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HYDROGENATION OF ETHYLENE OVER $LaNi_5H_{3.3}$

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The hydrogenation of ethylene was conducted at -78°C over $LaNi_5H_{3.3}$ both in the presence and absence of gaseous hydrogen, and it was found that hydrogen absorbed in $LaNi_5H_{3.3}$ showed far greater activity as compared with gaseous hydrogen under the experiment conditions.

Some activated intermetallic compounds of transition metals such as $LaNi_5$, $PrNi_5$, $LaCo_5$ etc. are well known to absorb appreciable amounts of hydrogen in atomic state at high pressure and desorb it rappidly at a reduced pressure. In combination with the convenient equilibrium pressure, this might enable these compounds to be used for the storage of hydrogen. From this point of view, a considerable amount of work has been done on the equilibrium properties between hydrogen and these compounds.1-4) Scarcely any studies have been concerned, however, with the chemical nature of the absorbed hydrogen.

This communication reports the hydrogenation of ethylene over $LaNi_5H_n$ which seems to be most promising among these compounds for the storage of hydrogen. $LaNi_5$ (from Moly Corp., 0.87 m^2/g) was activated according to the procedures reported by Kuijpers et al.1) The hydrogenation of ethylene was conducted at -78°C in a conventional gas circulation system having the reaction space of 300 cm^3 effective volume including the reactor. The product was analyzed by gas chromatography. About 0.40 g of $LaNi_5$ thus prepared was supported on glass wool in the reactor. It was again heated at 400°C under vacuum (ca. 4×10^{-5} mmHg) for 3 hr, exposed to hydrogen (40 cmHg, 99.99% pure hydrogen was further purified by passage through glass-bead traps cooled to -196°C.) at 400°C for 1 hr, cooled quickly to -78°C and kept for 2 hr at -78°C every time immediately before use.
The composition of the compound estimated from pressure drop of hydrogen was always maintained as $LaNi_5H_{3.3}$. Experiment 1 was conducted by admitting only ethylene (8.5 cmHg) after gaseous hydrogen in the reactor was quickly removed by evacuation. Experiments 2 and 3 were conducted by admitting the mixture of ethylene (8.5 cmHg) and hydrogen (15.3 and 36.2 cmHg) after gaseous hydrogen was removed. Experiment 4 was conducted by admitting the mixture of ethylene (8.5 cmHg) and hydrogen (36.0 cmHg) over $LaNi_5$ which was heated at 400°C in a vacuum for 3 hr and cooled slowly from 400°C to -78°C in the absence of hydrogen. Figures 1 and 2 show the time courses of hydrogenation rate and typical pressure changes during the reaction. We are first concerned with the initial fast reaction (A). Figure 1 clearly shows that the initial rate over $LaNi_5H_{3.3}$ is much faster than that over $LaNi_5$ (Experiment 4), and that it is almost independent of the pressure of gaseous hydrogen (Experiments 1, 2 and 3). This strongly implies that the initial fast reaction (A), except Experiment 4, proceeds with absorbed hydrogen. When gaseous hydrogen was absent (Experiment 1), the total pressure slightly increased at first and then reached a constant value (Figure 2, A).

The total number of hydrogen molecules which were used for the hydrogenation reaction (7.85×10^{-4} mol) and evolved from the alloy (7.35×10^{-4} mol) coincides exactly with the initial number of absorbed hydrogen molecules (1.53×10^{-3} mol). Therefore, the slight increase in the pressure is considered to be due to the hydrogen which was evoled by the recombination of hydrogen atoms on the surface. On the other hand, when a large amount of gaseous hydrogen was present(Experiment 3), the total pressure slightly decreased until ethylene was almost completely converted into ethane, then it significantly decreased (Figure 2, B). The decrease in the total pressure may be attributed mainly to the absorption of hydrogen into the alloy. It should be noted here that such a hydrogen absorption did not occur over the alloy used in Experiment 4. Experiment 5 was conducted with the same conditions as Experiment 1 over the alloy which was once used for the hydrogenation and then treated according to the procedure as shown in Figure 2, B . Figure 1 shows that the hydrogenation rate does not significantly differ from that of Experiment 1. Thus, the catalytic activity hardly decreases by the hydrogenation reaction. While, the slow reaction (B) is considered to proceed mainly with gaseous hydrogen, because the rate (B) is roughly proportional to the pressure of gaseous hydrogen except Experiment 4.

Kuijpers[1] measured in some detail the lattice parameters of $LaCo_5$ and $LaCo_5H_n$ by X-ray diffraction analysis and it was found that the lattice parameters of $LaCo_5H_n$ expand with increasing the content of absorbed hydrogen (n). Such a phenomenon can easily be expected also in the present alloy; the lattice parameters of $LaNi_5H_{3.3}$ are considered considerably expanded as compared with those of $LaNi_5$. It can also be considered that many of the characteristic physical properties of $LaNi_5$, such as surface area, concentration of defects, distribution of porosity etc. are different from those of $LaNi_5H_{3.3}$. The difference of the rate (B) between Experiments 3 and 4 may be attributed to these physico-chemical properties of the alloy.

From these results it can be concluded that the hydrogen absorbed in $LaNi_5$ alloy has a large activity for the hydrogenation of ethylene at such a low temperature as -78°C.

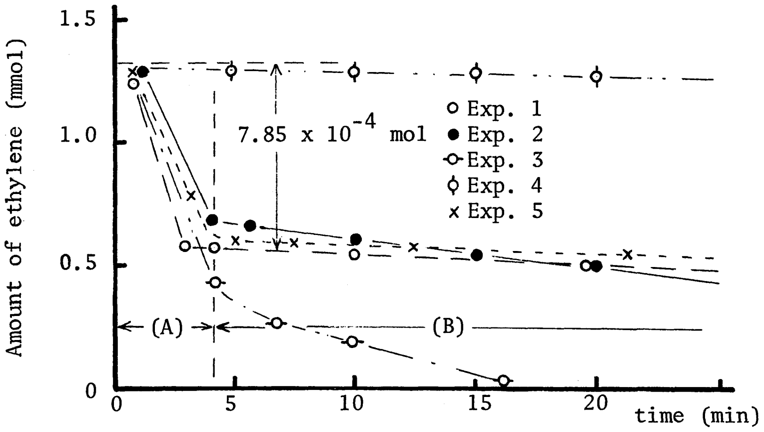

Figure 1. Time courses of the hydrogenation.

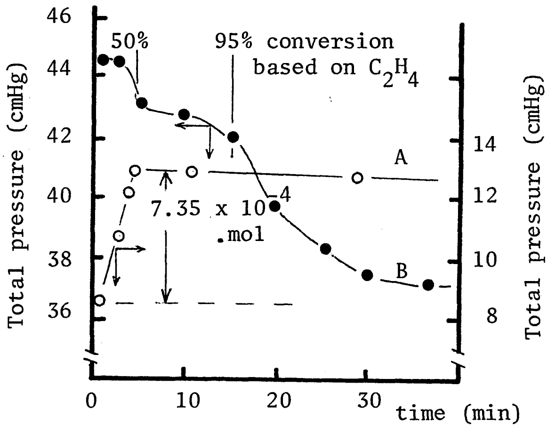

Figure 2. Variation of the gaseous total pressure (P) with time.

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