The Confinement of Hydrogen in $LaNi_5$ Hydride Using Surface Poisoning

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It has been found that an $LaNi_5$ hydride treated with a CO gas is stable in air at room temperature. The hydrogenation of acetophenone or 1-octene was performed using the CO-treated hydride. The reaction well proceeded and it was confirmed that hydrogen confined in the hydride can be available for reactions. The use of the CO-treated $LaNi_5$ hydride, therefore, can simplify the operation for hydrogenation.

$LaNi_5$ family alloys are well known to exhibit excellent rechargeable hydrogen storage properties at an ambient temperature and pressure.

An $LaNi_5$ hydride has an equilibrium pressure of as low as about 0.2 MPa at room temperature, hence it is unstable in air and must be handled under a hydrogen pressure of more than the equilibrium pressure. If it is possible to deal with the hydride under an atmosphere or an inert gas, some advantages would be available. For example, we do not need any heavy pressure vessels for hydrogen storage and transport.

It has been found that the surface treatment with a carbon monoxide gas is effective to confine hydrogen in the hydrogenated $LaNi_5$ and the resulting hydride is stable even in air at room temperature.[1] Our present concern is to clarify the mechanism of the confinement of hydrogen with the CO treatment, and how hydrogen confined in the hydride is taken out. To solve the problems, the hydrogenation of some organic compounds, such as acetophenone or 1-octene, was carried out using the $LaNi_5$ hydride treated with CO.

The hydrogenation reaction was done in a 32.3 ml stainless steel vessel fitted with a magnetic stirrer. The experimental procedure for obtaining the $LaNi_5$ hydride treated with CO has been previously described in detail.[1] Acetophenone (0.43 mmol) and xylene, or 1-octene (0.64 mmol) and cyclohexane were introduced by a pipette into the vessel in which about 2.3 mmol(1 g) $LaNi_5$ hydride powder treated with CO was presented. This operation was performed under an Ar atmosphere at room temperature. The total volume of solvent was 5.0 ml. The organic compounds used were obtained from Wako Pure Chemical Ind., and purities were as follows; 98.5% acetophenone, 95% 1-octene, 96% xylene and 99.5% cyclohexane. These were distilled before use. The hydrogenation reaction was performed for 14.4 ks at a given temperature. The stirrer was controlled at about 2000 rpm. Since the $LaNi_5H_x$ powder was suspended in the liquid as a slurry, the powder and solution were separated by filtration after reaction. The progress of hydrogenation reaction was determined by gas chromatographic analyses which were performed with Shimadzu GC-3BT for acetophenone (detector, TCD; carrier gas, He) and Shimadzu GC-8A for 1-octene (detector, FID; carrier gas, N_2) equipped with a column of 5% PEG 20M on Chromosorb W AW-DMCS (60/80 mesh) and of 20% PEG 20M on Shimalite NAW (60/80 mesh) respectively. To determine the change in hydrogenation concentration in the samples, X-ray diffraction measurements were taken of the hydride treated with CO gas. This procedure was described in detail elsewhere.[1]

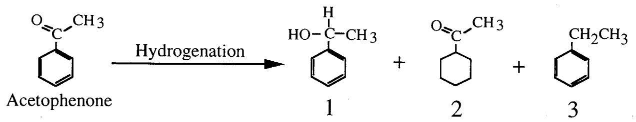

Table 1. Hydrogenation of acetophenone with the CO-treated $LaNi_5$ hydride

Temperature/K	Conversion/%[a]	Yield/%[a]			H / $LaNi_5$[b]
		1	2	3	
300	—[c]	—	—	—	5.9±0.2
333	10	6	—	—	0
363	9	5	—	—	0
373	53	50	1	2	0
383	60	52	1	6	0
393	94	77	15	3	0
300[d]	3	3	—	—	0

[a] Determined by GC analysis. [b] Hydrogen concentration in $LaNi_5H_x$ after reaction. (before reaction : x=6.7±0.2) [c] Not detected. [d] The reaction was carried out with the non-treated hydride.

Table 1 shows the results for hydrogenation of acetophenone with the $LaNi_5$ hydride treated with CO. No product was obtained at 300 K, whereas the reaction proceeded remarkably at more than 373 K. At 393 K, 1-phenylethanol which is the main product of the hydrogenation was obtained in a 77% yield. For the reaction at 300 K, the hydrogen concentration of 5.9±0.2 H/$LaNi_5$ was still remained in the alloy even after reaction for 14.4 ks (4 h). As for the reaction at more than 333 K, however, there was no hydrogen in the alloy after reaction. It has been already found that if the CO-treated $LaNi_5$ hydride is placed under an atmosphere at more than 333 K it desorbs hydrogen immediately. Therefore, the reaction appears to occur with gaseous hydrogen and the surface Ni on $LaNi_5$ as a catalyst.

For the hydrogenation of 1-octene, as shown in Table 2, a yield of main product, i.e. n-octane, was 95% at 313 K.

The results from the hydrogenation of acetophenone and 1-octene indicate that we can use hydrogen in the CO-treated $LaNi_5$ hydride without great difficulties. An advantage of the present technique is that the CO-treated hydride is easily handled in comparison with the non-treated one. Some investigations for the practical utilization of hydrogen storage alloys in organic synthesis have been done.[2-5] On the conventional technique for handling of the $LaNi_5$ hydride, to avoid the desorption of hydrogen from the hydride, the system is necessary to maintain a low temperature with appropriate cooling baths. The CO-treated hydride, however, can be handled in inert gas (even in air) at room temperature, so that both the substrate and the hydride can be introduced simultaneously into a reaction vessel.

The surface of $LaNi_5$ has been analyzed by means of X-ray photoelectron spectroscopy and Auger electron spectroscopy.[6] After the adequate activation process, the surface consists of islands of La_2O_3 or $La(OH)_3$ and metallic Ni. The surface Ni

Table 2. Hydrogenation of 1-octene with the CO-treated $\mathrm{LaNi_5}$ hydride

Temperature/K	Conversion/%[a]	Yield/%[a,b]	H / $\mathrm{LaNi_5}$[c]
273	17	6	6.4±0.2
295	21	7	6.1±0.2
300	98	89	6.1±0.2
313	100	95	3.4±0.2
273[d]	100	99	>6

[a] Determined by GC analysis. [b] Yield of n-octane. [c] Hydrogen concentra-tion in $\mathrm{LaNi_5H_x}$ after reaction. (before reaction : x=6.7±0.2) [d] The reaction was carried out with the non-treated hydride.

mainly acts as a catalysis for dissociation and recombination of the hydrogen molecule.[6,7] When the $\mathrm{LaNi_5}$ hydride are placed in a CO atmosphere, CO molecules adsorb on the surface Ni.[1] Since the adsorbed CO prohibits the recombination of hydrogen atoms from the hydride, hydrogen appears to be confined in $\mathrm{LaNi_5}$.

It was confirmed that the hydrogenation of 1-octene using the non-treated hydride proceeds perfectly at 273 K. CO molecules adsorbed on the Ni surface does not desorb at this temperature.[8] The hydrogenation of 1-octene using the CO-treated hydride, nevertheless, occurred to some extent at 273 K. This suggests that the recombination center on the Ni surface was not terminated with CO perfectly, although it is clear that the surface poisoning with CO hindered the reaction of 1-octene with hydrogen on the metallic Ni which appears to be an active site of hydrogenation. This matter may be undesirable for the storage of hydrogen for a long period. Therefore, further investigations for the condition of CO treatment and finding other poisoning materials, such as sulfur compounds, are necessary to confine hydrogen perfectly in the alloys.

It is noteworthy that a high yield, 89%, was obtained for the hydrogenation of 1-octene at 300 K with only a slight decrement of hydrogen concentration in the hydride. The decrement corresponded to a consumption of hydrogen for the hydrogenation. The fact means that hydrogen atoms in the hydride directly react with 1-octene before recombining to hydrogen molecules. It was found that the hydrogenation of 1-octene can be done by this method without using a pressure-stable vessel, such as autoclave, because the reaction with the CO-treated hydride are not attended by the increase of internal pressure in the system.

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