

## Hydrogenation on Supported Lanthanide–Palladium Bimetallic Catalysts: Appearance of Considerable Hydrogen Uptake

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Upon introducing of lanthanide metals (Ln: Eu or Yb) onto a Pd surface by the reaction of Pd/SiO<sub>2</sub> with Eu or Yb metal dissolved in liquid ammonia, the ability of considerable hydrogen uptake by the catalyst appeared during the hydrogenation reaction. Hydrogenation over supported lanthanide–palladium bimetallic catalysts was studied at 173–213 K, especially concerning the effects of the reactants, support materials, Pd particle sizes, and dispersion on the hydrogenation behavior with the hydrogen uptake. For the hydrogenation of ethene, propene, butene or butadiene, considerable hydrogen uptake occurred preferentially, followed by hydrogenation using the hydrogen taken up the catalyst. The hydrogenation occurred by a rate-limited hydrogen uptake process. In marked contrast to olefin and butadiene, no hydrogen uptake was observed for the hydrogenation of acetylene, indicating the progress of the reaction by a different mechanism. The support materials (SiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub>, ZrO<sub>2</sub>, MgO, and TiO<sub>2</sub>), Pd particle sizes and Pd dispersion in Pd/support were important factors in determining the hydrogen uptake by supported Ln–Pd catalysts and the resulting hydrogenation behavior.

There has been increasing interest in the properties of lanthanides (Ln), as well as such related compounds as heterogeneous catalysts.<sup>1)</sup> By using the dissolution of lanthanide metals (Eu and Yb) in liquid ammonia,<sup>2)</sup> we have developed methods for preparing novel catalysts containing lanthanides, and have demonstrated that they exhibit specific catalytic properties.<sup>3)</sup>

We have recently reported on an interesting hydrogenation behavior by SiO<sub>2</sub>-supported Ln–Pd bimetallic catalysts (Eu–Pd/SiO<sub>2</sub> and Yb–Pd/SiO<sub>2</sub>), obtained when Eu or Yb metal dissolved in liquid ammonia reacts with 5 wt% Pd/SiO<sub>2</sub>.<sup>4)</sup> Ln–Pd/SiO<sub>2</sub> shows synergetic effects between the lanthanide and palladium metal involving considerable hydrogen uptake during the hydrogenation of propene.

When the hydrogenation of propene was carried out at 193–263 K over Ln–Pd/SiO<sub>2</sub>, preferential hydrogen uptake by the catalyst occurred, followed by the hydrogenation of propene with a certain induction period. The amounts of hydrogen taken up by Yb–Pd/SiO<sub>2</sub> (Yb/Pd=0.43) exceeded 12 in H/Pd. However, this hydrogen uptake was not the solubility of hydrogen in palladium and/or lanthanide in the catalyst. The hydrogen taken up was highly reactive, and was completely consumed for the hydrogenation of propene. The hydrogenation rates on Pd/SiO<sub>2</sub> were given by  $v = kP_{H_2}$ , whereas for Ln–Pd/SiO<sub>2</sub> the rate dependence on the pressure was formulated as  $v = kP_{C_3H_6}/P_{H_2}$  (where  $k$  is a rate constant). The apparent activation energies were 48 kJ mol<sup>-1</sup> for 5 wt% Pd/SiO<sub>2</sub>, while those for Yb–Pd/SiO<sub>2</sub> (Yb/Pd=0.43) were no more than ca. 3 kJ mol<sup>-1</sup>. Extensive kinetic studies indicated that hydrogenation on Ln–Pd/SiO<sub>2</sub> proceeded ex-

clusively through a reaction path using the hydrogen taken up by the catalyst, and that it was by a rate-limited hydrogen uptake. However, it was found that hydrogen uptake occurred only in the presence of adsorbed propene on the catalyst.<sup>4)</sup> In the present study, the effects of the differences in the reactants used (ethene, propene, but-1-ene, *cis*-but-2-ene, *trans*-but-2-ene, buta-1,3-diene, and acetylene) on the hydrogenation behavior over SiO<sub>2</sub>-supported Ln–Pd were investigated. Moreover, to provide information regarding the factors responsible for the hydrogenation reactions with considerable hydrogen uptake, the influence of the support materials, Pd particle size and dispersion in the supported Pd catalysts as precursors were also studied.

### Experimental

**Materials.** Eu and Yb ingots (99.9%, Shin-Etsu Chemical Co., Ltd.) were used in the form of turnings or granules. SiO<sub>2</sub> (Degussa Aerosil 380) and ZrO<sub>2</sub> (Tosoh-Zirconia TZ-O) were commercially available. Al<sub>2</sub>O<sub>3</sub>, MgO, and TiO<sub>2</sub> (referred to as JRC-ALO-2, JRC-MGO-3, and JRC-TIO-4, respectively) were Reference Catalysts of the Catalysis Society of Japan.<sup>5)</sup> PdCl<sub>2</sub> (99.9%; Rare Metallic Co., Ltd.), Pd(NO<sub>3</sub>)<sub>2</sub> (99.9%; Wako Pure Chemical Ind., Ltd.) and (NH<sub>4</sub>)<sub>2</sub>[PdCl<sub>4</sub>] (Nacalai Tesque Inc.) were used without further purification. Ammonia (Iwatani Ind., Ltd.) was dried through a calcium oxide column and a sodium hydroxide column before use. Ethene, propene, but-1-ene, *trans*-but-2-ene, *cis*-but-2-ene, but-1,3-diene, and acetylene were of research purity, and further purified by triple distillation.

**Procedures of Catalyst Preparation and Catalytic Reactions.** Various oxide-supported Pd samples with various levels of Pd loading (0.2–30.0 wt%) were prepared by impregnating the support

materials ( $SiO_2$ ,  $ZrO_2$ ,  $Al_2O_3$ ,  $MgO$ , and  $TiO_2$ ) with aqueous solutions of the Pd metal salts. The impregnating slurry was vigorously stirred, dried, calcined at 623 K, and finally reduced at 623 K with flowing hydrogen at a standard pressure. Pd powders were conventionally prepared from  $Pd(NO_3)_2$  as follows. Aqueous ammonia was dropwise added to an aqueous solution of  $Pd(NO_3)_2$  to form precipitates. The resulting precipitates were filtered off, washed with distilled water, dried and reduced with hydrogen at 623 K.

The method of lanthanide addition to the Pd sample was described in earlier papers.<sup>4)</sup> In a typical preparation, reduced  $Pd/SiO_2$  was placed in a Schlenk tube containing a solution of liquid ammonia (15–20 cm<sup>3</sup>) at 198 K. Eu or Yb was added to the Pd sample suspended in liquid ammonia with vigorous stirring. Upon dissolution of the lanthanide metal in a liquid-ammonia solvent, a blue homogeneous solution was immediately formed, which was characteristic of the solvated electrons.<sup>2)</sup> The blue color gradually disappeared as a result of the reaction of the dissolved lanthanide metal with the Pd sample. Upon the disappearance of the blue color, the reaction tube was allowed to warm to room temperature, and the excess ammonia was pumped off, leaving supported Eu-Pd and Yb-Pd bimetallic catalysts. Unsupported Ln-Pd catalysts were similarly prepared using the Pd powder instead of supported Pd samples.

The catalytic reactions were performed on a recirculation reactor (ca. 253 cm<sup>3</sup>) equipped with a mercury manometer. Prior to each reaction, the catalyst was subjected to an evacuation treatment at 633 K for 2 h, set at 173–213 K of the reaction temperature; hydrogenation was then initiated by the admission of a mixed gas of the reactant and hydrogen. The reaction temperature was maintained constant within  $\pm 2$  K using such refrigerants as dry ice or liquid nitrogen. The reacting gas in the system was periodically collected by a gas sampler and analyzed using a Shimadzu TCD gas chromatograph (GC) with a column of active alumina or VZ-7. The gas composition during the reaction was determined by the material balance between the quantities of the reactants and hydrogenated products evaluated by GC, and by the changes in the total pressure in the gas phase. The carbon balance between the reactants and products during the reaction was usually retained. Moreover, it should be noted that notable adsorption or capillary condensation of the hydrocarbons was too small to be identified by manometric techniques. Therefore, the hydrogen uptake could be accurately determined from differences between the quantities of the hydrogen obtained from the drop in pressure and the hydrogen spent in the formation of hydrogenated products. The initial rates of the reactions were determined by measuring the slopes of the concentration–time curves. The accuracy of such measurements using GC and pressure changes was previously confirmed in the hydrogenation of propene, which was carried out in a recirculating reactor for a reference over 5 wt% Ni/ $SiO_2$  (JRC-S3-5Ni; Reference Catalyst of the Catalysis Society of Japan).<sup>5)</sup>

**Analyses.** IR spectra were recorded on a JASCO FT-IR 7000 spectrometer equipped with a MCT detector. The samples for the IR studies were prepared according to the method described above. To a liquid-ammonia solution of Eu or Yb metal was added, at 198 K, a disc of 5 wt%  $Pd/SiO_2$  that had been reduced at 623 K for 5 h. In a dry-argon glove bag, the thus-treated disc was carefully loaded into an IR cell of variable temperatures (193–673 K). The IR spectra were obtained from the ratio of the background spectrum of the catalysts to that of the species adsorbed on the catalysts. Extreme care was taken to prevent any contamination by air.

Temperature-programmed desorption (TPD) experiments were carried out at a constant heating rate of 10 K min<sup>−1</sup> in order to

increase the mass-spectrometer signal. After a thermal treatment of the catalyst at 633 K, hydrogen was adsorbed at 193 K, followed by evacuating the gas phase to ca.  $10^{-6}$  Torr (1 Torr = 133.322 Pa). The catalyst was heated in a programmed manner, and the desorbed hydrogen was continuously monitored by a quadrupole mass spectrometer (MS).

For hydrogenation using deuterium, the reaction was followed by a combination of measurement of GC and MS.

## Results and Discussion

**Hydrogenation Behavior of Olefin, Diene or Acetylene over Ln-Pd/ $SiO_2$ .**  $Pd/SiO_2$  was highly active for the hydrogenation of olefin, diene, and acetylene, even at low temperatures of around 190 K, whereas lanthanide metals exhibited very low or negligible activity under similar conditions.<sup>6,7)</sup> Upon the introduction of lanthanide onto a Pd metal surface, the catalytic properties for hydrogenation were drastically changed. When ethene, but-1-ene, but-2-ene or buta-1,3-diene was used, hydrogenation on Ln-Pd/ $SiO_2$  occurred in a way similar to the case of propene (Fig. 1 of Ref. 4). As shown in the examples of ethene (Fig. 1) and buta-1,3-diene (Fig. 2), preferential hydrogen uptake by the catalyst occurred during the initial step of the reaction, followed by hydrogenation with a certain induction period. The hydrogenation activity tended to decrease along with an increase in the lanthanide content in the catalyst.<sup>4)</sup> The Eu-Pd/ $SiO_2$  and Yb-Pd/ $SiO_2$  catalyst systems exhibited a similar hydrogenation behavior in the composition ranges studied.

The results for hydrogenation at 173–231 K over Yb-Pd/ $SiO_2$  (Yb/Pd = 1.0) are summarized in Table 1. In

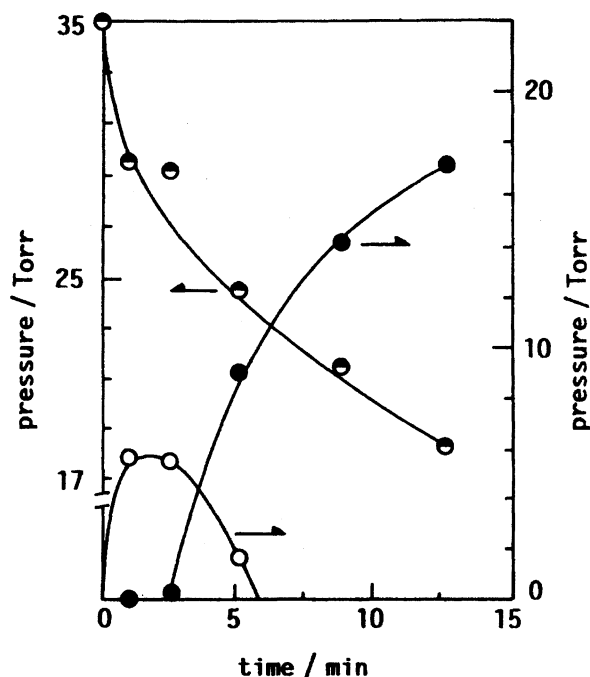


Fig. 1. Hydrogenation of ethene at 173 K over Yb-Pd/ $SiO_2$  (Yb/Pd = 1.0). ●: gaseous hydrogen; ○: hydrogen uptake; ●: ethane. The catalyst (0.046 g) was evacuated at 633 K for 2 h before the reaction.  $P(C_2H_4) = 35$  Torr,  $P(H_2) = 35$  Torr.

Table 1. Hydrogenation of Various Olefins or Dienes over Yb-Pd/SiO<sub>2</sub> (Yb/Pd = 1.0)<sup>a)</sup>

Reactant	Reaction temp K	H <sub>2</sub> uptake mmol g <sup>-1</sup>	Rate of H <sub>2</sub> uptake mmol min <sup>-1</sup> g <sup>-1</sup>	Rate of hydrogenation mmol min <sup>-1</sup> g <sup>-1</sup>
Ethene	173	1.6	1.8	1.0
	213	1.9	1.5	1.3
Propene	193	3.2	0.70	0.98
	193 <sup>c)</sup>	— <sup>b)</sup>	— <sup>b)</sup>	3.6 <sup>c)</sup>
	213	3.1	0.81	1.1
But-1-ene	213	2.5	0.65	1.3
<i>cis</i> -But-2-ene	213	2.1	0.48	0.94
<i>trans</i> -But-2-ene	213	2.7	0.55	1.2
Buta-1,3-diene	213	3.3	1.0	0.94

a) After the Yb-Pd catalysts prepared from 2 wt% Pd/SiO<sub>2</sub> (Pd dispersion: 37%) were evacuated at 633 K for 2 h, a gaseous mixture of reactant (35 Torr) and hydrogen (35 Torr) was admitted to initiate the reaction. b) The values were almost zero within detection limits. c) For comparison, the hydrogenation of propene was carried out on 2 wt% Pd/SiO<sub>2</sub> at 193 K.

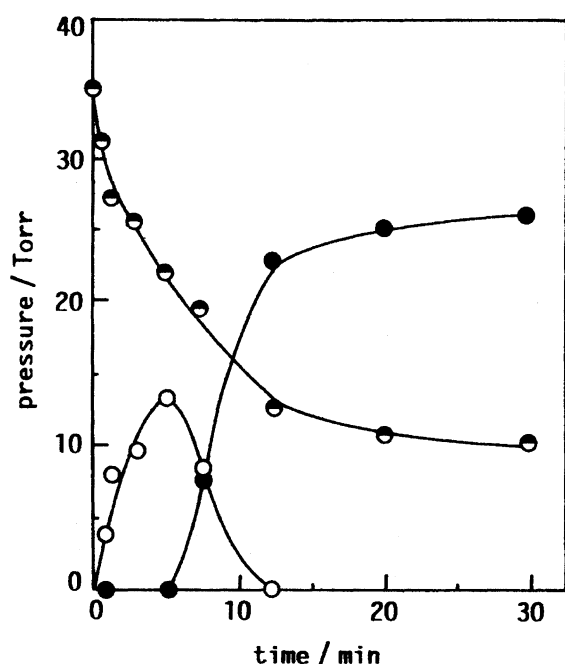


Fig. 2. Hydrogenation of buta-1,3-diene at 213 K over Yb-Pd/SiO<sub>2</sub> (Yb/Pd = 1.0). ○: gaseous hydrogen; ●: hydrogen uptake; ●: butene and butane. The catalyst (0.054 g) was evacuated at 633 K for 2 h before the reaction.  $P(\text{C}_4\text{H}_6) = 35$  Torr,  $P(\text{H}_2) = 35$  Torr.

kinetic measurements of the hydrogen uptake and hydrogenation, both rate dependences on the pressures were very similar, regardless of the reactants used. Their rates were approximately proportional to the pressure of olefin (or diene), and inversely proportional to the pressure of hydrogen. The apparent activation energies of hydrogenation were estimated to be 2–7 kJ mol<sup>-1</sup>, which were close to the activation energies for the hydrogen uptake. These results were also analogous to the results obtained for the hydrogenation of propene over Yb-Pd/SiO<sub>2</sub> (Yb/Pd = 0.43) (Figs. 9, 10 and 11 of Ref. 4). As shown in Table 1, an interesting feature is that the initial rates of hydrogenation at 213 K almost remained unchanged regardless of the reactants

used, and, moreover, they were very close to the rates of the hydrogen uptake. It is generally accepted that there is a difference in the reactivity of olefins for hydrogenation, which has often been discussed based on the effect of a steric hindrance;<sup>8)</sup> the reactivity of olefins is usually in the following order: ethene > propene > butene. From the fact that the hydrogenation rates were quite independent of the olefins used, it is consequently unlikely that the hydrogenation processes containing the addition of hydrogen with subsequent steps are involved in a rate-limiting step. Moreover, the similarity between the kinetics of the hydrogen uptake and hydrogenation leads to speculation that a possible path for the hydrogenation of such olefins or butadiene is closely associated with the hydrogen species taken up by the catalyst, and that the reaction proceeds by a rate-limited hydrogen uptake process.

For the hydrogenation of propene with deuterium, the observed distributions of deuterium in the propane product of Yb-Pd/SiO<sub>2</sub> (Yb/Pd = 0.43)-catalyzed reaction were recorded at the conversion of 46% as follows:  $d_0 = 26.6$ ;  $d_1 = 34.4$ ;  $d_2 = 25.0$ ;  $d_3 = 6.8$ ;  $d_4 = 3.4$ ;  $d_5 = 1.8$ ;  $d_6 = 1.8$ ;  $d_7 = 0.2$ ;  $d_8 = 0$ . This was very close to the results for pure 5% Pd/SiO<sub>2</sub>.

When acetylene was used in hydrogenation over Yb-Pd/SiO<sub>2</sub> (Yb/Pd = 1.5) at 193–208 K, the mode of hydrogenation was quite different from that observed for olefin or diene. Thus, for hydrogenation of acetylene at 203 K there was no indication of hydrogen uptake during the reaction, and no induction period for the hydrogenation was observed at all (Fig. 3). The hydrogenation kinetics on Yb-Pd/SiO<sub>2</sub> (Yb/Pd = 1.0) gave a 1st-order dependence of hydrogen, and was almost independent of the pressure of acetylene (Fig. 4). An activation energy of 22 kJ mol<sup>-1</sup> for the hydrogenation was determined, which was much larger than that observed for olefin or diene. These results strongly indicate that the hydrogenation of acetylene proceeds by a mechanism different from that associated with the hydrogen taken up. In the hydrogenation of acetylene (Fig. 3), the reaction proceeded in the same manner as the normal hydrogenation behavior on Pd catalysts;<sup>9)</sup> acetylene was selectively hydrogenated to

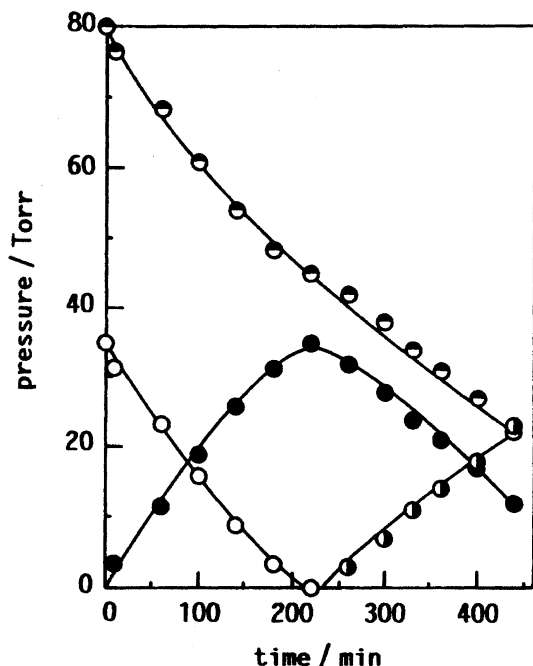


Fig. 3. Hydrogenation of acetylene at 203 K over Yb-Pd/SiO<sub>2</sub> (Yb/Pd=1.5). ○: gaseous hydrogen; ○: acetylene; ●: ethene; ●: ethane. The catalyst (0.068 g) was evacuated at 633 K for 2 h before the reaction.  $P(C_2H_2)=35$  Torr,  $P(H_2)=80$  Torr.

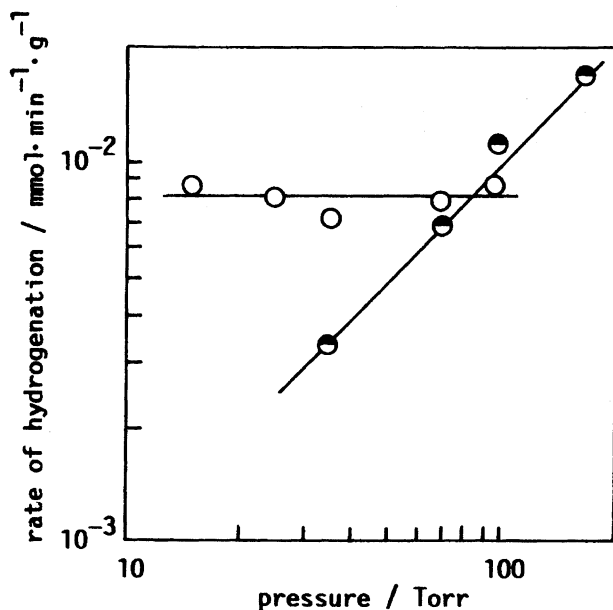


Fig. 4. Dependence of acetylene hydrogenation on pressures of hydrogen (●) and acetylene (○). Yb-Pd/SiO<sub>2</sub> (Yb/Pd=1.0) was evacuated at 633 K for 2 h before the reaction. The reaction was carried out at 193 K by the admission of a gaseous mixture of hydrogen and acetylene.

ethene, followed by the conversion of ethene to ethane. The difference in such hydrogenation behavior between olefin (or diene) and acetylene is due to the occurrence of considerable hydrogen uptake in one case, and not in the other.

The effects of co-existent olefin or diene, as well as propene,<sup>4)</sup> on the preferential hydrogen uptake were clear; it was observed only in the presence of ethene, butene or butadiene. However, these observations do not imply the formation of a hydrogen/olefin (or diene)-containing surface complex or a hydrogenated intermediate whose surface concentration builds up before any substantial desorption of hydrogenated products with a lapse of time corresponding to the induction period. This is because the carbon balance between the reactants and products was always maintained within the experimental error or ca. 1% during the hydrogenation. Ethene, propene, butene, and butadiene are reactants, and, at the same time, they are operative as promoters for hydrogen uptake. Hydrogen uptake along with subsequent hydrogenation processes proceeds in the presence of olefin or diene, in which a phenomenon similar to spillover may exist.<sup>10)</sup> Neikam and Vannice<sup>11)</sup> characterized perylene in Pt black/Ce-Y-zeolite as bridges between the Pt black and zeolite of the catalyst facilitating hydrogen migration. TPD studies of hydrogen also supported the effects of coexistent olefin or diene on the hydrogen uptake. The TPD measurements of Yb-Pd/SiO<sub>2</sub> were made (i) after a pretreatment of hydrogen of 35 Torr at 193 K for 0.5 h and (ii) after the occurrence of hydrogen uptake by the catalyst (exposed to hydrogen, followed by addition of propene at 193 K). Pure 5% Pd/SiO<sub>2</sub> was also used for a comparison. As shown in Fig. 5, for pure 5% Pd/SiO<sub>2</sub>, in agreement with previous desorption studies,<sup>12–14)</sup> hydrogen is present on/in palladium in three states, i.e., weakly adsorbed hydrogen, absorbed hydrogen, and strongly adsorbed hydrogen. The peaks of the TPD spectra corresponding to the absorbed hydrogen and the weakly chemisorbed hydrogen are at lower temperatures (<250–290 K). For Yb-Pd/SiO<sub>2</sub>, in which the hydrogen uptake was observed, the intensity of the hydrogen desorp-

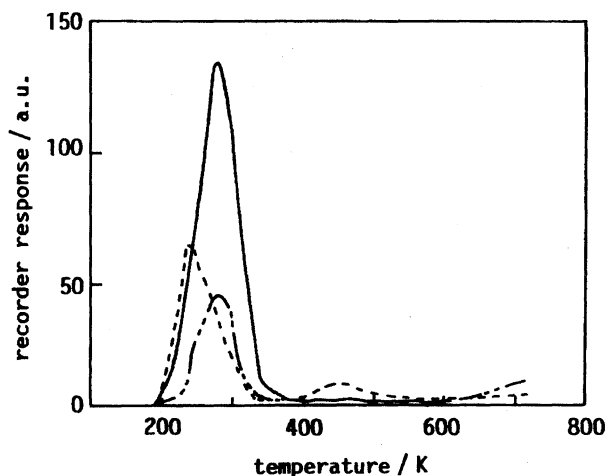


Fig. 5. TPD of hydrogen on 5 wt% Pd/SiO<sub>2</sub> and Yb-Pd/SiO<sub>2</sub> (Yb/Pd=0.67). TPD spectra were measured after pretreatment of 5 wt% Pd/SiO<sub>2</sub> (---) and Yb-Pd/SiO<sub>2</sub> (Yb/Pd=0.67) (-·-) with hydrogen (35 Torr) at 193 K for 0.5 h, and after occurrence of hydrogen uptake by Yb-Pd/SiO<sub>2</sub> (Yb/Pd=0.67) (—).

tion peak at around 280 K, probably weakly chemisorbed hydrogen, was evidently discerned to increase.

Considering the rapid hydrogenation processes (as described above), the reactivity of the hydrogen taken up by the catalyst is expected to be high. The results using different reactants and kinetic techniques strongly indicate that gaseous hydrogen is necessarily taken up to react with the olefin (or diene) and that the hydrogenation is controlled by hydrogen-uptake processes in the catalyst.

#### Effects of the Support, Dispersion, and Particle Sizes.

In the present catalyst system, the role of supports is important; unsupported Ln-Pd did not show such hydrogenation behavior as was observed in Ln-Pd/SiO<sub>2</sub>. For the hydrogenation of propene at 193 K over unsupported Yb-Pd (Yb/Pd = 0.03), a substantial bulk uptake of hydrogen occurred during the reaction (Fig. 6) and the formation of PdH was confirmed by X-ray diffraction of the catalyst after the

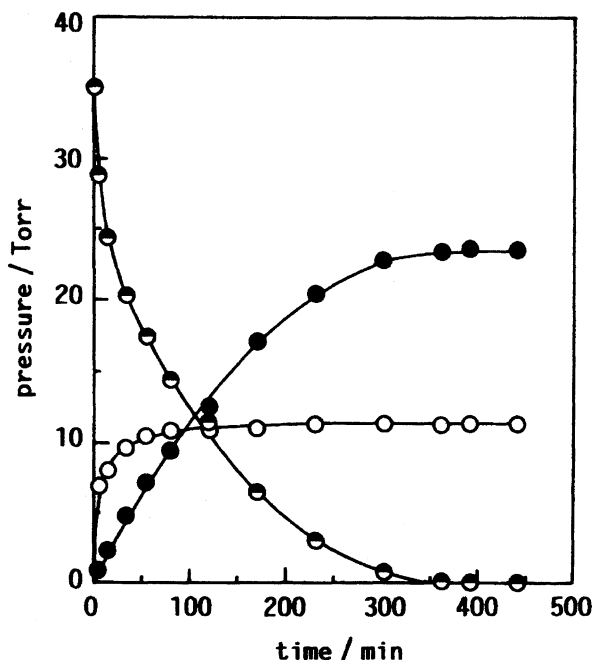


Fig. 6. Hydrogenation of propene at 193 K over Yb-Pd (Yb/Pd = 0.03). ○: gaseous hydrogen; ●: hydrogen uptake; ●: propane. The catalyst (0.098 g) was evacuated at 633 K for 2 h before the reaction.  $P(\text{C}_3\text{H}_6) = 34$  Torr,  $P(\text{H}_2) = 35$  Torr.

reaction.<sup>4)</sup> The hydrogen absorbed in the palladium was too stable to react with propene at such a low reaction temperature, and remained intact in the catalyst, as opposed to the results observed for SiO<sub>2</sub>-supported Ln-Pd.<sup>4)</sup> Thus, it now seems quite certain that the support plays an important part to take up hydrogen in this catalyst system and to induce subsequent reaction processes.

To evaluate and understand the nature of the hydrogen taken up by the supported Ln-Pd catalyst, IR measurements were performed. The IR spectra of Yb-Pd/SiO<sub>2</sub> (Yb/Pd = 0.43), which was exposed to (i) H<sub>2</sub> (35 Torr), (ii) H<sub>2</sub> (35 Torr) + C<sub>3</sub>H<sub>6</sub> (35 Torr) and (iii) H<sub>2</sub> (35 Torr) with subsequent addition of C<sub>3</sub>H<sub>6</sub> (35 Torr), showed negligible changes in the wavenumber ranges assigned to the adsorbed hydrogen, such as the molecular hydrogen (4200–3900 cm<sup>-1</sup>), hydride (ca. 2000 cm<sup>-1</sup>) and OH species on silica. Moreover, the IR spectra of the same catalyst using deuterium under the same conditions as those stated above showed no new absorption bands, particularly around 2750 cm<sup>-1</sup>, attributed to surface OD species on silica. The exchange of D<sub>2</sub> with surface OH groups on SiO<sub>2</sub> via supported Pt particles was first investigated using IR spectroscopy by Eischens et al.<sup>15)</sup> In contrast with the system containing spilt-over hydrogen by Yates et al.,<sup>16)</sup> it is unlikely that the support in Ln-Pd/SiO<sub>2</sub> acts as acceptor sites which can accommodate the taken up hydrogen species.

To provide information about the support materials and their related properties, alumina, titania, zirconia, and magnesia other than silica were examined. The characteristics of various 2 wt% Pd/supports as a precursor of supported Ln-Pd catalysts are summarized in Table 2. When the hydrogenation of propene was tested under the same conditions, only Ln-Pd/Al<sub>2</sub>O<sub>3</sub> exhibited a marked similarity to Ln-Pd/SiO<sub>2</sub> in the hydrogenation behavior:

- (1) considerable hydrogen uptake during the initial step.
- (2) hydrogenation using hydrogen taken up by the catalyst.
- (3) kinetic characteristics.

Ln-Pd/TiO<sub>2</sub>, Ln-Pd/ZrO<sub>2</sub>, and Ln-Pd/MgO did not show any hydrogen uptake at all throughout the reaction. Their rates of hydrogenation obeyed first-order kinetics with respect to the hydrogen pressure, regardless of the propene pressure. This was evidently quite different from the kinetic behavior observed when the hydrogen taken up by the

Table 2. Characteristics of Various Supported Pd (2 wt%) as a Precursor

Support	Surface area of support/m <sup>2</sup> g <sup>-1</sup>	Pd particle size <sup>a)</sup>	Pd particle size <sup>b)</sup>	Pd dispersion <sup>c)</sup>
		Å	Å	%
Silica	380	—	38	37
Alumina	285	36	52	26
Zirconia	13	90	93	15
Magnesia	13–19	59	78	18
Titania	50±15	157	220	6

The Pd particle sizes were deduced from a) the Scherrer equation and b) CO chemisorption measurements.  
c) The degree of Pd dispersion was calculated according to the equation:  $C/W \times 100$ , where C and W denote the CO chemisorption and content of Pd per unit weight of Pd/support, respectively.

Table 3. Effects of Pd/SiO<sub>2</sub> Precursors on the Hydrogenation of Propene over Yb–Pd/SiO<sub>2</sub> (Yb/Pd = 1.0)

Pd source	Pd/SiO <sub>2</sub> precursor			Hydrogenation of propene <sup>a)</sup>		
	Pd loading	Pd size <sup>b)</sup>	Pd dispersion <sup>c)</sup>	H <sub>2</sub> uptake	Rate of H <sub>2</sub> uptake	Rate of hydrogenation
	wt%	Å	%	mmol g <sup>−1</sup>	mmol min <sup>−1</sup> g <sup>−1</sup>	mmol min <sup>−1</sup> g <sup>−1</sup>
Pd(NO <sub>3</sub> ) <sub>2</sub>	5.0	274	5	— <sup>d)</sup>	— <sup>d)</sup>	0.14
PdCl <sub>2</sub>	30.0	210	7	— <sup>d)</sup>	— <sup>d)</sup>	3.2
Pd(NO <sub>3</sub> ) <sub>2</sub>	2.0	169	8	0.5	0.014	0.10
PdCl <sub>2</sub>	5.0	90	15	2.1	0.15	0.46
PdCl <sub>2</sub>	0.5	63	22	1.7	0.032	0.066
PdCl <sub>2</sub>	2.0	38	37	3.2	0.70	0.98
(NH <sub>4</sub> ) <sub>2</sub> [PdCl <sub>4</sub> ]	2.0	27	52	4.1	1.8	1.7

a) After the catalysts were evacuated at 633 K for 2 h, a gaseous mixture of reactant (35 Torr) and hydrogen (35 Torr) was admitted to initiate the reaction at 193 K. b) The Pd particle size was deduced from CO chemisorption measurements. c) The degree of Pd dispersion was calculated according to the equation:  $C/W \times 100$ , where  $C$  and  $W$  denote the CO chemisorption and content of Pd per unit weight of Pd/SiO<sub>2</sub>, respectively. d) The values were almost zero within detection limits.

catalyst was associated with the reaction path. Such a kinetic behavior was analogous to that of the hydrogenation of acetylene over Yb–Pd/SiO<sub>2</sub> (Fig. 4), which exhibited negligible hydrogen uptake. Hence, for the hydrogenation on Ln–Pd/TiO<sub>2</sub>, Ln–Pd/ZrO<sub>2</sub>, and Ln–Pd/MgO, the hydrogen uptake can not participate in the reaction, resulting in a different kinetic behavior. The enhanced adsorption of hydrogen is mainly centered on group-VIII metals supported on silica, alumina, zeolite or carbons.<sup>10)</sup>

As shown in Table 3, Pd/SiO<sub>2</sub> with various levels of Pd loading, Pd particle size and its dispersion was prepared by a conventional impregnation method using PdCl<sub>2</sub>, Pd(NO<sub>3</sub>)<sub>2</sub> or (NH<sub>4</sub>)<sub>2</sub>[PdCl<sub>4</sub>] as a starting material. Using Ln–Pd/SiO<sub>2</sub> prepared from such Pd/SiO<sub>2</sub> precursors, the hydrogenation of propene was carried out under the same conditions. The results summarized in Table 3 strongly suggest that hydrogen uptake is closely involved in the Pd particle size and dispersion, rather than the Pd sources and the amounts of loaded Pd; thus, the amounts of hydrogen uptake tend to decrease along with an increase in the Pd particle sizes, and are reduced to almost zero above 210 Å. In contrast with the unsupported Ln–Pd prepared from Pd powder (230 Å of average crystallite size evaluated from X-ray line broadening) (Fig. 6), the supported Ln–Pd catalysts showed no formation of  $\beta$ -hydride in the bulk, even for Ln–Pd/SiO<sub>2</sub> prepared from the Pd precursor with the largest Pd particle sizes (274 Å). Boudart et al.<sup>17)</sup> showed that the solubility of hydrogen in palladium increases linearly along with decreasing the percentage dispersion of the metal, and Aben<sup>18)</sup> has shown that the total hydrogen uptake in the  $\beta$ -hydride phase tends to increase along with increasing particle size. From the TPD results, hydrogen is considered to be present in weakly adsorbed states on the Ln–Pd catalyst, in which most of the hydrogen taken up migrates to the interface between the palladium and support of Ln–Pd/SiO<sub>2</sub>, acting as a hydrogen-acceptor site. This is consistent with the results from IR measurements and hydrogenation over unsupported Ln–Pd. It can therefore be speculated that the proportion of contacting surface between the palladium and silica is responsible for the degree of hydrogen uptake induced by the synergism of the bimetallic system.

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