Hydrogenation of Ethylene over Some Intermetallic Compounds

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The hydrogenation of ethylene was studied by passing a mixture of ethylene and hydrogen over $LaNi_5$, $PrCo_5$, $LaCo_5$, $CeCo_5$, and $SmCo_5$ in a temperature range from -85 to $-46°C$. The reaction was also carried out over $LaNi_5H_{2.4}$, $PrCo_5H_{2.4}$, $LaCo_5H_{1.9}$, $CeCo_5H_{1.7}$, and $SmCo_5H_{1.2}$ by admitting only ethylene under similar conditions. It was found that the reaction proceeded at much higher rates over the hydrides than over their corresponding metal alloys. The rate of hydrogen desorption from the hydrides was separately measured, and the rate-determining step of hydrogenation over the hydrides was concluded to be the migration process of absorbed hydrogen atoms from the bulk of the compounds onto the surface.

INTRODUCTION

Some activated intermetallic compounds of transition metals, such as $LaNi_5$, $PrCo_5$, $LaCo_5$, $CeCo_5$, etc., absorb appreciable amounts of hydrogen in atomic form under high pressures which desorb rapidly at reduced pressures, and a considerable amount of work has been done on the equilibrium between hydrogen and these compounds (*1*). Few studies, however, have been carried out so far on the reactivity of such absorbed hydrogen atoms (hydrides).

Recently Coon *et al.* (*2*) and Wallace *et al.* (*3*) have reported that these inter-metallic compounds catalyze the reaction of carbon monoxide and hydrogen to form methane at 250–300°C, and they also catalyze ammonia synthesis at 300–530°C. We have also studied the hydrogenation of ethylene over $LaNi_5H_n$ ($n = 0.62$, 0.92, 1.5, 2.1, and 2.4) and $PrCo_5H_{2.4}$ as well as over $LaNi_5$ and $PrCo_5$ in a temperature range from -60 to $-84°C$ and observed that the rates of hydrogenation over $LaNi_5H_n$ and $PrCo_5H_{2.4}$ are far greater than

those over $LaNi_5$ and $PrCo_5$ (*4–6*). These results strongly suggest that the reactivity of the hydride hydrogen is far greater as compared with that of gaseous hydrogen and that the hydrogenation takes place mainly by using the hydride. In this report more varieties of alloy hydrides were employed to examine the mechanism of the reaction in more detail.

EXPERIMENTAL

Preparation of $LaNi_5H_n$, $PrCo_5H_n$, $LaCo_5H_n$, $CeCo_5H_n$, and $SmCo_5H_n$. Binary alloys of $LaNi_5$, $PrCo_5$, $LaCo_5$, $CeCo_5$, and $SmCo_5$ were obtained from Moly Corp. The alloys were adequately washed with purified acetone and then treated at 450°C for several hours under vacuum (ca. 4×10^{-5} mm Hg). The alloys were exposed to a hydrogen pressure of 100 atm at 450°C, cooled step by step to room temperature, evacuated, and then gradually heated to 450°C under vacuum. By repeating such treatments the alloys are activated so that they absorb hydrogen quite rapidly at

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450°C. The compounds of LaNi₅Hₙ, PrCo₅Hₙ, LaCo₅Hₙ, CeCo₅Hₙ, and SmCo₅Hₙ thus obtained were preserved at room temperature under an atmospheric pressure of hydrogen.

Apparatus and procedure of the hydrogenation of ethylene. The hydrogenation of ethylene was studied in a conventional gas circulation system with a dead space of about 300 cm³ including the reactor. The reactor was a quartz tube about 17 cm long and 2.0 cm in diameter. It was confirmed that the speed of circulation pump used in the present system was sufficiently fast in comparison to the reaction rate.

The research grade ethylene used in this work was obtained from Takachiho Chemical Corp. and purified by the conventional method.

About 0.40 g of each alloy was supported on silica wool in the reaction tube. Prior to every measurement of the reaction the alloys were subjected to the following treatments: LaNi₅Hₙ, PrCo₅Hₙ, LaCo₅Hₙ, CeCo₅Hₙ, and SmCo₅Hₙ were heated at 400°C under vacuum (ca. 4 × 10⁻⁵ mm Hg) for 3 hr, exposed to hydrogen (30 to 40 cm Hg) at 400°C for 1 hr, cooled quickly to −78°C, kept at −78°C for 2 to 10 hr, and then quickly brought to a reaction temperature. The composition of the compounds was estimated from the pressure drop of hydrogen as LaNi₅H₂.₄, PrCo₅H₂.₄, LaCo₅H₁.₉, CeCo₅H₁.₇, and SmCo₅H₁.₂.

After the temperature of the catalyst, which was measured by a thermometer inserted at the center of the catalyst bed, reached a reaction temperature, the reaction tube was quickly evacuated to remove hydrogen in the gas phase, and then the reactant (ethylene or mixture of ethylene and hydrogen) was admitted. The reacting gas was analyzed by gas chromatography.

RESULTS AND DISCUSSION

The hydrogenation of ethylene was first carried out at −78°C by admitting the mixture of hydrogen (5.7 cm Hg, 0.90

mmol) and ethylene (8.5 cm Hg, 1.35 mmol) over LaNi₅, PrCo₅, LaCo₅, CeCo₅, and SmCo₅ which were heated at 400°C for 3 hr under vacuum (ca. 4 × 10⁻⁵ mm Hg) and cooled quickly to a reaction temperature in the absence of gaseous hydrogen. In these cases, the total pressure in the gas phase decreased gradually during the reaction. The number of moles of ethane formed in the reacting gas exactly agreed with that of hydrogen disappearing in the gas phase, which indicates that no gaseous hydrogen was absorbed by these alloys under the experimental conditions and that these alloys are free from hydrides.

The hydrogenation of ethylene was then studied at −78°C over 0.40 g of these alloys using various pressures of hydrogen and ethylene. The initial rates of the hydrogenation followed by gas chromatography are summarized in Table 1. The data shown in Table 1 lead to the following rate expression:

$$r = k_1 P_{H_2}^{1.0} P_E^0, \tag{1}$$

where r is the initial rate of the hydrogenation, k_1 is the rate constant, and P_{H_2} and P_E, are the initial pressures of hydrogen and ethylene, respectively. The rate constants obtained from the hydrogenation over these alloys at various temperatures under the same pressures of hydrogen (5.7 cm Hg) and ethylene (5.4 cm Hg) are shown in Table 2 together with the apparent activation energies. The activation energies obtained were almost the same in all cases, but the rate constants were significantly dependent upon the alloys.

The hydrogenation of ethylene was then conducted at −78°C over 0.40 g of LaNi₅H₂.₄ (containing 2.23 matom of H), PrCo₅H₂.₄ (2.22 matom), LaCo₅H₁.₉ (1.78 matom), CeCo₅H₁.₇ (1.57 matom), and SmCo₅H₁.₂ (1.08 matom) by admitting only ethylene (9.2 cm Hg, 1.46 mmol). The results obtained are shown in Fig. 1. Almost no change of the total pressure was observed until most of ethylene was converted into

ethane, but the analysis by gas chromatography showed ethane was being formed at a very high speed. It was also confirmed that the reacting gas contained only a trace of hydrogen in every case. Accordingly, it may be concluded that the ethylene was hydrogenated by the hydrogen in the hydrides.

The reaction was also studied at $-78°C$ over 0.40 g of the same catalysts by using various pressures of ethylene.

The following equation, which was pre-

TABLE 1

Rates of Hydrogenation Obtained under Various Pressures of Ethylene and Hydrogen at $-78°C$

Alloy	P_{H_2} (cm Hg)	P_E (cm Hg)	r (mmol of C_2H_6/ g of cat min)
LaNi$_5$	4.0	8.5	4.12×10^{-4}
	7.7	8.5	8.93×10^{-4}
	11.7	8.5	1.17×10^{-3}
	19.0	8.5	1.95×10^{-3}
	5.7	2.6	6.53×10^{-4}
	5.7	4.0	6.78×10^{-4}
	5.7	8.1	6.69×10^{-4}
	5.7	15.8	6.60×10^{-4}
PrCo$_5$	3.1	6.0	1.06×10^{-3}
	10.8	6.0	3.60×10^{-3}
	15.2	6.0	5.12×10^{-3}
	6.0	6.0	2.11×10^{-3}
	6.0	2.9	2.14×10^{-3}
	6.0	10.1	2.13×10^{-3}
LaCo$_5$	2.1	5.5	2.21×10^{-5}
	9.2	5.5	9.97×10^{-5}
	15.5	5.5	1.58×10^{-4}
	5.6	2.2	5.54×10^{-5}
	5.6	5.5	5.54×10^{-5}
	5.6	8.7	4.99×10^{-5}
CeCo$_5$	4.7	6.7	1.21×10^{-4}
	16.7	6.7	3.81×10^{-4}
	10.5	6.7	2.24×10^{-4}
	10.5	2.2	2.15×10^{-4}
	10.5	14.6	2.32×10^{-4}
SmCo$_5$	2.3	6.4	2.25×10^{-4}
	16.1	6.4	1.61×10^{-3}
	6.5	6.4	5.92×10^{-4}
	6.5	2.1	6.09×10^{-4}
	6.5	15.8	5.85×10^{-4}

TABLE 2

Rate Constants [k_1 in Eq. (1)] Obtained at Various Temperatures for the Reaction between Ethylene and Hydrogen over Different Alloys

Alloy	Temperature (°C)	k_1(g^{-1} of cat min^{-1})	E(kcal/mol)
LaNi$_5$	-60	9.42×10^{-4}	6.8
	-69	4.17×10^{-4}	
	-78	2.05×10^{-4}	
	-83	1.35×10^{-4}	
PrCo$_5$	-51	1.35×10^{-2}	6.9
	-57	9.00×10^{-3}	
	-65	4.91×10^{-3}	
	-73	2.95×10^{-3}	
	-78	1.70×10^{-3}	
LaCo$_5$	-46	5.05×10^{-4}	6.8
	-60	1.91×10^{-4}	
	-70	8.20×10^{-5}	
	-78	4.24×10^{-5}	
CeCo$_5$	-52	7.41×10^{-5}	6.4
	-60	5.00×10^{-5}	
	-70	2.45×10^{-5}	
	-78	1.23×10^{-5}	
SmCo$_5$	-48	5.19×10^{-5}	6.5
	-60	2.21×10^{-5}	
	-71	9.65×10^{-6}	
	-78	5.26×10^{-6}	

viously proposed in the hydrogenation of ethylene over LaNi$_5$H$_n$ (5), can be approximately applied for every case:

$$y = \tfrac{1}{2}(C_0 - C_t) \quad \text{or} \quad C_t = C_0 - 2y, \quad (2)$$

where y, C_t, and C_0 denote the amount of the resulting ethane (mmol of C_2H_6/g of cat) at time t, and the amounts of the hydride (matom of H/g of cat) at time t and 0, respectively. By using the data shown in Fig. 1, C_t was calculated according to Eq. (2) and $\ln C_t$ was plotted against the reaction time t (Fig. 2), which leads to

$$\ln C_t = -k_2 t + \ln C_0$$

or

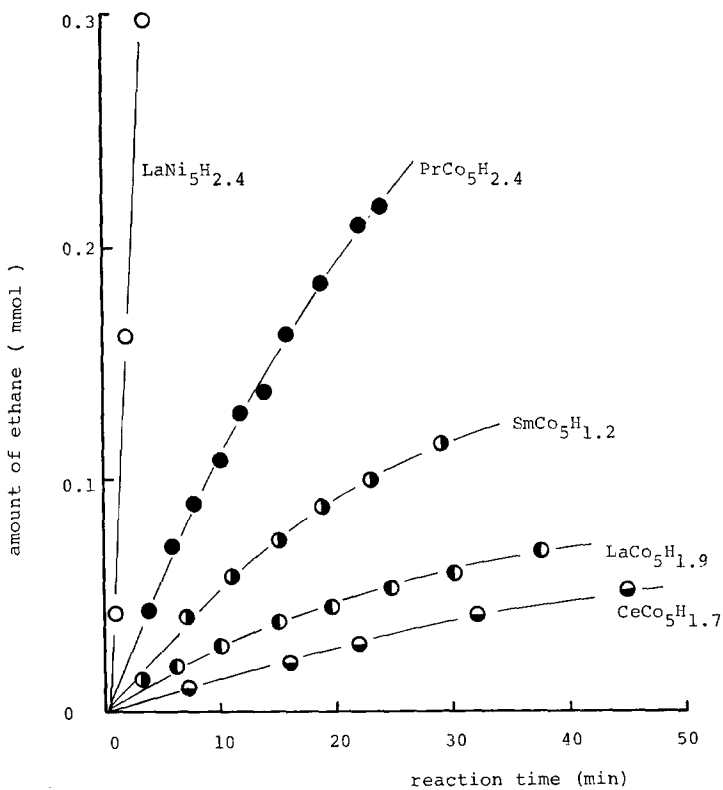$$r = \frac{dy}{dt} = \tfrac{1}{2}k_2 C_t = k_3 C_t, \quad (3)$$

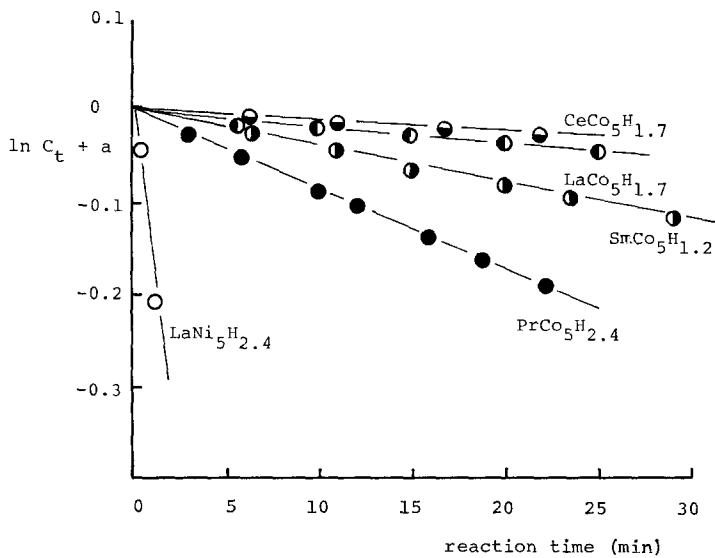FIG. 1. Hydrogenation of ethylene by alloy hydrides at $-78°C$ over 0.40 g of alloys in 9.2 cm Hg of ethylene.

FIG. 2. Plots of ln C_t vs reaction time t. Hydrogenation reactions were conducted at $-78°C$ over 0.4 g of each alloy in 9.2 cm Hg of ethylene. C_t represents the amount of the hydrides at time t. a, an arbitrary constant.

TABLE 3

Rate Constants [k_3 in Eq. (3)] Obtained with Various Pressures of Ethylene
and at Various Temperatures

Alloy	P_E (cm Hg)	k_3 at $-78°C$ (g^{-1} of cat min^{-1})	Temperature (°C)	k_3 at various temperatures (g^{-1} of cat min^{-1})	E(kcal/mol)
LaNi$_5$H$_{2.4}$	9.1	5.11×10^{-1}	-75	6.20×10^{-1}	5.7
	16.0	4.92×10^{-1}	-78	5.11×10^{-1}	
			-80	4.30×10^{-1}	
			-85	2.92×10^{-1}	
PrCo$_5$H$_{2.4}$	5.0	2.09×10^{-2}	-62	8.18×10^{-2}	6.0
	9.2	2.20×10^{-2}	-67	5.01×10^{-2}	
	16.1	2.15×10^{-2}	-69	4.18×10^{-2}	
			-78	2.20×10^{-2}	
LaCo$_5$H$_{1.9}$	5.8	4.09×10^{-3}	-66	9.08×10^{-3}	5.2
	9.1	4.15×10^{-3}	-72	6.10×10^{-3}	
	15.9	4.02×10^{-3}	-75	5.05×10^{-3}	
			-78	4.15×10^{-3}	
			-80	3.65×10^{-3}	
CeCo$_5$H$_{1.7}$	4.3	2.65×10^{-3}	-57	1.17×10^{-2}	5.7
	9.3	2.32×10^{-3}	-66	5.11×10^{-3}	
	16.1	2.40×10^{-3}	-78	2.32×10^{-3}	
SmCo$_5$H$_{1.2}$	4.5	1.11×10^{-2}	-65	2.88×10^{-2}	5.7
	9.2	1.21×10^{-2}	-72	1.55×10^{-2}	
	16.5	1.07×10^{-2}	-78	1.21×10^{-2}	

where r is the rate of the formation of ethane (mmol of C_2H_6/g of cat min) at time t, and k_2 and k_3 denote the rate constants (g^{-1} of cat min^{-1}) for the consumption of the hydrides and the formation of ethane, respectively. The values of the rate constant, k_3, obtained are summarized in Table 3. The data shown in Table 3 indicate that the rate constant, k_3, is independent on the pressure of ethylene. The hydrogenation of ethylene was also conducted at various temperatures over 0.40 g of the same catalysts using a constant pressure of ethylene (9.2 cm Hg). The values of k_3 obtained at various temperatures are also shown in Table 3 together with the apparent activation energies.

About 0.40 g of LaNi$_5$H$_{2.4}$, PrCo$_5$H$_{2.4}$, La Co$_5$H$_{1.9}$, CeCo$_5$H$_{1.7}$, and SmCo$_5$H$_{1.2}$ were prepared at $-78°C$ in the same reactor

according to normal procedures. They were briefly evacuated at $-78°C$ to remove ambient hydrogen, and then the pressure increase in the vessel was continuously measured. The initial rate of hydrogen desorption from the hydrides obeyed Eq. (3) in every case. The rate constants, [k_3 in Eq. (3)], for the desorption obtained at various temperatures are shown in Table 4 together with the apparent activation energies. In most cases both the values of k_3 and the apparent activation energies are very close to those of the hydrogenation of ethylene (Table 3). These results strongly indicate that the rate-determining step of ethylene hydrogenation by hydride hydrogen is the migration of hydrogen in the hydrides from the bulk to the surface, which was previously suggested in the case
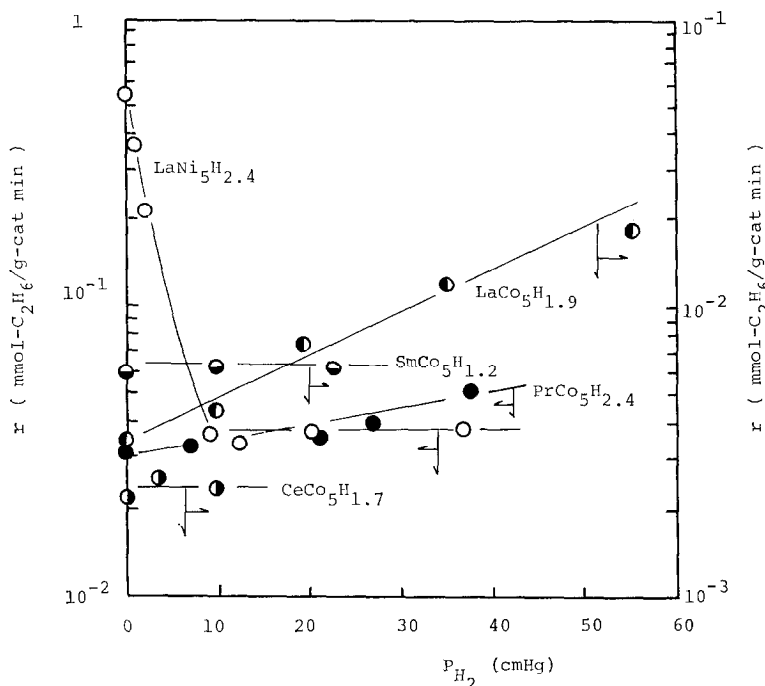
FIG. 3. Dependence of r on the pressure of hydrogen. Hydrogenation reactions were conducted at $-78°C$ over 0.40 g of each alloy.

of $LaNi_5H_n$ (5), and also that it is independent of ethylene pressure.

Then, the hydrogenation of ethylene was conducted at $-78°C$ over 0.40 g of the same catalysts using the mixture of hydrogen and ethylene. The initial rates, r, followed by gas chromatography (Table 5) were almost independent of the pressure of ethylene. In the cases of hydrogenation over $LaNi_5H_{2.4}$, $CeCo_5H_{1.7}$, and $SmCo_5H_{1.2}$, the total pressure remained almost unchanged until most of ethylene was converted into ethane and then decreased gradually. The decrease in the total pressure may be attributed to the absorption of gaseous hydrogen into the alloy. In fact, it was confirmed at $-78°C$ over the activated $LaNi_5$ alloy by using the mixture of hydrogen (12.5 cm Hg) and ethane (7.5 cm Hg) that gaseous hydrogen was absorbed at a considerably high speed. This implies that ethane produced during the hydrogenation hardly blocks the hydrogen adsorption, but ethylene seems to retard the hydrogen

absorption (5). Over other hydrides, the total pressure decreased gradually from the initial stage of the hydrogenation reaction. The decrease in the total pressure in these cases may be attributable to the consumption of gaseous hydrogen by the hydrogenation of ethylene. Figure 3 shows the dependence of the initial rates of hydrogenation on the hydrogen pressure. With increasing hydrogen pressure, the hydrogenation rate was markedly diminished in the case of $LaNi_5H_{2.4}$, hardly affected in the cases of $CeCo_5H_{1.7}$ and $SmCo_5H_{1.2}$, and accelerated to some extent in the cases of $PrCo_5H_{2.4}$ and $LaCo_5H_{1.9}$, respectively. However, the precise mechanism for such a different effect of hydrogen over various alloy hydrides is left to be studied in the future.

Then, the hydrogenation of ethylene was conducted at $-78°C$ over several kinds of $LaCo_5H_n$ which were prepared by evacuating $LaCo_5H_{1.9}$ for 4 to 16 hr under vacuum (ca. 4×10^{-5} mm Hg) at -78,

TABLE 4

Rate Constants [k_3 in Eq. (3)] Obtained at Various Temperatures in the Desorption of Hydride

Alloy	Temperature (°C)	k_1 (g^{-1} of cat min^{-1})	E (kcal/mol)
LaNi$_5$H$_{2.4}$	−60	3.82 × 10^{-1}	5.3
	−69	2.15 × 10^{-1}	
	−78	1.10 × 10^{-1}	
	−84	6.74 × 10^{-2}	
PrCo$_5$H$_{2.4}$	−48	1.72 × 10^{-1}	6.0
	−56	1.02 × 10^{-1}	
	−62	6.01 × 10^{-2}	
	−78	2.20 × 10^{-2}	
LaCo$_5$H$_{1.9}$	−55	3.05 × 10^{-2}	5.4
	−60	2.30 × 10^{-2}	
	−65	1.59 × 10^{-2}	
	−78	6.78 × 10^{-3}	
CeCo$_5$H$_{1.7}$	−48	2.49 × 10^{-2}	6.2
	−63	8.28 × 10^{-3}	
	−78	2.32 × 10^{-2}	
SmCo$_5$H$_{2.4}$	−50	1.48 × 10^{-1}	6.1
	−60	7.74 × 10^{-2}	
	−70	4.30 × 10^{-2}	
	−78	2.30 × 10^{-2}	

−50, −20, and 0°C and quickly bringing it to the reaction temperature. The amounts of hydride left in the alloys after the evacuation (prior to the hydrogenation) were also estimated as follows: Each alloy hydride was heated at 400°C for 1 hr under a reduced pressure, and the hydrogen evolved in the gas phase was measured by collecting with a Toepler pump. The amounts of hydrogen evolved are shown in Table 6, which clearly shows that most of the hydride hydrogen is left in the bulk hydride under these evacuation conditions at lower temperatures. The hydrogenation of ethylene over these hydrides was examined at −78°C by admitting only ethylene (5.2 cm Hg) over 0.40 g of the evacuated alloy hydrides. The hydrogenation of ethylene hardly took place over these evacuated alloys. That is, the hydride

hydrogen left in the alloys no longer comes out under these conditions, in contradiction to the fact that most of the hydride hydrogen easily comes out during the hydrogenation of ethylene under similar conditions as described above. The precise reason is, however, not clear at present.

The hydrogenation of ethylene was carried out at −78°C over the evacuated alloys by admitting the mixture of hydrogen (19.5 cm Hg, 3.09 mmol) and ehtylene (5.8 cm Hg, 0.92 mmol). As shown in

TABLE 5

Rates of Hydrogenation Obtained with Various Pressures of Ethylene and Hydrogen at −78°C

Alloy	P_{H_2} (cm Hg)	P_E (cm Hg)	r (mmol of C$_2$H$_6$/ g of cat min)
LaNi$_5$H$_{2.4}$	37.0	2.1	3.44 × 10^{-2}
	37.0	4.6	3.90 × 10^{-2}
	37.0	8.5	3.92 × 10^{-2}
	37.0	14.3	3.73 × 10^{-2}
	1.1	8.5	3.83 × 10^{-1}
	2.0	8.5	2.25 × 10^{-1}
	9.5	8.5	3.70 × 10^{-2}
	12.6	8.5	3.44 × 10^{-2}
	20.5	8.5	3.79 × 10^{-2}
PrCo$_5$H$_{2.4}$	21.5	4.0	3.55 × 10^{-2}
	21.5	9.2	3.46 × 10^{-2}
	21.5	15.8	3.43 × 10^{-2}
	7.0	9.2	2.34 × 10^{-2}
	27.0	9.2	4.02 × 10^{-2}
	38.2	9.2	5.11 × 10^{-2}
LaCo$_5$H$_{1.9}$	19.4	2.1	7.60 × 10^{-3}
	19.4	5.7	7.30 × 10^{-3}
	19.4	14.0	7.73 × 10^{-3}
	10.1	5.7	4.22 × 10^{-3}
	35.1	5.7	1.25 × 10^{-2}
	55.3	5.7	1.89 × 10^{-2}
CeCo$_5$H$_{1.7}$	10.3	4.4	2.36 × 10^{-3}
	10.3	8.6	2.51 × 10^{-3}
	10.3	16.1	2.41 × 10^{-3}
	3.5	4.4	2.65 × 10^{-3}
SmCo$_5$H$_{1.2}$	9.4	4.7	6.35 × 10^{-3}
	9.4	9.1	6.93 × 10^{-3}
	9.4	15.7	6.71 × 10^{-3}
	2.2	4.7	6.83 × 10^{-3}
	22.5	4.7	6.52 × 10^{-3}

TABLE 6

Effect of the Evacuating Temperature on the Catalytic Activity for the Hydrogenation of Ethylene (5.8 cm Hg) in the Presence of Hydrogen (19.5 cm Hg)

Evacuation temperature in the pre-treatment (°C)	Remaining hydride hydrogen, $LaCo_5H_n$ (ml)	r (mmol of C_2H_6/ g of $LaCo_5$ min)
-78^a	—	4.10×10^{-3}
-50^b	$17.5, n = 1.7$	1.24×10^{-3}
-20^b	$16.3, n = 1.6$	5.30×10^{-4}
0^b	$14.7, n = 1.4$	1.67×10^{-4}

[a] Evacuating time, 16 hr.
[b] Evacuating time, 4 hr.

Table 3, the initial rates followed by gas chromatography remarkably decreased with an increase in the evacuating temperature.

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 concentration of the hydride (n). Such a phenomenon can also be expected in the present case. In addition, many of the characteristic physical properties of the alloy, such as concentration of defects, distribution of pores, etc., are considered to depend on the content of the hydride (n), the evacuation conditions of the alloy, and the kind of the alloys. These physicochemical properties of the alloy might affect the rate of the hydrogenation.

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