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Behavior of Hydrided and Dehydrided $LaNi_5H_x$ as an Hydrogenation Catalyst

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The catalytic properties of varying phase compositions of $LaNi_5H_x$ were studied using the hydrogenation of 1-undecene as a model reaction. All experiments were carried out with the catalyst in liquid suspension at 308 K under varying pressures of hydrogen. The H content of the catalyst particles was tracked during the course of each experiment. Four types of catalytic behavior were observed and are catalogued in turn. While the metal solid solution phase (α-$LaNi_5H_x$) exhibits catalytic properties, catalytic activity is significantly enhanced by the presence of the hydride phase (β-$LaNi_5H_x$) in the particle bulk even though the surface composition of the particle is likely unchanged. It was concluded that several factors contribute to this enhancement: (1) the hydride phase acts as a reservoir of H atoms which communicate with the surface via microcracks and grain boundaries; (2) the substantial increase in bulk volume upon the conversion of the metal to the hydride phase enlarges these conduits and facilitates said communication; (3) weak chemisorption of hydrogen on the surface, due to the high hydrogen atom activity when the hydride phase is present, increases the amount of labile hydrogen. © 1992 Academic Press, Inc.

INTRODUCTION

A recurring question in the use of palladium or other hydride-forming metals as hydrogenation catalysts is whether the active catalytic species is the hydride phase, the metal phase, or both under a given set of reaction conditions (*1*). For example, palladium hydride is stable and could readily form under the conditions of temperature and pressure where most catalytic hydrogenations are executed (*2*). In practice, however, the chemical potential of hydrogen at the catalyst surface may be below that required to maintain the metal in the hydrided state because of competition for H atoms at that surface. Thus, it is possible for the catalyst to exist in three different states during the course of the reaction: as a single-phase hydride, as a metal phase with hydrogen in solid solution, or as a mixture of both. It is the prime purpose of this paper to quantitatively determine the difference in catalytic activity of a metal hydride former in these various states, thereby gaining an insight into their respective catalytic mechanisms. The catalyst that we examine in this context is the intermetallic compound $LaNi_5$. It was chosen because $LaNi_5$ hydride can be readily formed or decomposed at or near room temperature over a pressure range of 1 to 10 atm, a mild regime which is conducive to the elimination of undesirable side reactions and is readily accessible by our apparatus. A simple reaction, the hydrogenation of 1-undecene, was selected as the vehicle to carry forward our study.

$LaNi_5$ and its hydride have been previously examined in this context. Soga *et al.* (*3*) studied the hydrogenation of ethylene gas in the presence of H_2 at 190–213 K and both hydrided and dehydrided $LaNi_5$. They found that the reaction proceeded predomi-

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nantly by extraction of hydrogen from the hydride phase, which consequently decomposed and did not reform. However, dehydrided $LaNi_5$ was demonstrated to have catalytic activity although the reaction rates were much lower than those observed when the hydride phase was present (see Discussion). Others (*4, 5*) have examined a number of AB_5 intermetallic compounds (A = rare earth metal and B = Ni) to determine their efficacy as catalysts in the synthesis of ammonia and the reduction of CO at elevated temperatures (>575 K). In both cases the intermetallic compound decomposed to form an oxide or nitride phase plus elemental Ni; however, this mixture exhibited significant catalytic activity, behaving much like elemental Ni on a metal oxide support. Thus, in view of previous results, it was a secondary purpose of this work to determine whether either phase of $LaNi_5H_x$ has any significant catalytic activity in a simple hydrogenation reaction near room temperature in an environment where decomposition of the intermetallic is avoided.

METHODS

The apparatus consisted of a calibrated hydrogen gas reservoir, a fore-pressure regulator, a pressure–vacuum manifold, temperature and pressure transducers, and a 300-ml reaction vessel. The latter was obtained from the Parr Instrument Co. (Moline, Il, Parr 4500); it was constructed of stainless steel and fitted with a sealed magnetic stirrer. An associated controller/tachometer (Parr 4843) was used for temperature and stirrer control. Additional temperature control capability was attained by virtue of an internal heat exchanger through which a heat transfer fluid was circulated. The preparation of metal hydride slurries has been described in detail previously (*6, 7*) and only a brief summary will be given here. $LaNi_5$ was obtained from the Ergenics Corp. (Wyckoff, NJ) and had a stated purity of 99%. X-ray diffraction data indicated that it was single phase with hexagonal lattice parameters of a = 5.018 Å and c = 3.987 Å. 1-undecene and *n*-undecane were obtained from Aldrich Chemical Co. (Milwaukee, WI); all the solvents were distilled before use and were 99+% pure, as determined by gas chromatographic analysis. These solvents were chosen because their low vapor pressure is experimentally desirable.

The experiments were carried out as follows. An ≈6-g sample of granular $LaNi_5$ was introduced into the reactor and activated by hydriding and dehydriding in direct contact with H_2 gas after which 100 ml of *n*-undecane was introduced. Before each experiment the sample, in liquid suspension, was then subjected to a series of hydriding/dehydriding cycles, which is necessary to assure reproducible behavior; in this case the alloy was subjected to ≈1000 cycles before the first reported experiment and about 10 before each subsequent experiment. The solids in suspension were equilibrated at 308 K under an appropriate H_2 pressure; stirring was stopped and hydrogen was vented until the pressure was 1 atm. When the system is quiescent virtually no H_2 desorption takes place from either the solvent or the solids over a period of several minutes. A measured amount of undecene (10 ml) was quickly introduced into the reactor, which was immediately sealed. The reactor gas space was quickly evacuated and then flushed with hydrogen. Hydrogen was then added to the reactor through the pressure regulator, the stirrer was turned on and controlled at 1070 rpm, and the reaction was carried out under a constant hydrogen pressure at 308 K. The total time for the introduction of the undecene sample was ~120 s. In repeat experiments, ~10 ml of undecane was removed before introduction of the sample in order to maintain the liquid volume approximately constant in all experiments.

The course of the hydrogenation was followed as a function of time by two different techniques. (1) The reservoir pressure, reactor pressure, reactor temperature, and room temperature were measured and digitized by a data logger at time intervals of 5 s to 1 h. The data were sent to an associated computer and stored for later retrieval and reduction. (2) The hydrogenation reaction was momentarily interrupted at periodic intervals, a small sample of the liquid phase was taken by syringe, and the undecene/undecane ratio was determined via gas chromatography using a flame ionization detector. This required stirring to be stopped and venting the reactor to 1 atm. After sampling the reactor was sealed and the reaction restarted as described above. The conversion/time data were corrected for the sampling interruption.

In order to determine the initial H/$LaNi_5$ ratio, the labile hydrogen inventory, H_{2m}, was measured at the end of the experiment. This was done by venting hydrogen from the reactor into an evacuated, calibrated reservoir until the pressure in the reactor was <1 atm, thereby decomposing the hydride phase. Then,

$$(H/LaNi_5)_{initial} = 2(H_{2u} + H_{2m} + H_{2r} - H_{2a} - H_{2gd})/0.0134, \quad (1)$$

where H_{2u} is equal to the moles of undecene reacted, H_{2a} is the moles of H_2 added from the gas reservoir, H_{2gd} is the correction for the final amount of H_2 in the gas and liquid phases, H_{2r} is the estimate of residual hydrogen remaining in the solids (see below), and 0.0134 is the moles of $LaNi_5$ catalyst. The initial H/$LaNi_5$ ratio can also be closely estimated by inspection of the isotherms in Fig. 1, making due allowance for the direction from which equilibrium is approached.

Equilibrium pressure/composition isotherms for the $LaNi_5$/H system were obtained with the alloy particles suspended in *n*-undecane as previously described (*6*).

PRESSURE/COMPOSITION ISOTHERMS

The nonstoichiometric hydride phase of $LaNi_5$ was first prepared by van Vucht *et al.* (*8*). The thermodynamic behavior of a given metal/hydrogen system is conveniently represented by a family of pressure/composition isotherms. Such a diagram for the $LaNi_5$/H system is shown in Fig. 1 with the overall chemical reaction. Two isotherms are shown; they have been displaced slightly to the right to account for residual hydrogen remaining in solid solution in the metal phase at an equilibrium pressure of 0.1 atm. This corresponds to a composition of $LaNi_5H_{0.3}$ as estimated from other similarly treated samples in which the residual H content was determined analytically. First we will address the absorption isotherm; as hydrogen is added to $LaNi_5$ it will dissolve in the metal lattice to form a hydrogen solid solution (α) phase in which, ideally, the H concentration in the metal will be a linear function of the square root of the equilibrium hydrogen pressure. Eventually the system departs from ideal behavior, primarily due to elastic interactions, and the hydride (β) phase precipitates. At this point the isotherm forms a plateau which persists until the α phase is entirely converted to the β phase. In the hydride region of the phase diagram the isotherm steepens as the limiting concentration is approached. The desorption isotherm behaves similarly except that equilibrium is approached by removing hydrogen from the system. There is a hysteresis gap between the isotherms in the pressure plateau region which is about 0.3-atm wide. Thus it is possible to prepare and maintain the solids in the α or β phases at virtually the same temperature and pressure by approaching equilibrium from different directions, e.g., see type 1 and type 2 behavior below.

RESULTS

Table 1 lists pertinent parameters for the hydrogenation experiments. The reaction rates are calculated from the slope of the linear portion of the plot of the undecene/undecane ratio vs time as determined by periodic GC analysis of the liquid phase. There was no indication in the chromatogram of components produced by side reactions.

We have observed four qualitatively different types of catalytic behavior for

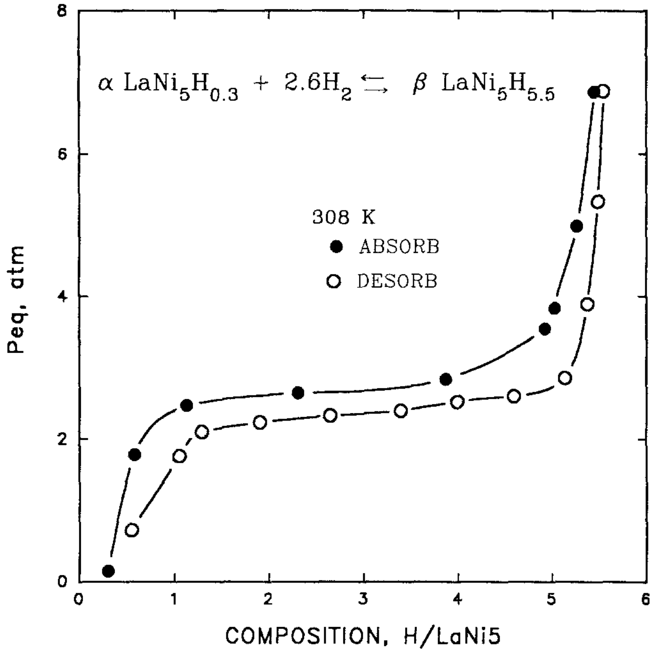

FIG. 1. Pressure/composition isotherms for the $LaNi_5/H$ system after approximately 1000 hydriding/dehydriding cycles. The phase compositions in the equation correspond to those at the isotherm extremities.

$LaNi_5H_x$ which are represented in Figs. 2–7. In each figure there are plots of three variables vs time: (1) the moles of H_2 introduced into the system as determined from the pressure change in the calibrated gas reservoir; (2) the moles of H_2 reacted with undecene as calculated from periodic determination of the undecene/undecane ratio; (3) the $H/LaNi_5$ ratio in the solids as determined from the difference between the amount of H_2 added from the gas reservoir, the amount required to convert the alkene to the mea-

TABLE 1

Hydrogenation of 1-Undecene $LaNi_5H_x$ Catalyst 308 K

Expt.	P_{H2},(atm)	Rate,[a] $dC_{11}H_{22}/dt$ (mol/s)10^5	Charge, $C_{11}H_{22}$(mmol)	Turnover[b] frequency $C_{11}H_{22}$(site·s)$^{-1}$
1	2.48	5.88	47.0	0.84
2	2.42	0.88	44.7	0.13
3	3.21	3.71	44.9	0.46[c]
4	4.14	9.92	44.1	1.22[c]
5	3.14	2.06	42.7	0.30
6	4.20	5.36	39.1	0.76

[a] Hydrogenation rate based on undecene/undecane ratio (see text).
[b] Based on surface area of dehydrided catalyst = 0.79 m^2/g (see text).
[c] Based on surface area of hydrided catalyst = 0.91 m^2/g (see text).

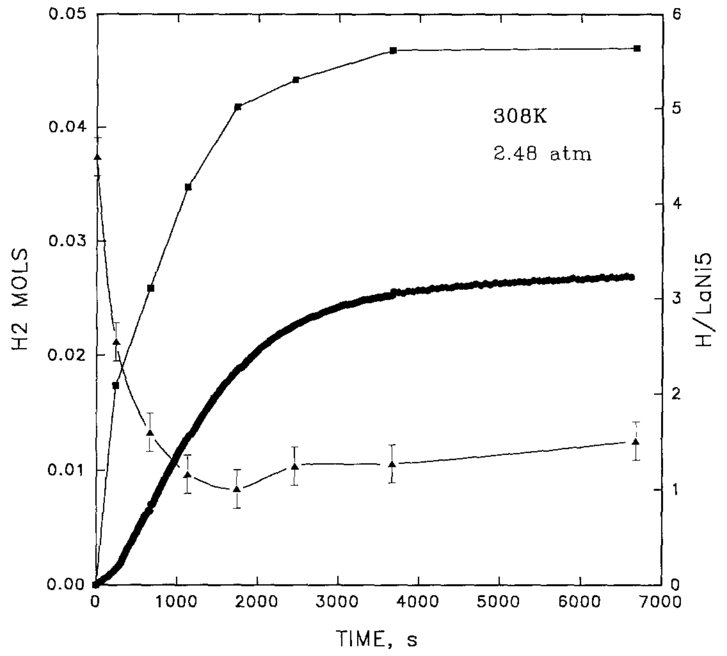

FIG. 2. Figures 2–7 show various types of catalytic behavior: left axis, ●, moles of H_2 introduced from gas reservoir; ■, moles of H_2 reacted with 1-undecene; error ≈ symbol size. Right axis, ▲, with error bar, catalyst composition, H atoms (moles of $LaNi_5$)$^{-1}$.

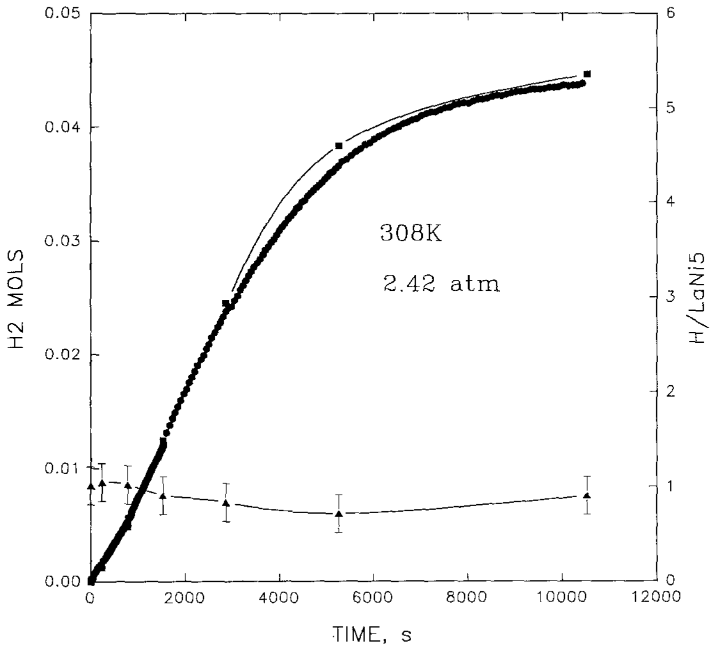

FIGURE 3

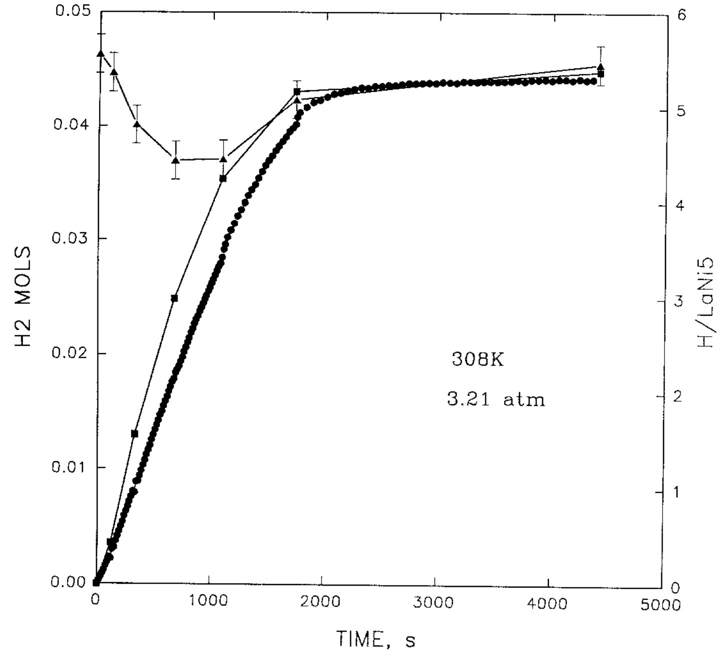

FIGURE 4

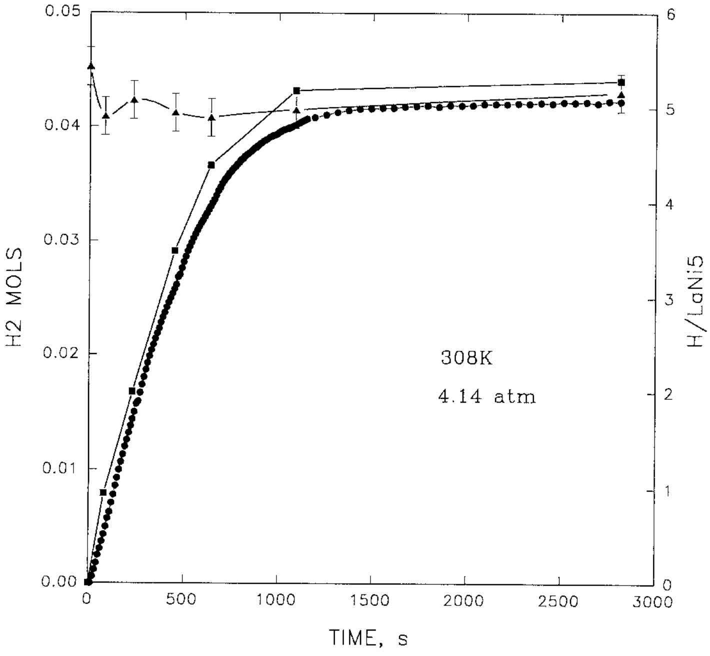

FIGURE 5

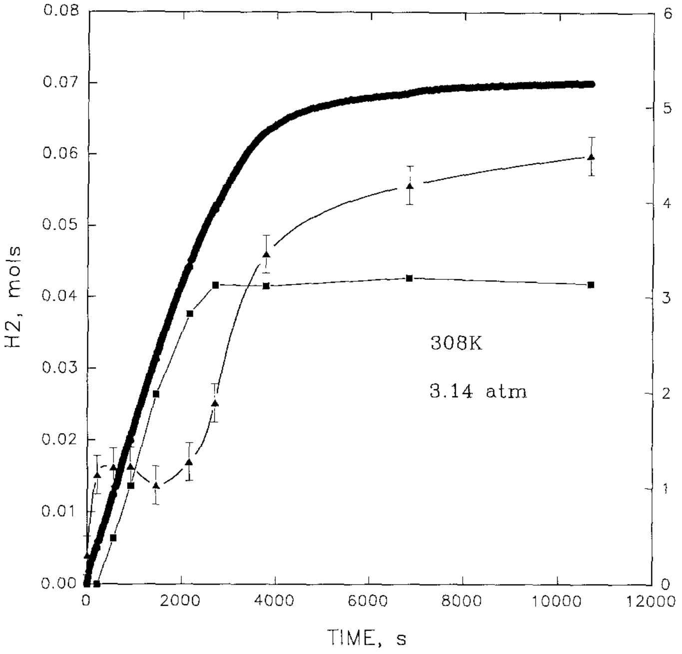

FIGURE 6

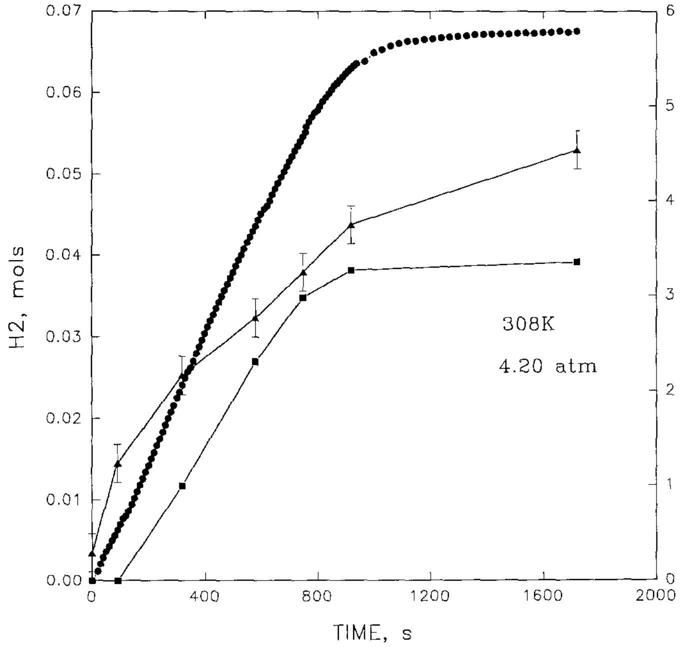

FIGURE 7

sured value, and the initial $H/LaNi_5$ ratio, i.e.,

$$(H/LaNi_5)_t = (H/LaNi_5)_{initial} + (H_{2a} - H_{2u})_t/0.0134, \quad (2)$$

where H_{2a} and H_{2u} refer to the quantities defined in Eq. (1) at time t.

Type 1 Behavior (Fig. 2)

$LaNi_5H_{4.5}$ was prepared by equilibrating the system at 10 atm pressure of H_2 at 308 K. Hydrogen was slowly vented until the pressure was 2.48 atm, when the system was reequilibrated; thus the pressure was within the hysteresis gap and the solids composition approximated that at the end of the desorption pressure plateau.

Type 2 Behavior (Fig. 3)

A suspension of $\alpha LaNi_5H_{1.0}$ was prepared. Equilibrium was approached by the addition of H_2, i.e., by equilibrating the $LaNi_5H_x$ suspension at 1 atm pressure and subsequently increasing the pressure to 2.42 atm and reequilibrating.

Type 3 Behavior (Figs. 4 and 5)

β-$LaNi_5H_{5.5}$ was prepared by equilibrating the system at 3.21 atm (Fig. 4). This composition is within the single-phase hydride region of the phase diagram. A similar experiment is shown in Fig. 5, which was carried out at H_2 pressure of 4.14 atm.

Type 4 Behavior (Figs. 6 and 7)

$LaNi_5H_{0.3}$ was prepared by equilibrating the system at a pressure of 1 atm. After addition of the alkene reactant the pressure was increased to 3.14 atm, at which value the experiment was immediately begun (Fig. 6). This experiment was repeated (Fig. 7) with the experimental pressure increased to 4.2 atm.

DISCUSSION

Our results will be interpreted using as a frame of reference the reported nature of the surface of $LaNi_5$, a kinetic model for the formation and decomposition of $LaNi_5$ hydride and the physical change accompanying phase conversion.

The surface of polycrystalline $LaNi_5$ that has been subjected to many hydriding/dehydriding cycles was studied using X-ray photoemission spectroscopy, Auger electron spectroscopy, and magnetic susceptibility techniques (*9*). Substantial surface segregation occurs and there is a surface enrichment of La to give a La/Ni $\approx$ 1; the La is associated with oxygen but Ni remains metallic. The magnetic susceptibility measurements indicated the latter is present as clusters on the surface containing about 6000 atoms. Thus, the surface of highly cycled $LaNi_5$ appears to consist of islands of La associated with oxygen as La_2O_3 or $La(OH)_3$ and Ni. The oxygen species, which we will designate as La_2O_3, was produced by the presence of small amounts of oxygen present initially in the alloy and in the H_2 gas. It was proposed (*9, 10*) that such surface disproportion into a stable oxide and an easily reduced transition metal is the mechanism by which an aggressive catalytic surface is formed, readily capable of dissociating the H_2 molecule. Indeed the mechanism seems generally applicable to other intermetallic hydrides in which the metal components consist of a metal from Groups II–IV of the periodic table and a transition metal, e.g., Mg_2Ni, Mg_2Cu, and TiFe (*11*). Since no surface species forms a hydride phase under our experimental conditions there should be no chemical difference in the surface composition between a hydrided and dehydrided particle. However, there is a bulk volume expansion of >20% in the $\alpha \rightarrow \beta$ conversion, which may induce a great deal of strain in the surface layer and enhance effects due to microcracks, porosity, defects, etc.

The kinetics of the formation (*12*) and the decomposition (*7*) of $LaNi_5$ hydride have been found to obey a shrinking core reaction model. This model specifies that the rate-limiting process is the solid state transformation taking place at the interface between the β and the α phases of $LaNi_5H_x$. Thus in

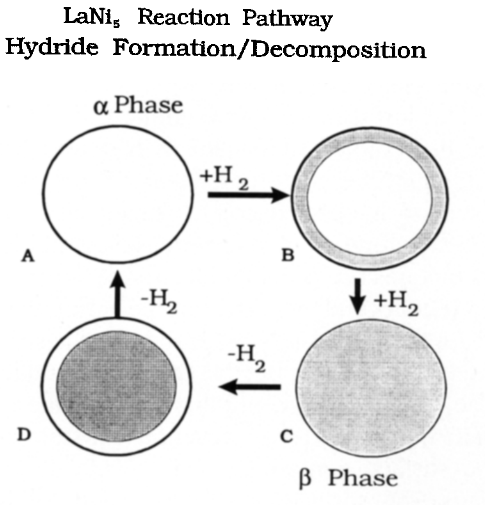

FIG. 8. The kinetics of the formation and decomposition of β-$LaNi_5H_x$ obey the shrinking core model (*7*, *12*); consequently the subsurface phase composition depends on reaction direction and initial composition. This is illustrated above using idealized, spherical particles.

hydride formation a growing product layer of β $LaNi_5H_x$ proceeds from the surface inward; in hydride decomposition the reaction also proceeds from the surface inward but now the growing layer is α-$LaNi_5H_x$. These reaction pathways are illustrated in Fig. 8. We note that the same model can account for the decomposition of β-$Pd_{0.85}Ni_{0.15}H_x$ (*13*), suggesting that Pd itself may behave similarly.

In type 1 behavior hydrogen is extracted rapidly from the hydride, which consequently decomposes (C → D, Fig. 8). In the experiment illustrated in Fig. 2, the final H/$LaNi_5$ ratio is 1.64, thus the phase conversion is not quite complete. The hydride is not regenerated because the pressure is below the equilibrium absorption plateau pressure (it should be noted that after many hydriding/dehydriding cycles the plateaus in Fig. 1 become more sloping, thus a small amount of reformation may occur as indicated in Fig. 2 by a slight increase in H content of the solids near the end of the hydrogenation). There is an immediate decrease in H/$LaNi_5$ at the start of the reaction with a consequent growing subsurface layer of α-$LaNi_5H_x$ in the catalyst particles. It is of interest to compare this behavior to that of type 2 as represented in Fig. 3 where the entire particle is α-$LaNi_5H_x$. Though the catalyst surface is the same in both cases in the latter there is essentially no H contribution from the solids over the entire course of the reaction; almost all of the reactant H_2 is supplied from the gas phase and the reaction rate (expt. 2, Table 1) is much slower, even though the experiments were carried out at the same temperature and pressure. We therefore conclude that the unreacted core hydride phase acts as an internal reservoir which supplies atomic hydrogen to the particle surface as it is consumed by the alkene and accounts for the higher reaction rate and, further, that in both cases the particle surface is catalytically active with respect to alkene reduction.

We note that type 1 behavior is essentially what Soga *et al.* observed (*3*) in the hydrogenation of ethylene using $LaNi_5$ hydride. In the present instance the hydride phase was not reformed because the H_2 pressure was too low, whereas in the work of Soga *et al.* it did not reform because the presence of gaseous ethylene greatly inhibited absorption of hydrogen by the alloy, although the partial pressure of hydrogen was sufficient for hydride formation. Nevertheless, in both cases the surfaces of the alloy particles exhibited catalytic activity and were probably similar in composition.

Upon prior equilibration at higher pressures type 3 behavior is encountered. In this case the initial solid composition lies within the single phase hydride region (C, Fig. 8). At 3.21 atm H_2 pressure (Fig. 4) there is a substantial hydrogen contribution from the solids permitting the formation of a small amount of subsurface α-$LaNi_5H_x$. However, this is transient and, upon completion of the hydrogenation, the H content of the solids increases to nearly its initial value. At the higher pressure of 4.14 atm (Fig. 5) the solids change composition only slightly over the course of the reaction and it appears that no subsurface α phase is ever formed. In the latter experiment, the H_2 pressure is slightly less than that used in experiment 6, yet the reaction rate is by far the highest observed. This is attributed to the fact that the catalyst was in the hydrided state from the very beginning, whereas in experiment 6 it was initially in the dehydrided state and strongly competed for hydrogen over the course of the reaction. Obviously fully hydrided particles greatly enhance catalytic activity.

Type 4 behavior is more complex. The solids are initially equilibrated at 1 atm and only α-$LaNi_5H_x$ is present. There is competition for hydrogen by both the solids and the alkene from the very start of the experiment. At a pressure of 3.14 atm (Fig. 6) there is no uptake of H_2 by the alkene for the first 209 s when the H content of the solids corresponded to $LaNi_5H_{1.2}$, indicating precipitation of a subsurface layer of β-$LaNi_5H_x$ (A → B, Fig. 8). At this point the hydrogenation reaction commences, after which the solids composition remains essentially constant until the alkene hydrogenation is almost complete. At a higher experimental pressure (Fig. 7) the system behaved similarly; again all of the initial hydrogen was absorbed by the solids and the alkene did not react until $H/LaNi_5 > 1.2$ ($t > 90$ s). After this the hydrogen activity was high enough to support a fairly rapid uptake of hydrogen by both the catalyst and the alkene. In this single case the H_2 turnover frequency is 1.04 molecules $site^{-1}\ s^{-1}$ and significantly exceeds that of $C_{11}H_{22}$ (experiment 6, Table 1) because the catalyst is absorbing hydrogen while the hydrogenation is proceeding. The fact that no alkene reduction was observed in either experiment until a subsurface hydride phase formed is another confirmation of the effect of the β phase on catalyst potency.

Types 2, 3, and 4 behavior are those most likely to be encountered in practice where the alkene/catalyst ratio is high (in contrast to the studies described herein) when essentially all of the reactant H_2 must be supplied from the surrounding liquid phase. In this situation the $LaNi_5/H$ system, irrespective of its initial state, will quickly reach a steady state condition in which the solid will be single phase α or β or a mixture of both, as determined by the hydrogen atom activity, a_H, at the particle surface, which is a function of the competition for hydrogen by the alkene and a_{H2} in the liquid phase. At steady state, when a_H is low, there will be no hydride phase present and the alkene reduction rate will be low. At some higher a_H ($a_H > a_{Hplateau}$) a hydride phase will be present and the rate will be moderate. If a_H is high enough the entire particle will be in the hydrided state and the alkene reduction rate is maximized.

The turnover frequencies for the experiments listed in Table 1 are based on the following assumptions: the catalytic species consists of nickel clusters which occupy 50% of the surface; each Ni atom is an active site; the Ni atom surface density, Ni_{atom}, corresponds to the density of the (111) crystallographic plane and is equivalent to 1.85×10^{15} atoms/cm^2. The surface area of the dehydrided catalyst was 0.79 m^2/g, as determined by BET measurements after the final experiment. The turnover frequency, T_f, is calculated as

$$T_f = (dC_{11}H_{22}/dt)N/(Ni_{atom} \times S_{eff} \times W),$$

where $dC_{11}H_{22}/dt$ is the reaction rate in moles $C_{11}H_{22}$/s, N is Avogadro's number, S_{eff} is one-half the surface area/g, and W is the weight of $LaNi_5$, i.e., 5.79 g. It is of interest to note that if the basal plane of hexagonal $LaNi_5$ was chosen as the catalyst surface, T_f doubles even if the entire surface area is used, because the density of the surface metal atoms is reduced to 4.6×10^{14} atoms/cm^2 due to the lower atomic packing in $LaNi_5$. However, it should be noted that neutron diffraction results of β-$LaNi_5D_7$ indicate that the solids expand 23% upon forming the deuteride phase relative to the deuterium free alloy (*14*) and the density decreases from 8.28 to 6.73 g/cc; the hydride phase behaves similarly (*8*). Assuming spherical particles, the passage from the metal to the hydride phase will increase the surface area to 0.91 m^2/g, effecting a corresponding decrease in T_f provided there is also a concomitant and proportional increase in active sites on the particle surface. In experiments 3 and 4 the particle bulk consisted essentially of the hydride phase throughout the entire reaction, thus the turnover frequencies were calculated using the hydrided surface area; in all other experiments the measured surface area of the dehydrided solids was used.

There are several mechanisms which can account for the increased catalytic activity when the hydride phase is present in the bulk particle. First, we believe, as suggested previously (*10*), that the absorption of hydrogen by $LaNi_5$ proceeds by dissociative chemisorption of H_2 on the Ni surface clusters followed by transport of H atoms from the particle surface to the bulk solid via the interface between the Ni clusters and the La_2O_3 surface precipitates. These pathways, though tortuous, communicate between the particle surface and the underlying $LaNi_5$ substrate. Additional pathways consist of microcracks which have been observed in transmission electron micrographs in highly cycled, dehydrided $LaNi_5$ (*15*). The large volume expansion $LaNi_5H_x$ undergoes when fully hydrided should greatly facilitate H atom transport in both directions by widening the conduits between the surface and the underlying $LaNi_5H_x$, possibly even exposing it directly to adsorbed surface species. If it is only partially hydrided the transport will be decreased proportionately, perhaps less if the hydride phase is immediately below the surface layer (B, Fig. 8). Thus, the hydride phase not only provides a reservoir of hydrogen atoms, it also facilitates their transport between the bulk particle and the catalyst surface.

Another factor which affects surface hydrogen mobility is that at high surface coverage the enthalpy of chemisorption is greatly reduced (*16*). In the case of palladium black it is reduced from 110 to 40 kJ(g atom $H)^{-1}$. It is this weakly chemisorbed hydrogen that is in dynamic exchange with the absorbed hydrogen in the solids and H_2 in the surroundings, in this case in the liquid phase. Thus, when the hydride phase is present there is a significant amount of weakly chemisorbed hydrogen on the surface which is highly labile. At lower H_2 activities the surface coverage is reduced and the heat of chemisorption is more exothermic, thus surface H atoms are less labile and, consequently, less reactive. This effect does not require that $LaNi_5$ be directly exposed on the surface.

Finally we note that there is a substantial difference in the electronic band structure of the metal and the hydride phase of $LaNi_5$ (*17*). This difference, of course, could readily account for variation in catalytic activity between the hydride and the metal phase. However, it is unlikely that any substantial amount of $LaNi_5$ is exposed on the particle surface of highly cycled material and, consequently, it is difficult to assert that the change in electronic band structure is responsible for the enhanced catalytic activity of partially or wholly hydrided catalyst. Type 1 behavior, in which the hydride core is rapidly shrinking but still significantly affects the reaction rate, supports this view. This is an important distinction between ternary hydride formers, such as $LaNi_5$, and Pd, for which there is no ambiguity concerning the exposure on the surface of the bulk component.

SUMMARY

We have found both α-$LaNi_5H_x$ and β-$LaNi_5H_x$ to be catalytically active for the hydrogenation of 1-undecene. The β hydride phase is a more aggressive catalyst than the α solid-solution phase and significantly enhances activity even when present in the solids as a minor component. While the active surface species is believed to be nickel clusters in both cases, the increased activity observed when the hydride phase is present is attributed to three factors: (1) the presence of a highly concentrated reservoir of hydrogen atoms; (2) the expansion of the catalyst particle due to the lower density of the hydride phase, facilitating migration of H atoms between the surface and the bulk hydride phase via pathways formed by microcracks and interfacial phase boundaries; (3) weak chemisorption of H, which occurs at high H activities associated with the presence of the hydride phase, thus increasing the amount of labile, surface hydrogen and effecting a consequent increase in the hydrogenation rate.

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