Ultrafine Palladium Particles supported on Chelate Resin–Metal Complexes: Promotion Effect of Lanthanide Ions on Catalytic Activity†

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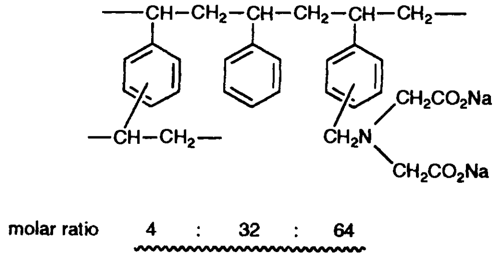
Dry beads of chelate resin–metal complexes have been prepared as catalysts from a resin based on polystyrene functionalized by tridentate iminodiacetate (ida) moieties by both complexing of metal ions and supporting of ultrafine palladium particles. Two methods were employed. When $[PdCl_4]^{2-}$ ions were contacted with a chelate resin without metal ions (acid type) or with divalent metal ions, ultrafine palladium particles, produced by subsequent reduction, were distributed only on the surface of the resin. On the other hand, when $[PdCl_4]^{2-}$ ions were contacted with a chelate resin having trivalent metal ions (which has anion-exchange ability), the palladium particles were distributed uniformly in the resin. The supported ultrafine palladium particles catalyse the hydrogenation of C=C bonds, the activity greatly depending on both the metal ions co-ordinated to the ida moieties and the distribution of the palladium particles in the resin. While catalysts with palladium particles on the surface of the resin had higher catalytic activity than those with particles inside the resin, palladium particles supported on chelate resin–lanthanide complexes had higher activity than those supported on resin–divalent metal complexes in spite of the uniform distribution of the palladium particles in the resin in the case of the lanthanide complexes. The promotion effect of the co-ordinated lanthanide ions varied with the atomic number of the latter, catalysts with unstable numbers of 4f electrons showing the highest catalytic activity.

Homogeneous dispersions of ultrafine palladium particles with protective colloids give highly selective and active catalysts.[1,2] Supporting the metal particles on a solid polymeric support results in a peculiar reactivity and the easy and repeated use of the metal particles as the catalyst.[3–5]

In order to prepare the supported metal particles cross-linked polymers can be used, *e.g.* a polystyrene-based chelate resin (cr) functionalized by iminodiacetate (ida) moieties, as shown in Scheme 1. Various metal ions can co-ordinate to the ida moieties.[6,7] Different chemical species can be accumulated in the small spaces of the resin through ion exchange in the case of metal ions and through ion exchange or co-ordination to the ida moieties in the case of noble metal ions. This makes it easy to investigate the interaction between metal ions and noble metal particles.

In our previous work the specific surface area of the chelate resin was found to increase both upon washing with an organic solvent miscible with water, such as ethanol, and upon complexing with multivalent cations.[8] When the porous chelate resin–metal complexes (cr–M; M = Na^+, Mg^{2+} or Al^{3+}) were used as supports for ultrafine platinum particles the catalytic activity for hydrogenation of cyclic olefins increased in the order $Na^+ < Mg^{2+} < Al^{3+}$, which corresponded to the increase in the surface area of the resin complexes.[6]



Scheme 1 Chemical structure of the chelate resin

Lanthanides (rare earths) have been investigated and utilized in many fields.[9] Lanthanide-catalysed reactions are currently of great interest. For example, a study of supported catalysts for synthesis gas conversion[10] showed the first promotion effect of a lanthanide overlayer on the adsorption and the reaction of an alkene on a transition-metal surface. The promotion effect of lanthanides is attractive from the viewpoint of heterogeneous catalysis. Imamura *et al.*[11,12] found that the catalytic activity for the hydrogenation of ethene showed a tendency to be larger over lanthanide-doped transition-metal catalysts compared with the undoped catalysts. They concluded that the additional presence of lanthanides strongly influenced the state of adsorption of hydrogen in the subsequent activation process, resulting in an enhanced ability of this surface to dissociate hydrogen. It is well known that lanthanides combine with the 3d-transition metals to give a large number of alloys or intermetallic compounds,[13] many of which absorb hydrogen copiously. The alloy $LaNi_5$ is considered a paradigm and can absorb hydrogen even at around 173 K.[14] As regards the adsorption characteristics and hydrogenation of ethene, lanthanides and transition metals were more efficient when they were used together than separately. Therefore, immobilization of both lanthanide and transition metals on resin beads having an accumulation effect is suitable for an investigation of the promotion effect by lanthanides and of the interaction between two immobilized species. Li and Binglin[15] found that the promotion effect of anchored lanthanide (Ln) ions upon the hydrogenation activity of a palladium catalyst supported on resin beads varied with the atomic number of the lanthanide. In their study, when the number of f electrons of the lanthanide was 0, 7 or 14 the polymer-bound Pd–Ln catalyst possessed the highest hydrogenation activity. However, it is open to question why this should be so, and how lanthanides in general enhance the catalytic activity.

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† *Non-SI units employed:* Torr ≈ 133 Pa, atm = 101 325 Pa.

In the present study we used chelate resin–metal complexes dried from ethanol as supports for ultrafine palladium particles produced by reduction of $[PdCl_4]^{2-}$ after immobilization on the supports. Sodium, magnesium, aluminium, and a series of lanthanides were used as complexing metal ions. So, the chelate resin contains two kinds of metal: the ultrafine palladium particles act as the catalyst, whereas the sodium, magnesium, aluminium, or lanthanide ions make the chelate resin porous and interact with the palladium particles. By using the chelate resin functionalized by the ida moieties the interaction between the metal ions and the palladium particles can easily be examined. The activities of the catalysts prepared by two methods for the hydrogenation of acrylic acid are considered, as is the relationship between the catalytic activity and the surface area of the support.

Experimental

Materials.—A chelate resin containing iminodiacetic acid moieties (abbreviated as cr, Diaion CR-10; mean bead diameter 0.5 mm, chemical structure as in Scheme 1) was obtained from Mitsubishi Chemical Industry Co. It was used in the swollen state as obtained or in the dry state by drying after washing with a large amount of ethanol which is a poor solvent for the resin. The extent of cross-linking is 5% (w/w), and two thirds of the styrene is functionalized by ida moieties, as determined by elemental analysis. One gram of the dry resin was determined by pH titration to contain 2.57 mmol of iminodiacetic acid moieties.

Poly(*N*-vinyl-2-pyrrolidone) (K30, average molecular weight 40 000; Tokyo Kasei Chemical Co.) was used without further purification as the standard protective polymer for ultrafine palladium particles.

Metal salts used for the complexation with the ida moieties, such as $MgCl_2{\cdot}6H_2O$, $AlCl_3{\cdot}6H_2O$, $Al_2(SO_4)_3$, $ScCl_3{\cdot}6H_2O$, $YCl_3{\cdot}6H_2O$, $CeCl_3{\cdot}6H_2O$, $NdCl_3{\cdot}6H_2O$, $GdCl_3{\cdot}6H_2O$, $TbCl_3{\cdot}6H_2O$, $ErCl_3{\cdot}6H_2O$, $YbCl_3{\cdot}7.2H_2O$ and $LuCl_3{\cdot}7.2H_2O$, were obtained from Nakalai Tesque, Inc. and Soekawa Chemicals, and used as received without further purification. Other reagents such as solvents and substrates were all of guaranteed grade and used as received without further purification. Highly purified hydrogen (99.99%) from Nippon Oxygen Co. was used for catalytic hydrogenation reactions.

Preparation of the Catalysts.—The ultrafine palladium particles supported on the chelate resin–metal complexes were prepared by two methods, differing in the order of 'complexing of the metal ions' and 'supporting of the ultrafine palladium particles'.

Method 1 (*complexing of metal ions after supporting palladium particles*). The commercial chelate resin was shaken with an excess of hydrochloric acid to produce the acidic form of the chelate resin (abbreviated cr–H), and the palladium ions were immobilized on 7 g of this by contact with 0.1 mmol of palladium(II) chloride (Kojima Chemical Co.) in water at pH 1. The resulting cr–H–Pd^{II} was neutralized by sodium hydroxide to give cr–Na–Pd^{II} followed by the reduction of the palladium ions by an aqueous solution of $LiBH_4$ (22.8 mmol) to give cr–Na–Pd. In order to exchange the metal ions complexed with the resin, an aqueous solution of each metal chloride (3.09 mmol) was added to cr–Na–Pd (0.8 g), resulting in cr–Pd–M.

Method 2 (*supporting of palladium particles after complexing of metal ions*). First, cr–M complexes were prepared by shaking a mixture of the corresponding metal chloride (3.09 mmol) and cr–Na (0.8 g, containing 2.06 mmol of ida in the dry state) in water for 1 d. Then, palladium ions (11.4 μmol) were immobilized on each cr–M complex, followed by reduction to produce ultrafine palladium particles by the same treatment as described above, giving cr–M–Pd.

Each catalyst was washed with ethanol (50 cm^3) four times and dried at room temperature under vacuum.

Homogeneous dispersions of ultrafine palladium particles were prepared by alcohol reduction of $PdCl_2$ in ethanol–water (1:1 v/v) in the presence of poly(*N*-vinyl-2-pyrrolidone) (pvp) in air.[16] The dispersions, protected by poly(*N*-vinyl-2-pyrrolidone), Pd(pvp), are brown and are stable for months at room temperature. The formation of ultrafine palladium particles was confirmed by the electronic spectrum and transmission electron microscopy (TEM).

Measurements.—The electronic spectra of $[PdCl_4]^{2-}$ and the lanthanide ions in the supernatant were measured with a Hitachi model 340 spectrophotometer. The reduction of the $[PdCl_4]^{2-}$ on the chelate resin was confirmed by the electronic spectra with the same spectrophotometer equipped with an integrated reflection apparatus. The concentration of typical metal ions in the supernatant was measured by inductively coupled plasma (ICP) absorption with a Nippon Jarrell-Ash ICAP-575 instrument. The amount of metal ion complexed was calculated from the discrepancy between the amount initially charged and that remaining in the supernatant after complexation.

The Brunauer–Emmett–Teller (BET) surface area and pore-size distribution of the dry catalyst was measured at 77 K with a Micromeritics ASAP 2000 instrument. The sample was completely dried by heating at 95 °C until the pressure in the sample tube became less than 10 mTorr before the measurement. The BET surface area was calculated from the amount of nitrogen adsorbed at 77 K. The pore-size distribution was obtained from the isothermal for nitrogen adsorption and desorption at 77 K.

Scanning electron microscopy (SEM) and electron-probe microanalysis (EPMA) on the catalysts were carried out by the use of a Hitachi model X-650 micro-scanning X-ray analyser, the resolution of the X-ray image being around 100 Å. The sample beads were cut at around the maximum diameter with a stainless-steel cutter and then coated with carbon so that cross-sections of the beads could be measured by irradiation with an electron beam. The metal distributions were evaluated from the intensity of the characteristic X-ray.

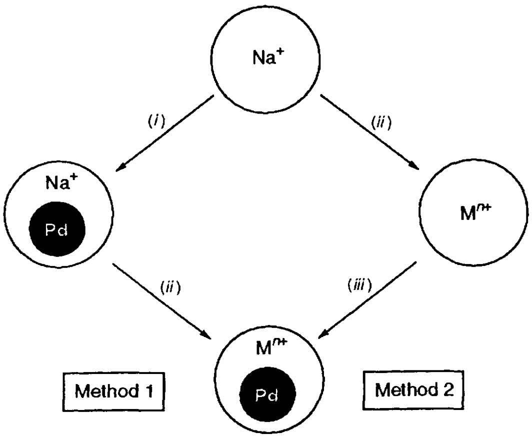
Elemental analysis of the Al(cr) complexed resin was carried out in order to estimate the ratio of co-ordinating Al^{3+} ions to the ida moieties.

Catalytic hydrogenation of various olefins was carried out as follows: the catalyst (0.8 g, containing 11.4 μmol of Pd) in ethanol was stirred in a flask (50 cm^3) at 30 °C under 1 atm of hydrogen until no further hydrogen was taken up. Then, the reaction was started by the addition of the substrate in a small amount of ethanol to give a total volume of 20 cm^3. The hydrogen uptake was measured with a gas burette to determine the initial rate of hydrogenation.

Results and Discussion

Catalyst Preparation.—Two methods were employed as illustrated in Scheme 2. In method 1, the immobilization of $[PdCl_4]^{2-}$ ions on cr–H (acid form of chelate resin) was carried out by mixing the latter with a hydrochloric acid solution of $PdCl_2$. The supernatant changed from yellowish brown to colourless upon immobilization of palladium ions to produce cr–H–Pd^{II}. From the electronic spectrum of the supernatant about 98% of the palladium ions were immobilized. Ultrafine palladium particles were produced by reduction of the palladium ions by $LiBH_4$ after neutralization of the cr–H–Pd^{II} to cr–Na–Pd^{II}. This was revealed by a colour change from yellow to grey. From the electronic spectra, the cr–Na–Pd has a gently tailing absorption in the visible region due to the surface plasmon resonance, which is absent for the cr–Na–Pd^{II}. It was confirmed from the electronic spectrum of the palladium ions rinsed from 2.0 g cr–Na–Pd by contacting with 10 cm^3 of 0.5 mol dm^{-3} hydrochloric acid solution that 97.3% of the immobilized palladium ions were reduced to atoms. The cr–H has no anion-exchanging ability, which suggests that the palladium ions $[PdCl_4]^{2-}$ approach the cr–H resin by diffusion, making complexes with the ida moieties on the surface, which are difficult to move inside the resin. Thus, the palladium ions are expected to be immobilized only on the surface of the resin beads, which is actually observed in TEM photographs of the reduced resins. Each cr–Pd–M was easily prepared by the conversion of cr–Na–Pd into cr–Pd–M by ion exchange as detailed in the Experimental section. Fig. 1 shows the TEM photographs of cr–Pd–Mg, cr–Pd–Al and cr–Pd–Nd.

In method 2 immobilization of $[PdCl_4]^{2-}$ ions on each cr–M was carried out by mixing the latter with a hydrochloric acid solution of $PdCl_2$. The supernatant changed from yellowish brown to colourless within 15 min in the case of cr–M^{3+} and within 1 h in the case of cr–Mg. From the electronic spectra of the supernatant more than 99.9% of the $[PdCl_4]^{2-}$ ions were immobilized. Reduction of the palladium ions was revealed by the colour change from yellow to grey. The ionic condition of the cr–M^{3+} was found to be different from that of the cr–Mg complex,[6] which probably caused the difference in the immobilization behaviour of $[PdCl_4]^{2-}$. The amount of Na^+ and Mg^{2+} taken up exactly balances that of the anionic group, whereas the amount of M^{3+} adsorbed exceeds it resulting in a surplus of positive charge. In other words, the M^{3+} ions partly form 1 : 1 complexes with the ida moieties, as shown in Scheme 3. Elemental analysis of cr–Al indicated that the ratio of co-ordinated Al^{3+} ions to the nitrogen atoms contained in the ida moieties was 0.801 : 1, consistent with the Al^{3+} : ida ratio obtained from the ICP measurement shown in Table 1. Thus, the anionic $[PdCl_4]^{2-}$ can approach the cr–Mg by diffusion, and, therefore, distributes only on the surface of cr–Mg in the same way as on cr–H. In the case of M^{3+}, however, the surplus of the positive charge is responsible for the interaction of the cr–M^{3+} with the $[PdCl_4]^{2-}$ anions. It is clear from the TEM photographs of cr–Mg–Pd, cr–Al–Pd and cr–Nd–Pd shown in Fig. 2 that the palladium particles are distributed on the surface of cr–Mg, but uniformly inside the cr–Al resin.



Scheme 2 Preparation of ultrafine palladium particles supported on the chelate resin–metal complexes. (*i*) H_2PdCl_4, NaOH, $LiBH_4$; (*ii*) M^{n+}; (*iii*) H_2PdCl_4, $LiBH_4$

Characterization of the Catalysts.—The distributions of typical metal ions and their counter anions in cr–M–Pd were measured by EPMA. Each metal ion was distributed uniformly. The counter anions used for the preparation of the cr–M complexes were detected only in cr–Al–Pd with uniform distribution, which suggests that cr–M^{3+} possesses anion-exchange ability.

Since the highly porous cr–M in water, which is a good solvent for the chelate resin, is in a rubber state, direct removal of water makes the pores shrink. However, by changing the solvent from water to ethanol, which is a poor solvent for the resin, a phase transition takes place from a rubber to a glass state, resulting in the cr–M remaining porous after the removal of the ethanol.[17,18] Thus, cr–M dried from ethanol has a large surface area and the pore structure is preserved, though it still

Table 1 Specific surface areas and mole ratios of the metal ions co-ordinated to the ida moieties

	Surface area/m^2 g^{-1}		
Metal ion, M^{n+}	cr–Pd–M (Method 1)	cr–M–Pd (Method 2)	M : ida
Na^+	—	1.56	2.0
Mg^{2+}	4.67	8.50	1.0
Al^{3+}	9.54	6.97	0.77

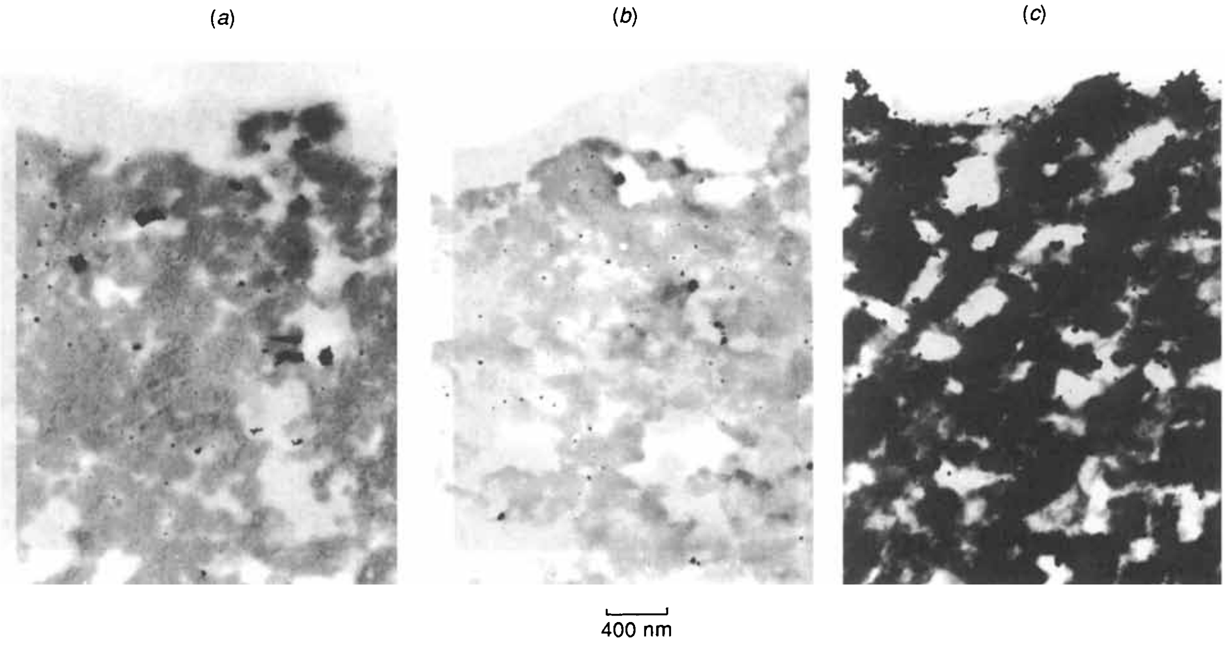
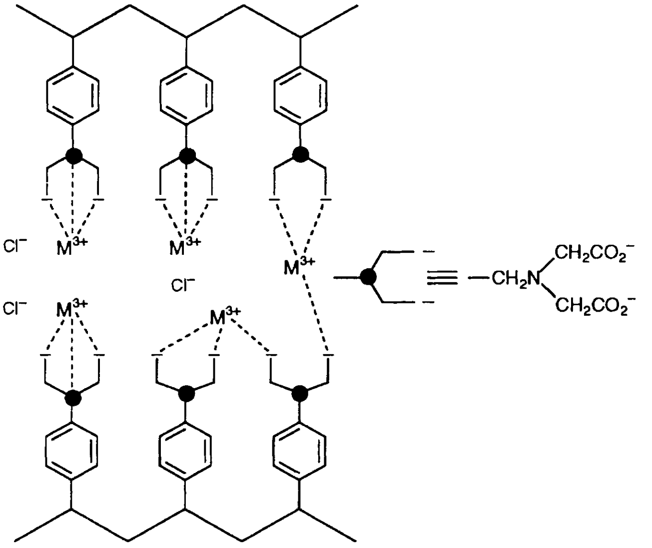


Fig. 1 Representative transmission electron micrographs of the ultrafine palladium particles in slices of the cr–Pd–Mg (*a*), cr–Pd–Al (*b*) and cr–Pd–Nd beads (*c*). The magnification factor is 30 000

has water molecules co-ordinated to the metal ions. The surface area of the cr–M can be increased both by complexing with multivalent cations and by drying after washing with an organic solvent miscible with water.[19]

Table 1 shows the specific surface area and the molar ratio of typical metal ions to the ida moieties of the chelate resin in various preparations. The specific surface area increases with increasing valence of the complexed metal ion, which might be explained in terms of the binding of the cations to the resin, as mentioned above.

Table 2 shows the specific surface area and the molar ratio of lanthanide ions to the ida moieties. There are no large differences in the specific surface areas. While the mole ratio of the M^{3+} ions required to balance the anionic groups of the chelate resin is 0.67:1, the amounts of Nd^{3+}, Gd^{3+} and Er^{3+} ions co-ordinated to the ida moieties exceeds this, resulting in the anion-exchange ability and the uniform distribution of palladium particles as mentioned above. Although the ratio of 0.67:1 was not reached with Ce^{3+}, Tb^{3+} and Yb^{3+} ions, the palladium particles are uniformly distributed in the resin and have a small particle size according to the TEM photographs.



Scheme 3 Chemical structure of the cr–M^{3+} complex

While there can be no doubt that $[PdCl_4]^{2-}$ ions were immobilized by anion exchange because of the distribution and size of the ultrafine palladium particles, the reason for the uniform distribution in these cases is not known. Possibly the co-ordinated metal ions in the resin were partly leached by contact with a HCl solution of $PdCl_2$ (H_2PdCl_4) at pH 2.4.

Pore-size distributions before and after supporting the ultrafine palladium particles on cr–Al and cr–Nd are shown in Figs. 3 and 4, respectively. Although the distributions of both chelate resin–metal complexes have a maximum at ≈40 Å in diameter, these peaks disappear on supporting the ultrafine palladium particles. Since the actual ion-exchange site in the resin is not on the surface of the pores but actually in the gel, the palladium ions $[PdCl_4]^{2-}$ are uniformly immobilized to the ion-exchange sites in the gel. However, the coagulation of palladium atoms requires an open space to form particles. Therefore, the disappearance of these pores and the decrease in specific surface area upon supporting palladium particles suggests that the ultrafine palladium particles occupy the pores of ≈40 Å in diameter of the chelate resin–metal complexes. A similar observation was also made for platinum particles,[6] the size of which is under 40 Å, strongly suggesting that the platinum atoms coagulate in the pores and that the size of the resulting particle is controlled by the pore size.

Table 2 Specific surface areas and mole ratios of the rare-earth metals co-ordinated to the ida moieties

	Surface area/m^2 g^{-1}		
Metal ion, M^{n+}	cr–Pd–M (Method 1)	cr–M–Pd (Method 2)	M:ida
Sc^{3+}	7.65	10.1	n.d.
Y^{3+}	7.47	5.47	n.d.
Ce^{3+}	11.3	13.0	0.62
Nd^{3+}	8.86	10.7	0.71
Gd^{3+}	5.68	11.8	0.81
Tb^{3+}	7.37	33.4	0.60
Er^{3+}	6.47	10.8	0.74
Yb^{3+}	7.14	10.6	0.59
Lu^{3+}	6.57	5.62	n.d.

n.d. = Not determined.

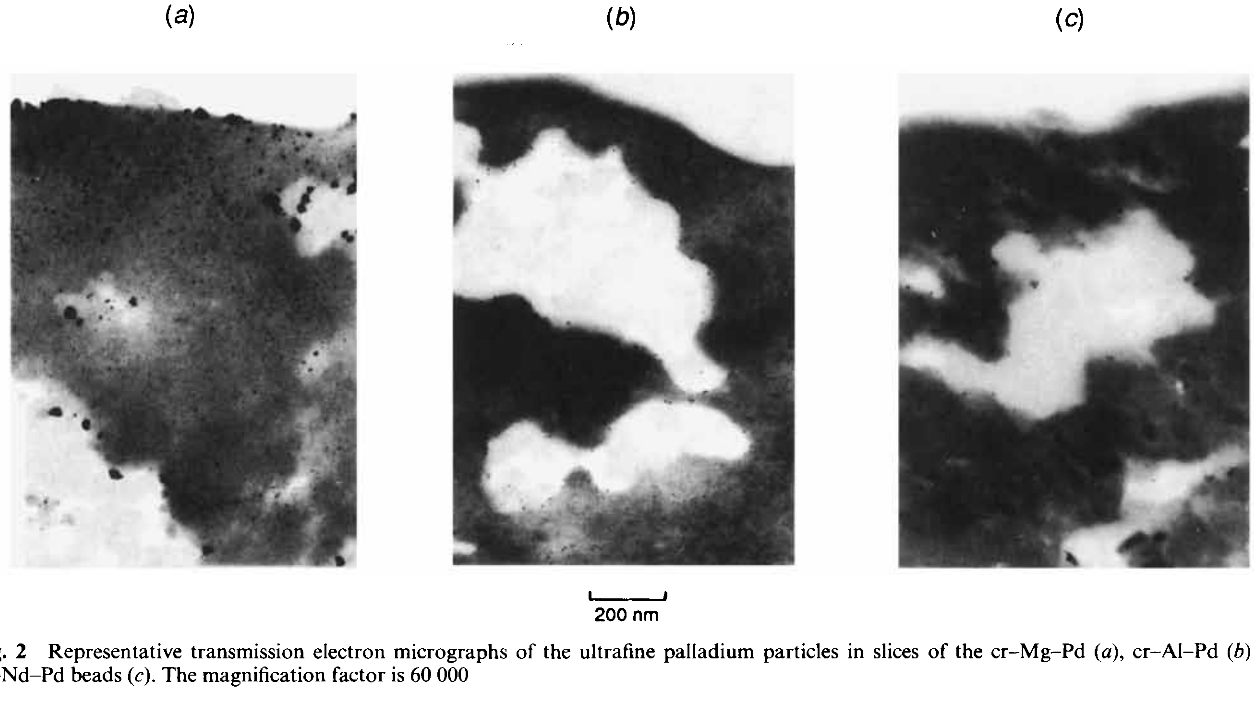


Fig. 2 Representative transmission electron micrographs of the ultrafine palladium particles in slices of the cr–Mg–Pd (*a*), cr–Al–Pd (*b*) and cr–Nd–Pd beads (*c*). The magnification factor is 60 000

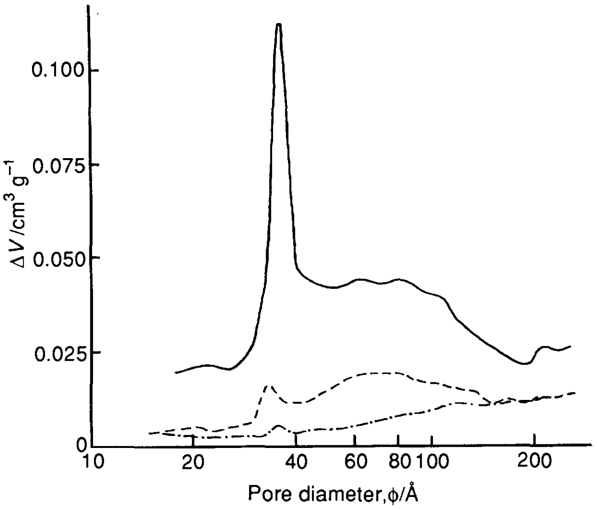


Fig. 3 Pore-size distributions of cr–Al (——), cr–Pd–Al (– – –) and cr–Al–Pd (— · —) dried from ethanol; ΔV is the sum of the volumes of the pores having diameters between φ and φ + Δφ

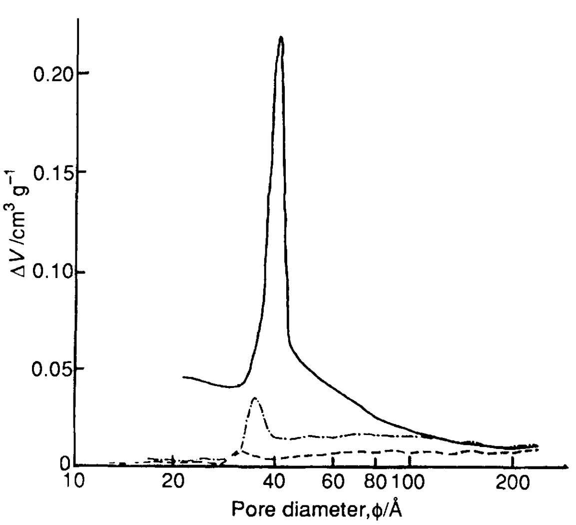


Fig. 4 Pore-size distributions of cr–Nd (——), cr–Pd–Nd (– – –) and cr–Nd–Pd (— · —) dried from ethanol

Table 3 Catalytic activities of palladium particles supported on chelate resin-typical metal complexes

	Catalytic activity*/mmol H_2 (mol Pd)$^{-1}$ s^{-1}	
Metal ion, M^{n+}	cr–Pd–M (Method 1)	cr–M–Pd (Method 2)
Na^+	—	151
Mg^{2+}	3.2	166
Al^{3+}	8.5	120

* Initial rate of hydrogenation of acrylic acid (0.5 mmol) in ethanol at 30 °C under an atmospheric pressure of hydrogen; amount of Pd was 11.4 μmol.

Catalytic Activity in Hydrogenation of C=C *Bonds*.—Since hydrophilic chelate resins favour hydrophilic substrates,[20] both cr–Pd–M and cr–M–Pd catalysts dried from ethanol were applied to catalysis of the hydrogenation of acrylic acid in ethanol under an atmospheric pressure of hydrogen at 30 °C. Table 3 shows the initial rates (catalytic activities) of hydrogenation of the catalysts. The only product detected is propionic acid. The catalytic activities of cr–M–Pd (preparation method 2) are much higher than those of cr–Pd–M (method 1) in spite of their lower surface areas. This phenomenon seems to be a function of the order of addition of the metal ions and the ultrafine palladium particles. It is thought that, since the ultrafine palladium particles have a negative charge in the case of the palladium particles prepared by $NaBH_4$ reduction of $PdCl_2$ in water,[21] the metal ions were partly adsorbed on the palladium surface, interfering in the approach of hydrogen or substrates to the palladium surface. The hydrogenation of cycloocta-1,3-diene (cod) over Pd(pvp) was carried out in ethanol at 30 °C under 1 atm hydrogen in the presence of three kinds of metal chlorides (NaCl, $MgCl_2$ and $AlCl_3$) at the same M : Pd ratio as that in the resin system. The addition of metal chloride to the system made the catalytic activity of Pd(pvp) decrease drastically. This phenomenon is characteristic of the metal particles because it was not observed in the heterogeneous system of a commercial palladium black catalyst.

As for the cr–M–Pd catalysts prepared by method 2, adsorption of metal ions on the ultrafine palladium particles is not expected to occur, because the supporting of the palladium particles is the last stage of the procedure. Therefore, the catalytic activity is expected to increase with increasing surface area of the catalyst, *i.e.* in the order $Na^+ < Mg^{2+} < Al^{3+}$. However, cr–Al–Pd actually has a lower activity than those of cr–Mg–Pd and cr–Na–Pd. This was also observed in the hydrogenation of cod and hex-1-ene as shown in Table 4. In cr–Mg–Pd or cr–Na–Pd almost all the palladium particles are located near the surface of the resin, whereas in cr–Al–Pd they are distributed uniformly as shown in Fig. 2. Therefore, hydrogen and the substrate can easily approach the palladium particles on the surface of cr–Mg–Pd or cr–Na–Pd, while it is not so easy to approach the palladium particles inside the cr–Al–Pd catalyst. This is the reason why cr–Al–Pd has a larger surface area but lower catalytic activity than those of cr–Mg–Pd.

Poisoning Effect of Chloride Ions on Ultrafine Palladium Particles in cr–Al–Pd.—As mentioned above, cr–Al–Pd has mobile anions inside the resin. Thus, these anions may affect the catalytic activity of the palladium particles. Fig. 5 shows the hydrogenation curves of acrylic acid and cod over cr–Al–Pd catalysts, prepared independently from $Al_2(SO_4)_3$ and $AlCl_3{\cdot}6H_2O$. It is clear that the cr–Al–Pd prepared from $Al_2(SO_4)_3$ has a much higher catalytic activity than that of the resin prepared from $AlCl_3{\cdot}6H_2O$. The chloride ions seem to have a poisoning effect on the ultrafine palladium particles. To investigate this the hydrogenation of cod was conducted in ethanol by the addition of NaOH or NaCl using the homogeneously dispersed Pd(pvp) catalyst at the same Na : Pd ratio as in the resin system. Although the catalytic activity increased upon the addition of NaOH, the addition of NaCl made the activity decrease by one-fifth.

Factors affecting Catalytic Activity.—To summarize the results so far, three factors affect the catalytic activity of ultrafine palladium particles supported on the chelate resin–metal complexes.

(*i*) Order of addition of metal ions: the addition of metal ions in the presence of ultrafine palladium particles makes the catalytic activity decrease drastically. The addition of metal ions before the palladium particle formation is preferred to that after the particle formation.

(*ii*) Distribution of the ultrafine palladium particles: catalysts with the palladium particles on the surface have higher activity than those with the palladium particles distributed uniformly in the resin.

(*iii*) Counter anion (in the case of M^{3+}): the catalytic activity decreases in the presence of chloride ions inside the resin. Sulfate or hydroxide is preferred to chloride ions.

To increase the catalytic activity, (*i*) and (*ii*) are important factors in the present system.

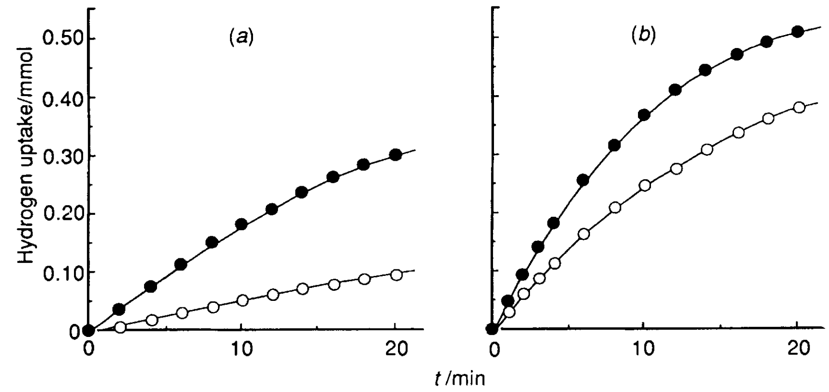


Fig. 5 Effect of counter anions (●, SO_4^{2-}; ○, Cl^-) on the catalytic activity of the ultrafine palladium particles in the hydrogenation of cycloocta-1,3-diene (0.5 mmol) over cr–Pd–Al (*a*) and cr–Al–Pd (*b*) in ethanol at 30 °C

Table 4 Catalytic activities for the hydrogenation of various substrates (0.5 mmol)

	Catalytic activity/mmol H_2 (mol Pd)$^{-1}$ s^{-1}		
Catalyst *	cod	Hex-1-ene	Acrylic acid
cr–Na–Pd	122	77.0	151
cr–Mg–Pd	144	109	166
cr–Al–Pd	63.5	61.4	120

* Amount of Pd charged was 11.4 μmol.

Table 5 Catalytic activities of palladium particles supported on chelate resin–rare-earth metal complexes

	Catalytic activity */mmol H_2 (mol Pd)$^{-1}$ s^{-1}	
Metal ion, M^{n+}	cr–Pd–M (Method 1)	cr–M–Pd (Method 2)
Sc^{3+}	26.6	84.0
Y^{3+}	12.8	129
Ce^{3+}	24.5	57.1
Nd^{3+}	72.2	172
Gd^{3+}	40.6	151
Tb^{3+}	57.1	98.7
Er^{3+}	49.7	166
Yb^{3+}	49.4	122
Lu^{3+}	51.4	107

* Initial rate of hydrogenation of acrylic acid (0.5 mmol) in ethanol at 30 °C under an atmospheric pressure of hydrogen; amount of Pd was 11.4 μmol.

Promotion Effect of Lanthanide Ions on the Catalytic Activity of Ultrafine Palladium Particles.—A series of rare-earth metals were used to co-ordinate to the ida moieties. The catalytic activities of cr–Pd–M prepared by method 1 and cr–M–Pd prepared by method 2 are shown in Table 5. The product of hydrogenation of acrylic acid in each case is propionic acid. As a whole, the catalytic activity of cr–Pd–M is lower than that of cr–M–Pd, owing to both the adsorption of rare-earth-metal ions on the ultrafine palladium particles and the poisoning effect of chloride ions. It is clear that the catalytic activity of the ultrafine palladium particles is promoted by the rare-earth-metal ions, especially by the lanthanide ions (abbreviated as Ln). The activity of each cr–Pd–Ln is three to nine times higher than that of cr–Pd–Al.

Since the cr–Ln^{3+} complex has anion-exchange ability, the ultrafine palladium particles are distributed uniformly in cr–Ln–Pd, as shown in Fig. 2. Moreover, the lanthanide salt used to prepare the cr–Ln^{3+} complex is the chloride, which is cheap and easily available; chloride ions are therefore present in the resin. However, all the cr–Ln–Pd resins show high catalytic activities in spite of some negative factors, such as the distribution of the ultrafine palladium particles and the effect of chloride ions. The catalytic activity of cr–Nd–Pd prepared from $Nd(NO_3)_3{\cdot}6H_2O$, 185 mmol H_2 (mol Pd)$^{-1}$ s^{-1}, is higher than that of cr–Nd–Pd prepared from $NdCl_3{\cdot}6H_2O$, 172 mmol H_2 (mol Pd^{-1}) s^{-1}. Among the cr–Ln–Pd resins, the catalytic activities of cr–Nd–Pd and cr–Er–Pd are especially higher than that of cr–Mg–Pd (*cf.* Fig. 6), where the ultrafine palladium particles are distributed on the surface and chloride ions are not present inside. However a direct comparison between cr–Ln–Pd and cr–Mg–Pd is not reasonable because they have different distributions of the palladium particles. Since we have focused on the promotion effect of lanthanide ions on the catalytic activity, *i.e.* the interaction between the lanthanide ions and the palladium particles, a comparison of the activity between cr–Ln–Pd and cr–Al–Pd is reasonable.

For catalysts prepared by method 2, the distribution of the palladium particles depends on the valency of the co-ordinating metal ions, as mentioned above. While bulk palladium aggregates can be observed for cr–M^+–Pd and cr–M^{2+}–Pd, cr–M^{3+}–Pd has a uniform distribution of the small palladium particles. In general, a catalyst with palladium particles on the surface of the resin has higher catalytic activity than those with the small palladium particles uniformly distributed and firmly fixed to the resin. The fact that lanthanide ions (Ln^{3+}) could promote the less-active palladium particles under disadvantageous conditions is significant.

Fig. 7 shows the relationship between the catalytic activity and atomic number of the lanthanide in the chelate resin. Lanthanides with unstable 4f electrons give a prominent acceleration effect on the catalytic activity of the ultrafine palladium particles supported on the chelate resin. In other words, the catalyst shows high activity for the hydrogenation of acrylic acid when the number of 4f electrons is not 0, 7 or 14. It follows from Table 2 that these differences in catalytic activities are not caused by differences in the specific surface areas of the catalysts.

In order to investigate the interaction between the lanthanide ions and the ultrafine palladium particles, the hydrogenation of acrylic acid in ethanol catalysed by the homogeneously dispersed Pd(pvp) catalyst was carried out in the presence of $NdCl_3$. Fig. 8 demonstrates the change in the catalytic activity upon addition of various amounts of $NdCl_3{\cdot}6H_2O$. The catalytic activity gradually decreases with increasing amount of neodymium ions added, which is thought to be caused mainly by the adsorption of Nd^{3+} on the ultrafine palladium particles, preventing substrates from approaching their surface. Therefore, it is concluded that an adequate distance between the ultrafine palladium particles and the lanthanide ions is necessary for a promotion effect of the latter.

In method 2 the ultrafine palladium particles are supported after the co-ordination of the lanthanide ions to the ida moieties

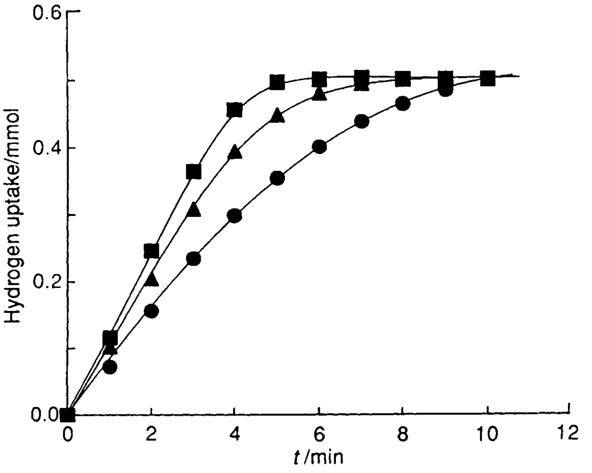


Fig. 6 Hydrogenation of acrylic acid (0.5 mmol) catalysed by cr–Mg–Pd (▲), cr–Al–Pd (●) and cr–Nd–Pd (■) in ethanol at 30 °C under an atmospheric pressure of hydrogen

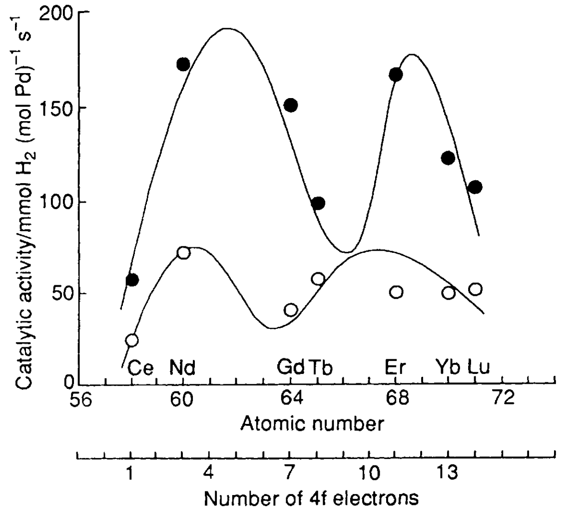


Fig. 7 Relationship between the catalytic activity and the atomic number of the co-ordinated lanthanide ion in cr–Pd–M (○) and cr–M–Pd (●)

so there is an adequate distance between them without adsorption. We cannot say for certain how the promotion effect occurs, but two hypotheses can be proposed. One is a through-space electron interaction between the lanthanide ions and the ultrafine palladium particles. This interaction seems to accelerate the rate of adsorption of the substrate and/or hydrogen because the hydrogenation is first order in the substrate concentration, as shown in Fig. 9. The lanthanides with unstable 4f electrons are thought to exhibit stronger interactions than those with stable 4f electrons, *i.e.* 0, 7 or 14.

A second hypothesis is an interaction between the lanthanide ions and substrates. The rate of adsorption of the substrate may be accelerated by its co-ordination to the lanthanide ions and/or the ultrafine palladium particles. In this case, lanthanide ions would favour co-ordination of substrates, while the ultrafine palladium particles would favour adsorption and dissociation of hydrogen. In general, the co-ordination number of lanthanide ions is greater than six and those in the chelate resin are likely to have vacant sites. It is known[19] that iron(II) ions in the resin have a co-ordination number of four and they too have vacant site(s), to which an NO molecule can be bound.

There remain many questions to elucidate and it is worthwhile to examine the promotion effect of lanthanides in more detail.

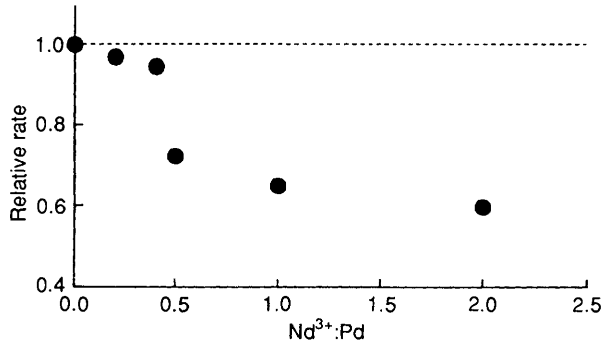


Fig. 8 Influence of the addition of Nd^{3+} ions on the catalytic activity of ultrafine palladium particles in the Pd(pvp) homogeneous system

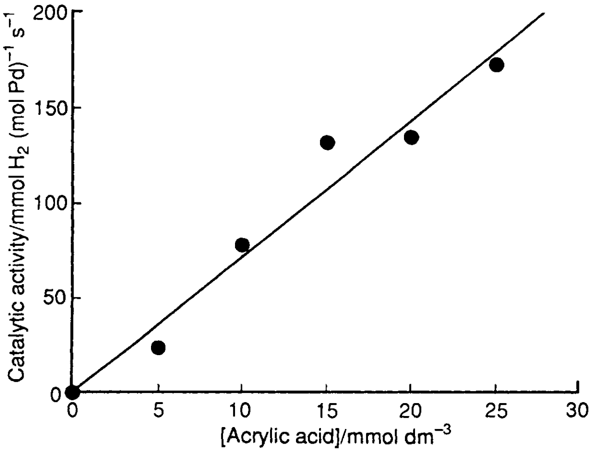


Fig. 9 Dependence of the catalytic activity of cr–Nd–Pd on the substrate concentration in the hydrogenation of acrylic acid (0.5 mmol) in ethanol at 30 °C under an atmospheric pressure of hydrogen

Acknowledgements

We thank Dr. Koichi Adachi for the measurement of transmission electron micrographs and Mr. Toru Nishimura for his technical advice on measuring the specific surface areas. This work was supported by a Grants-in-Aid for Scientific Research (C) (No. 01550611) and (B) (No. 05453141) from the Ministry of Education, Science and Culture, Japan.

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Received 6th April 1994; *Paper* 4/02068E