

Metal Hydride Catalysis—Water Formation on Exposure of LaCo_5H_z to O_2 *

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The formation of H_2O upon exposure of LaCo_5H_z to O_2 is studied at various temperatures in the vicinity of room temperature. In the equilibrium range of α and β hydride phases a predominantly linear dependence of rate on z (first-order rate law) is observed. Near room temperature no concomitant metal oxidation occurs, as the metal matrix can be rehydrided. The process is therefore a catalytic one. At higher temperatures the predominantly first-order reaction is modified by at least two concurrent reactions. They involve reaction of gas phase hydrogen and partial metal oxidation. Similar reactions of metal hydrides with NO and CO are briefly discussed.

Introduction

This study explores details in the process of an H_2O formation reaction when a metal hydride (LaCo_5H_z) is exposed to O_2 around ambient conditions. LaCo_5H_z was chosen because formation of this hydride is relatively slow. This allows us to determine more accurate kinetic data of the H_2O formation reaction and avoids effects stemming from local heating due to heat of this reaction.

H_2O formation has been long known to occur when H_2 and O_2 were brought in contact over a catalyst such as Pt . More recently, a large class of hydrides of intermetallics composed of components other than noble metals (such as LaNi_5) was found (1, 2) to form H_2O without concomitant metal oxidation (safe for microscopic processes leading to a catalytically active surface)

when exposed to O_2 around ambient conditions. One of these studies (1) showed that deuterium in the metal deuteride rather than available gas phase H_2 reacted with O_2 . The process therefore has to take place catalytically on the hydride surface as the metal matrix can be fully rehydrided and does not participate in the reaction.

A catalytic surface activity for intermetallics in question is already implied in the hydriding process. One step on H_2 absorption entails the dissociation of the H_2 molecule at the metal surface. As shown by example of LaNi_5 (for references see recent reviews on hydride phenomenology, (3, 4)) this surface is characterized by a segregation of fine transition metal particles and of the rare earth which binds the oxidizing impurities. In this way clean metallic surface sites are obtained which can act catalytically in dissociating H_2 . These sites, however, can act equally well as a meeting ground of activated H , supplied in enormous quantities from the bulk of the hy-

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drude (especially near or at the α - β phase transition) and an oxygenating atmosphere which will be reduced in the process.

This metal hydride catalysis should be contrasted with catalytic methanation and ammonia synthesis (5, 6) over similar intermetallics. Here the intermetallic compounds are exposed at elevated temperatures (700 K) to a mixture of H_2 and oxidizing gases. In the process the intermetallic partly breaks up into rare earth oxides or nitrides and fine transition metal particles. At the temperatures in question, the latter are well-known catalysts for the reactions in question. It appears that in this process the catalytic activation through oxidative segregation of the intermetallic has been carried to an extreme. At the same time, however, special opportunities with catalysis involving the metal hydride (enormous supply of activated H and involvement of α - β hydride phase transition) have been lost.

Experimental

$LaCo_5$ was prepared by induction melting on a water-cooled copper boat under argon. Purity of all metals was 99.9% or better and purity of all gases was 99.995% or better. $LaCo_5$ was subsequently annealed for 24 hr at 900°C under argon in sealed quartz tubing with the sample enclosed in tantalum foil. X-ray characterization was performed to verify phase purity.

The hydriding behavior of $LaCo_5$ has been described previously. Two hydride phases (β , γ) of approximate composition $LaCo_5H_{3.4}$ and $LaCo_5H_{4.3}$, respectively, were identified (7).

All samples (~0.5 grams) were initially hydrided and subsequently exposed to oxygen in an apparatus utilizing calibrated volumes (~25 cm³ total) of known temperature. The sample chamber (~4 cm³) was contained in a constant temperature oil bath and the sample temperature was moni-

tored directly by a thermocouple which was in contact with a small copper holder containing the sample.

Initial hydriding was achieved at H_2 pressures on the order of 10 atm. Before any water formation studies were performed, the samples were cycled through 5 hydrogen absorption-desorption processes to approach limiting particle size. After hydriding, the pressure of hydrogen was kept such that it remained well above the plateau pressure of the α - β transition.

The reaction of the metal hydride with O_2 was carried out as follows. While the initial H_2 pressure was well above the plateau pressure, oxygen was introduced such that the partial pressure of hydrogen at the start of the reaction corresponded to the plateau pressure. Therefore on H_2O formation the metal hydride was undergoing only the β - α transition (rather than changes in composition within the β phase range). Only the last stages of the catalytic reaction involved the metal hydride in the α phase. This procedure was followed because it was desired to maintain a constant chemical potential of α and β phases during the majority of the reaction. Initial partial pressures varied from 1 to 2 atm for oxygen and 0 to 0.3 atm for hydrogen. The water formation reaction was monitored by recording the total pressure change with time.

After each water formation experiment the sample was rehydrided to the maximum extent possible. First vacuum was placed on the sample overnight at room temperature to remove all water in the system. Next the sample was subjected to a temperature of approximately 140°C for one to two hours under vacuum. Then the sample was rehydrided at around 40°C.

Results and Discussion

When $LaCo_5H_z$ is exposed to O_2 a characteristic decay of total pressure with time is observed. It will be shown that only the

hydrogen in the metal hydride reacts for some initial period of time. For this period ΔP is proportional to Δz . The pressure decay is represented in Fig. 1 as a plot of $\ln z/z_0$ vs time where z_0 is the initial amount of hydrogen in the metal hydride. The plots shown are for the first water formation experiments on each of three samples employed (Exp. 1.1, Exp. 2.1, and Exp. 3.1; experiment numbers indicate sample (first number) and run (second number)).

In the most straightforward case (Fig. 1, Exp. 1.1) one observes, after an initial induction period, a linear dependence of $\ln z/z_0$ vs time upon exposure of LaCo_5H_2 to O_2 at 23°C . There is no complication from reaction of gas phase hydrogen with O_2 in this case because the hydrogen present in the gas phase is only 1% of the total amount of hydrogen in the hydride.

This linear dependence (first order) can also be observed in similar reactions per-

formed at $\sim 40^\circ\text{C}$ (Exp. 2.1) (giving a rough value for activation energy of 10 kcal). Here, however, values of z/z_0 to only 0.5 are shown due to a change in the reaction pattern thereafter. This change may be connected with an interfering action from gas phase H_2 with O_2 . The onset of this reaction is observed as a rather dramatic increase of rate of reaction over a short period of time. To support the notion that this sudden increase is due to a gas phase reaction, an experiment was performed in which the partial pressure of hydrogen was increased after a reaction time of 2 hr. No effect was observed until 4 hours later when a quite dramatic drop in pressure occurred which corresponded rather well to the onset of this gas phase reaction which initiated (at 40°C) during the later stages of the H_2O formation reaction ($\sim 60\%$ metal hydride reacted).

Several other more qualitative experiments were performed to widen the perspective on catalytic H_2O formation. Experiments 2.2 and 2.3 were both concerned with the effect of changing the pressure of oxygen. In Exp. 2.2 the initial partial pressure of oxygen was reduced significantly as compared to the earlier run at 40°C . This caused a catastrophic process to occur. The reaction proceeded at a much faster rate as compared to the previous 40°C run and significant metal oxidation may be indicated by an excessive pressure change. A slight temperature rise of the sample was also noticed during the initial rapid change of pressure at the very start of the experiment. It is assumed that initial self-heating started such a catastrophic process although it is not clear why this occurred on lowering the O_2 pressure.

Exp. 2.2 could not establish the dependence of reaction rate on oxygen pressure. This was accomplished in Exp. 2.3 in the following manner. The initial oxygen partial pressure was set at 1.7 (used in the initial 40°C run) and then decreased by about one

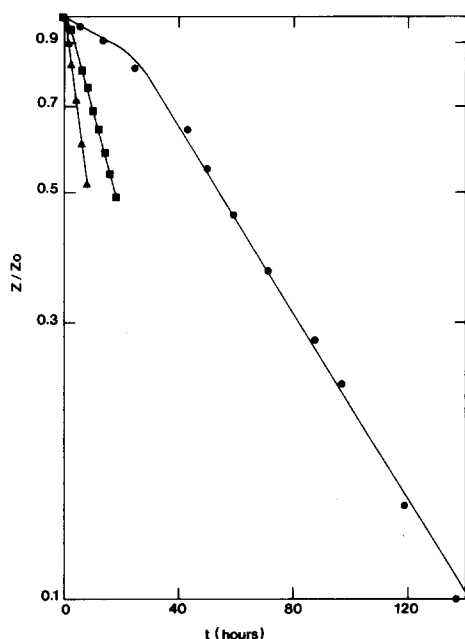


FIG. 1. $\ln z/z_0$ vs time. ● Exp. 1.1, 23.4°C , $z_0 = 3.4$; ▲ Exp. 2.1, 39.1°C , $z_0 = 3.5$; ■ Exp. 3.1, 37.4°C , $z_0 = 3.0$. Experiment numbers indicate sample (first number) and run (second number).

half after the reaction was well underway. This experiment clearly showed that there was no dependence of oxygen pressure on time once an experiment was begun. Therefore no change of reaction rate occurred after changing the partial pressure of oxygen.

Several experiments were also performed at 55°C. Here it was observed that both the metal hydride and gas phase reaction apparently start almost simultaneously since no dramatic change in rate was observed at later times. In addition the pressure change observed exceeded that due only to water formation from the available hydrogen and it is therefore assumed that oxidation of the sample was taking place. Except for Exp. 2.2 all other reactions at lower temperatures did not show excessive pressure drops even though they were continued to apparent completion.

Each of the three samples, after completion of water formation studies, was analyzed for the amount of hydrogen absorption. X-ray diffraction patterns were also obtained. A sample on which only a room temperature water formation experiment was performed showed complete regeneration of the metal hydride under 50 atm H_2 at 300 K. Two other samples which formed H_2O at 55°C showed only partial regeneration to about 50 to 75% of the initial hydride. X-ray diffraction analysis in all cases showed $LaCo_5$ but no indication of La_2O_3 . However, the quality of the diffraction patterns had deteriorated.

H_2O formation experiments were also carried out in a special gas confluence arrangement. $LaNi_5H_6$ was enclosed in tubing and exposed at about 15°C to a flow of H_2 of about 1 atm (a condition suitable to maintain the β phase hydride). Into the down stream portion of the hydride sample, a capillary was inserted which supplied a stream of O_2 at approximately 1 atm. This arrangement also produced the expected H_2O formation which was monitored by passing the gas mixture through a cold trap.

However, in this case H_2O formation was observed even after 36 hr. This considerably extends the period which produced substantial amounts of H_2O when the metal hydride was exposed to O_2 only, in a conventional manner. This special confluence method may be quite generally employed as an interesting novel route for catalysis based on metal hydrides. It can be assumed that H_2O formation in this case takes place in the region of the intermetallic hydride where O_2 and H_2 streams merge (bi-functional catalyst).

Finally, results of independent studies with other oxygenating atmospheres shall be mentioned. Exposure of Zr_2PdH_z to NO shows (8) strong onset of a reduction reaction around 120°C. Products are not identified yet. When $ThRhH_3$ is exposed (9) to CO, methanation occurs around 200°C. While matrix oxidation is observed in this case, indications are that a first step involves reaction of H, from the solid, with CO. Subsequently O reacts with Th possibly involving H_2O as an intermediary. Bursts of methane formation are observed near the α - β phase transition.

The increased bond order in O_2 , NO, and CO are reflected in the increasing temperatures for onset of the reduction reaction. At these higher temperatures matrix oxidation becomes a problem.

It should also be mentioned that H_2O formation data (1) on $LaNi_5H_6$ previously presented as $\ln p_{O_2}$ vs time also indicate reactions of first order (8) with respect to hydrogen concentration in the matrix (z) when plotted in the manner of the present study.

A relationship between the catalytically active surfaces of metal hydrides and the ones of oxidized rare earth-transition metal compounds is obvious. It can be assumed that in both cases the catalytically active species are clean transition metal particles (Ni). In the case of metal hydride catalysis these will be present only in minute quanti-

ties on the surface of the hydride originating from trace surface segregation. In the case of the decomposed intermetallics this surface segregation (catalytic activation) has been carried to an extreme. However, metal hydrides bring special opportunities to reduction catalysis in the form of vast reservoirs of active H and an involvement of the α - β phase transition.

Synthesis of more complex chemicals (e.g., amino acids) is also a possibility with metal hydrides. This may have prebiotic implications. It has also been pointed out (2) that catalytic reduction reactions are of possible technological potential (fuel cells, catalytic heating, isotope separation, or chemical synthesis).

Conclusion

Data of this study allow one to make two important points. One concerns the fact that when LaCo_3H_z is exposed to O_2 of order 1 atm at near ambient conditions, H_2O formation is observed without noticeable

matrix oxidation. However, at higher temperatures some concomitant matrix oxidation does occur. A second point pertains to the fact that, *cum grano salis*, one can speak of the water formation reaction as first order with respect to hydrogen concentration in the matrix (z).

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