be explained on the basis of earlier proposals that the metal *d*-band is filled by 1*s* electrons from hydrogen atoms.

INTRODUCTION

The elucidation of the mechanism of catalytic activity of metals in hydrogenation reactions is closely connected with the knowledge of the role played by hydrogen adsorbed on the catalyst surface. This hydrogen can either enhance or inhibit hydrogenation depending on the form in which it is present at the metal/reactants interface. Various authors have investigated the effect of the hydrogen preadsorption on the catalytic activity of nickel, palladium (or their alloys with the IB Group metals) in some test reactions involving hydrogen, usually in the para–ortho hydrogen conversion, hydrogen–deuterium equilibration, ethylene hydrogenation. However, there are many fewer data in the literature for the catalytic effect of hydrogen preabsorption in nickel or palladium resulting in the formation of the respective β hydride phases, in which hydrogen is placed in octahedral positions of the fcc parent metal lattice.

In the case of palladium the catalytic behavior of the hydride phase in the parahydrogen conversion was investigated by Scholten and Konvalinka (*1*), but the first report is due to Couper and Eley (*2*). A change in the catalytic activity of palladium and palladium–gold alloys (rich in palladium) ascribed to the respective hydride formation was observed by Dickens *et al.* (*3*) in the heterogeneous atomic hydrogen recombination. All the results pointed to the poisoning effect of "hydride" hydrogen.

This effect was confirmed in detailed studies on the catalytic activity of the β hydride phases of nickel and nickel–copper alloys in atomic hydrogen recombination (*4,5*) and ethylene hydrogenation (*5,6*). The present paper deals with investigations of the kinetics of the parahydrogen conversion catalyzed by thin films of nickel and nickel hydride. The preliminary results concerning the catalytic activity of a nickel–copper alloy film were reported earlier (*5*).

EXPERIMENTAL METHODS

Nickel Film Deposition

The films were deposited on the inner surface of a cylindrical Pyrex glass vessel (Fig. 1) of 3 cm diam sealed directly to a conventional high vacuum system. Before the nickel film deposition the nickel wire (spec. pure, manufactured by Johnson-Matthey) was well outgassed and the vessel was baked out in a vacuum of 10^{-6} Torr (1Torr = 133.3 N m^{-2}). During the metal deposition the temperature of the support was maintained at 77°K. The evaporation was carried out at the rate of 10–30 Å min^{-1}. The final nickel deposit was 200–400 Å thick. The nickel films were annealed in hydrogen for about 1 hr at 195°K.

Parahydrogen Conversion Rate

The kinetics of the para–ortho conversion were determined in an apparatus similar to that described by Eley and Rideal (*7*). The 300 ml reactor, protected from both sides by means of liquid nitrogen traps, was evacuated to 10^{-6} Torr. Hydrogen obtained electrolytically was filtered through a heated palladium thimble and then enriched to 51% in its para modification on active charcoal at 77°K (after the previous outgassing at 700°K).

The composition of the hydrogen was determined by a micro-Pirani gauge described by Bolland and Melville (*8*). During the measurements the temperature of the tungsten filament of the gauge was about 200°K, the pressure in the gauge was constant and amounted to 50 Torr. The maximum difference between the resistance readings corresponding to normal and paraform enriched hydrogen was about 4%.

The rate of conversion was measured at various hydrogen pressures ranging from 1 to 30 Torr. Since the system investigated obeyed first order kinetics the experimental rate constants were determined from the equation $k_e = (1/t) \ln (c_0/c)$ (c_0 and c are concentrations of the p-H_2 in excess of the equilibrium value at time zero and t, respectively). The measurements were performed within the temperature range 165–195°K using suitable cooling mixtures (*n*-propanol, toluene).

Preparation of Nickel Hydride Films

Nickel hydride samples were prepared by the method described by Palczewska and Janko (*9*), i.e., nickel film deposits were exposed to atomic hydrogen produced in molecular hydrogen in an electrodeless rf discharge. The rf coil for the discharge was situated directly over the reactor, the walls of which were covered with the evaporated nickel film sample (Fig. 1).

The transformation of the nickel film into the hydride phase was followed by observation of its resistance change. As Baranowski and Bauer have stated previously (*10*) the resistivity of nickel undergoes a considerable change in consequence of the transformation into nickel hydride. A similar effect was observed for nickel and nickel hydride thin films in our experiments. The resistance of the nickel hydride film was about 50% lower at 195°K than that of the initial nickel film at the same temperature.

When producing atomic hydrogen in a glass vessel one has to take into account the simultaneous formation of water as a consequence of hydrogen atoms reacting with the glass surface (*11*). This contamination of the molecular and atomic hydrogen mixture is adsorbing on the film sample and influences its catalytic activity. Therefore, the eventual catalytic effect of the exposure of nickel to atomic hydrogen is attributable to some extent to partial coverage of the film surface by H_2O molecules.

With the aim of eliminating the catalytic effect of H_2O adsorption we compared the

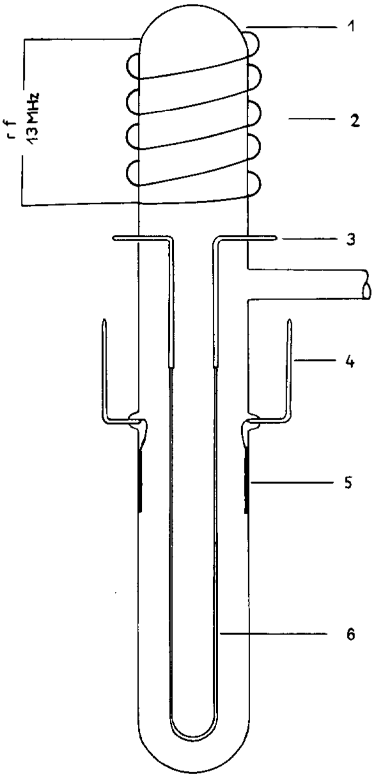

FIG. 1. Reaction vessel for measuring the rate of parahydrogen conversion on nickel and nickel hydride films. (1) quarz tube; (2) rf coil, (3 and 4) tungsten leads; (5) platinum foils (electrical contact with the film layer for resistance measurement); (6) nickel wire.

catalytic activity of the nickel film transformed into hydride with that of the nickel film on which a suitable quantity of water vapor had been preadsorbed.

Procedure

The kinetics of p-$H_2 \rightarrow o$-H_2 were studied at various pressures and temperatures, though the temperature had to be low on account of nickel hydride instability at higher temperatures under not sufficiently high pressures (*12*). First, the freshly evaporated nickel sample covered with preadsorbed water was used as catalyst. Then the film was exposed to atomic hydrogen for 1 hr at 195°K and simultaneously the change of resistance was observed, thus giving evidence of nickel film transformation into its hydride phase. The catalytic activity of this film was then compared with the first one.

In separate experiments the catalytic effect of the film preexposure to molecular hydrogen was also investigated. The conversion rates on nickel films preexposed to atomic hydrogen, but at higher temperature, when the hydride could not form, were measured as well.

RESULTS

The results of the measurements performed are shown in Table 1. The experimental rate constants k_e (min^{-1}) are expressed as absolute rates (*13*) $k_m = Nk_e/60g$ (N = the number of molecules in the reaction volume; g = the mass of the film in mg).

The catalytic activity of freshly deposited nickel films is very high; its value is far beyond the range of the measurement ($k'_m \gg 1 \times 10^{18}$ moles s^{-1} mg^{-1}). The adsorption of H_2O molecules (in an amount comparable with that formed during the electrodeless rf discharge[1]) caused a marked decrease of activity (k''_m of the order of 10^{17} molecules s^{-1} mg^{-1}). k''_m was only slightly temperature dependent, the apparent activation energy amounting to about 2 kcal/mole.

After the transformation of the nickel film into its hydride phase, the catalytic activity decreased considerably: the k'''_m value was now of the order of 10^{15} molecules s^{-1} mg^{-1}. The apparent activation energy kept its low value of about 1 kcal/mole.

The ratio of the rates k''_m/k'''_m determining the loss of catalytic activity due to the "hydride" hydrogen was high and at 195°K and 15 Torr it was equal to about 300. As within the experimental error the activation energy for both kinds of catalyst samples is almost unchanged, the observed

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[1] A larger quantity of introduced water vapor had practically no effect on the catalytic activity of the film.

TABLE 1
RATE OF PARAHYDROGEN CONVERSION ON DIFFERENT CATALYST SPECIMENS[a]

T (°K)	p (Torr)	k_e (min^{-1})	k_m (molecules s^{-1} mg^{-1})
195	1.85	>7	$>1.4 \times 10^{18}$ (a)
195	1.90	2.5	5.1×10^{17} (b)
195	5.0	0.58	3.1×10^{17} (b)
195	14	0.39	5.8×10^{17} (b)
195	25	0.23	6.2×10^{17} (b)
167	2.0	0.80	1.7×10^{17} (b)
170	14.5	0.18	2.8×10^{17} (b)
195	1.60	3.6×10^{-3}	0.61×10^{15} (c)
195	15.5	1.1×10^{-3}	2.1×10^{15} (c)
195	23.5	0.8×10^{-3}	2.0×10^{15} (c)
180	2.0	2.7×10^{-3}	0.58×10^{15} (c)
180	16	0.93×10^{-3}	1.6×10^{15} (c)

[a] (a) Pure nickel film freshly evaporated. (b) The same film after preadsorption of water. (c) The nickel film after exposure to H atoms during 1 hr at 195°K.

lowering of catalytic activity seems to depend on the respective large decrease (amounting to about 10^3) of the preexponential factor in the Arrhenius equation.

In separate series of experiments the evaporated nickel films were heated for a long time in molecular hydrogen at 300, 373 or 600°K. Under these conditions hydrogen was dissolving in nickel forming the α solid solution. Then the conversion rates were determined on such films at 195°K. Only a slight decrease of the rate values (caused by the diminishing surface area of films) could be observed for the films treated at 300 and 373°K. A larger effect appeared for the film heated previously at 600°K, but even in this case the decrease of the k_m value was one order of magnitude smaller than that attributed in the previous experiments to the hydride formation (Table 2).

For films preexposed to atomic hydrogen at high temperatures (i.e., at 300 or 600°K), the poisoning effect comparable with that appearing at 195°K was still noticeable in the first case, whereas it completely disappeared in the second, one, for films which had been heated at 600°K.

The catalytic activity of films previously poisoned by the "hydride" hydrogen could regain their former high catalytic activity after heat treatment at 600°K.

DISCUSSION

As stated in our previous investigations of the catalytic effect of the hydride forma-

TABLE 2
RATE OF PARAHYDROGEN CONVERSION AT 195°K ON NICKEL FILMS AFTER HYDROGEN PRESORPTION AT DIFFERENT TEMPERATURES

p (Torr)	k_m (molecules s^{-1} mg^{-1})	Remarks
1.9	$>1.3 \times 10^{18}$	Film freshly evaporated
1.9	8.0×10^{17}	After annealing in H_2 at 300°K
1.8	2.5×10^{17}	After annealing in H_2 at 373°K
2.0	3.7×10^{16}	After annealing in H_2 at 600°K
1.9	1.5×10^{17}	After exposure to H atoms at 600°K
1.9	7.2×10^{15}	After exposure to H atoms at 300°K
2.0	$<8 \times 10^{14}$	After exposure to H atoms at 195°K

tion in nickel and nickel–copper alloy foils and films (*4,5,6,14*) this effect always consisted in a considerable poisoning of the initial metal catalyst. The present results concerning the parahydrogen conversion confirm the former observations.

A similar poisoning effect in parahydrogen conversion was observed for palladium hydride (*1,2*).

The analysis of the kinetics of the reaction reveals that in general form our results confirm those obtained by Scholten and Konvalinka (*1*) for the specimens of palladium which had been "cracked" in consequence of disintegration of its crystallites in the α–β phase transition. The activation energy for our nickel hydride samples retains the low value characteristic of the nickel catalyst itself, but the preexponential factor decreases markedly. This means that it is possible to interpret the experimental results by assuming that on the nickel hydride catalyst sample the parahydrogen conversion is proceeding on scarce active patches on the surface of the film. They are represented probably by nickel crystal planes, which are not transformed into hydride. There is experimental evidence in the literature directly confirming surface heterogeneity of specimens of nickel transformed into its hydride phase (*15*).

We suggest that "hydride" areas of the film do not take any important role in the reaction studied and thus represent a strongly poisoned part of a catalyst surface.

The observed lack of uniformity of the surface of the polycrystalline nickel hydride films studied, leading to the coexisting areas of nickel and nickel hydride, may occur as a consequence of the structure sensitive rates of heterogeneous atomic hydrogen recombination on nickel crystallites and/or hydrogen–nickel interaction leading to the hydride phase formation (*16*).

An alternative explanation, similar to that of Scholten and Konvalinka (*1*), could refer to the process of disintegration of film crystallites during their slow (at 195°K) $\beta \rightarrow \alpha$ transformation, when the rf discharge was switched off. This effect has been recognized and described in the literature [e.g., Ref. (*17*)]. If the hydride layer is present during the catalytic reaction as a skin enveloping nickel kernels, the cracking of crystallites will expose fresh active nickel planes. The evidence based on the low preexponential factor value proves that they are not numerous.

A separate problem, which cannot be resolved as yet, is the poisoning effect observed at higher temperatures such as 300°K and also ascribed to nickel hydride in the film catalyst. The assumption of a high stability of a thin surface layer of hydride far beyond the thermodynamic conditions known for the bulk nickel hydride phase (*12*) would necessitate the special thermodynamic treatment of a superficial nickel hydride phase. The suggestion was put forward also by Scholten and Konvalinka (*1*).

The poisoning effect of nickel or palladium hydrides in reactions of hydrogenation may be interpreted in terms of the electronic structure of those particular "alloys." The 1*s* electrons of hydrogen atoms built into the nickel or palladium lattice, will contribute to filling the *d*-band of the parent metal and in consequence will decrease the catalytic activity. The experimental evidence and theoretical considerations (*18*) are still supporting this general approach to the elucidation of the poisoning effect shown by metal hydride phase in catalytic hydrogenation reactions (*2*).

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