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Colloidal Palladium Supported on Chelate Resin Containing Iminodiacetic Acid Groups as Hydrogenation Catalyst

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ABSTRACT

Colloidal palladium supported on a chelate resin containing iminodiacetic acid groups was prepared by refluxing the palladium chelate resin in methanol-water. Using the resin-supported colloidal palladium as a catalyst, cyclopentadiene was hydrogenated to cyclopentene in 97.1% selectivity at 100% conversion of cyclopentadiene under 1 atm of hydrogen in methanol at 30°C. Finely dispersed metal particles ranging from 10 to 60 Å in diameter were observed in the resin by electron microscopy. Both x-ray microanalysis for palladium and elution analysis of palladium ion with an aqueous solution of ethylenediaminetetraacetic acid disodium salt demonstrated the existence of large amounts of palladium ion complexes in the resin. The amount of palladium metal in the resin was estimated to be about 5% of the total palladium. Since the resin, after removal of most of the ionic palladium, exhibited almost the same catalytic activity as before, it was concluded that the finely dispersed metal particles are the active species in the catalyst.

INTRODUCTION

There have been many recent attempts to prepare heterogeneous catalysts by supporting homogeneous transition metal complexes with organic polymers [1]. Such heterogeneous catalysts have advantages over homogeneous analogs in stability and ease of recovery and are, in some cases, superior in activity and selectivity.

We previously reported that highly active and selective catalysts for hydrogenation of olefins and dienes could be prepared from rhodium(III) or palladium(II) complexes of polymers bearing carboxyl groups or iminodiacetic acid groups by activation with refluxing methanol-water [2-6]. It was found that the use of polymers with functional groups that coordinate weakly to metal ions, such as poly(vinyl alcohol) and poly(N-vinyl-2-pyrrolidone), resulted in the formation of very finely dispersed metal colloids that were efficient hydrogenation catalysts [7-10]. A catalyst prepared from palladium(II) chloride and styrene-divinylbenzene copolymer carrying iminodiacetic acid groups showed a very high selectivity for the hydrogenation of dienes to monoenes. At the beginning of the investigation, the active species of this resin-supported Pd catalyst was thought to be a polymer complex because of the strong coordinating ability of iminodiacetic acid groups and because of the high selectivity. However, we have found that very finely dispersed colloidal palladium has high selectivity as a catalyst for the hydrogenation of dienes to monoenes [11] and that palladium salts are rather easily reduced to the metal even in the presence of polymeric ligands, compared to other noble metal salts. Accordingly, it appears likely that the active species of the resin-supported Pd catalyst is actually finely dispersed metal on the resin. In the present paper we describe detailed studies of the catalyst prepared from palladium chloride and chelate resin with iminodiacetic acid groups.

EXPERIMENTAL

Materials

A chelate resin with iminodiacetic acid groups attached to a styrene-divinylbenzene copolymer matrix, Diaion CR10 (Mitsubishi Chemical Ind. Co.) (1) was used as a supporting polymer. Resin 1 contains macropores and consists of white, opaque, spherical particles with a size range 297-1190 μm in the swelled state. One milliliter of the acid form of Resin 1 was found to contain 1.5 mmol of iminodiacetic acid groups by measurement of the exchange capacity with sodium hydroxide. Resin 1 for catalyst preparation was washed before use with hydrochloric acid and water to convert the iminodiacetate groups from the sodium salts to acids.

Palladium(II) chloride (guaranteed reagent grade) was obtained

from Kojima Chemical Co. Commercial reagent-grade methanol was used after distillation under argon, and distilled water was redistilled under argon. Commercial hydrochloric acid and sodium hydroxide were used without further purification.

Cyclopentadiene was obtained by pyrolysis of dicyclopentadiene (Yoneyama Chemicals Co.) and was distilled under argon. 1,3- and 1,5-Cyclooctadiene were used after distillation of the commercial materials.

N-Benzyliminodiacetic acid was obtained from Aldrich Chemical Co. Five percent Pd on charcoal (Nippon Engelhard, Ltd.) was used for comparison of catalytic properties. Ethylenediaminetetraacetic acid disodium salt dihydrate and 2-nitroso-1-naphthol were obtained from Tokyo Chemical Industry Co.

Commercial pure-grade hydrogen (Nippon Oxygen Ltd., 99.99999% purity) was passed through a Deoxo column (Nippon Engelhard, Ltd.) before use to remove trace amounts of oxygen. Argon (pure grade) was obtained from Takachiho Chemical Co.

Preparation of Palladium Catalyst Supported on the Chelate Resin with Iminodiacetic Acid Groups

Water was added to 20 mL of Resin 1 in the acid form in a flask to form 80 mL of aqueous resin mixture, which was then partly neutralized by 4 mL of 1 N sodium hydroxide solution and shaken for 1 h. Palladium chloride (70.9 mg, 0.4 mmol) dissolved in 0.1 N hydrochloric acid (30 mL) was added to the flask, which was then shaken for 1 h. The molar ratio of iminodiacetic acid groups to palladium atoms was 75. After the resin chelated with Pd(II) was washed with water, it was mixed with 1 N sodium hydroxide solution (25-30 mL) and shaken for 1 h, bringing the pH of the solution to about 11. The resulting resin was washed with water, 80 mL of 1:1 methanol-water was added, and the mixture refluxed under argon for 6 h. The color of the resin was altered from pale yellow to pale gray. The resin was then washed with water or methanol and preserved under water or methanol. One milliliter of Resin 1-Pd in methanol contains 18.5 μg -atom of palladium.

Hydrogenation Procedure

Dienes were hydrogenated as 0.2 M solutions in methanol at 30.0°C under 1 atm hydrogen. Resin 1-Pd (2.7 mL in methanol, containing 50 μg palladium) was placed in a 100-mL flask attached to a thermostated shaker (Tokyo Rikakikai Co.). The methanol was decanted, and the atmosphere in the flask was replaced with hydrogen. Methanol (18 mL) was added, and the flask was shaken for 1 h until the methanol was saturated with hydrogen. A methanol solution of cyclopentadiene (2 mL, 2M) was added, and the flask was shaken vigorously with the pressure in the flask being kept at 1 atm with hydrogen. The rate of hydro-

genation was determined by the rate of hydrogen uptake, expressed as mol $H_2/(g\text{-atom Pd}\cdot s)$ divided by the amount of palladium in the catalyst. Hydrogenations in other solvents were carried out in a similar way. The products were analyzed by GLPC (liquid phase, silicone OV-101 at 20°C; 0.28 mm diameter \times 30 m glass capillary column; flame-ionization detector).

Electron Microscopy

Samples of Resin 1-Pd were molded in methacrylate resin and sliced into 500 Å sections. The sliced sections were supported on copper grids, coated with a collodion film with a carbon layer, and mounted in an electron microscope, Hitachi Model HU-12, operated at 75 kV. The magnification was 150 000.

X-Ray Microprobe Analysis

The surface or a sliced section of Resin 1-Pd was covered with carbon and analyzed with an EDAX 707A energy-dispersion type X-ray analyzer (Si(Li) semiconductor detector) attached to a Hitachi HSM-2B scanning electron microscope. A beam of 30 kV at 5.0×10^{-10} A was used. Palladium and sodium were determined from the x-ray intensities of PdL_{α} and NaK_{α} line emissions, respectively.

RESULTS

Determination of Preparative Conditions of Palladium Catalyst

The chelate Resin 1 was characterized by titrating the acid form of resin beads in 1 M NaCl solution with 1 N sodium hydroxide solution (Fig. 1). When the degree of neutralization was over about 50%, the pH of the solution increased rapidly. Since palladium chloride is easily transformed to hydrate or hydroxide in an alkaline solution, the chelation of palladium ion with Resin 1 was carried out at low pH (about 3).

Catalysts were prepared by using various amounts of Pd per unit volume of resin. Their activities and selectivities in the hydrogenation of cyclopentadiene are plotted in Fig. 2. The initial rate of hydrogenation of cyclopentadiene, v_1 , and the ratio of v_1 to v_2 , the rate of subsequent hydrogenation of cyclopentene, were used as a measure of the activity and selectivity, respectively (*vide infra*). The activity of the catalyst is very low at low Pd/resin ratios, and

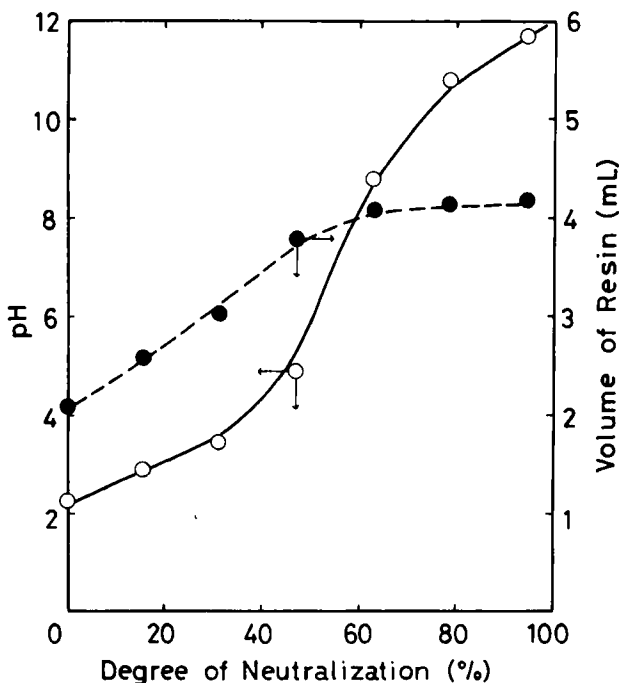


FIG. 1. Dependence of pH (○) and resin volume (●) upon the degree of neutralization of Resin 1 in 1 M NaCl aqueous solution.

the v_1/v_2 ratio is rather low at the high Pd/resin ratio. From these results, 20 μg -atom of palladium per mL of resin was selected for preparation of the catalyst.

After palladium chloride was chelated with Resin 1, the resulting resin in water was treated with 1 N sodium hydroxide solution before refluxing in methanol-water. The pH of the refluxing solution can be varied with the amount of 1 N sodium hydroxide solution used. The effect of the pH is shown in Fig. 3. Catalysts prepared at $\text{pH} < 8$ had no activity, and catalysts prepared at $\text{pH} > 10.5$ show a decreasing v_1/v_2 ratio although their activity increases.

Catalysts were prepared by varying the refluxing time under the standard conditions (Fig. 4). The v_1 value increases with refluxing time up to about 3 h. The v_1/v_2 ratio is almost constant with refluxing time from 40 min to 9 h.

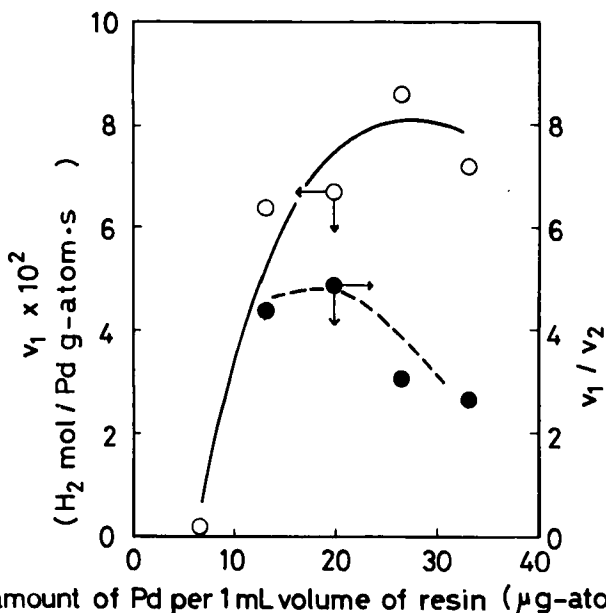


FIG. 2. Dependence of catalytic activity (v_1 , \circ) and selectivity (v_1/v_2 , \bullet) for hydrogenation of cyclopentadiene on the charged amount of Pd chelated on 1 mL of Resin 1; the preparation procedures of the catalysts were the same as the standard one except for the charged amount of Pd, and hydrogenations were carried out under the standard condition except for the amount of Pd.

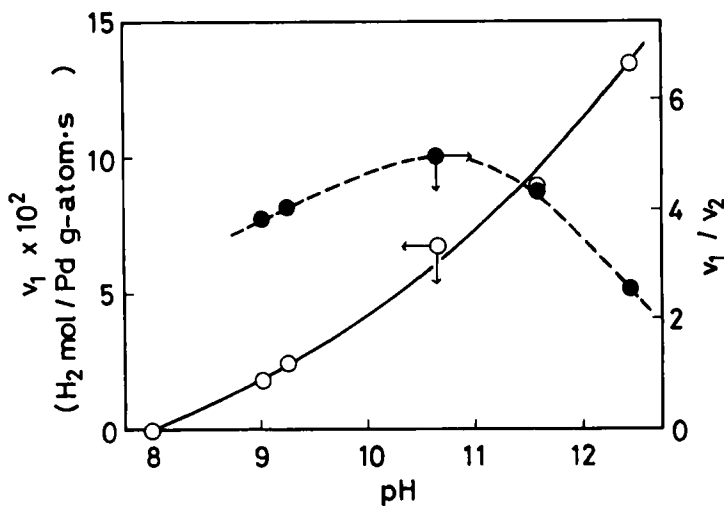


FIG. 3. Dependence of catalytic activity (\circ) and selectivity (\bullet) for hydrogenation of cyclopentadiene upon pH of the aqueous solution before refluxing in methanol-water for activation; the other procedures and hydrogenation conditions were the standard ones.

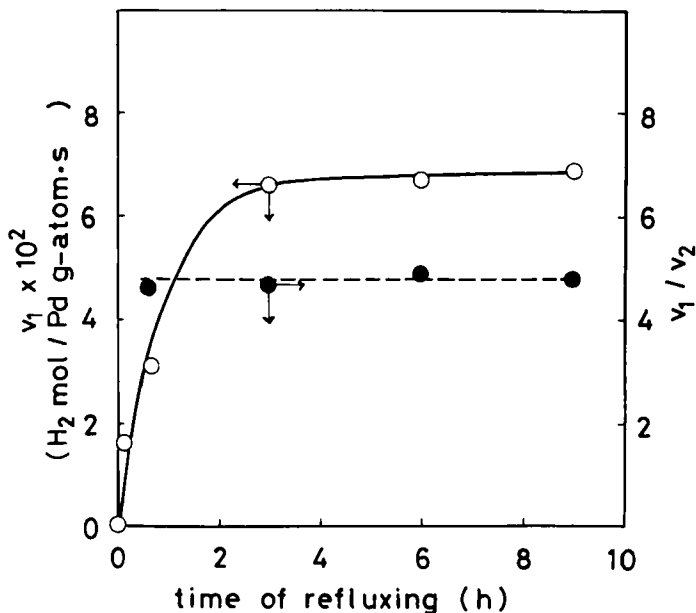


FIG. 4. Dependence of catalytic activity (\circ) and selectivity (\bullet) for hydrogenation of cyclopentadiene upon the refluxing time in methanol-water; the other preparation procedures and the hydrogenation conditions were the standard ones.

Elution of Palladium Ion from Resin 1-Pd with an Aqueous Solution of Ethylenediaminetetraacetic Acid Disodium Salt

In order to separate ionic palladium from palladium metal in Resin 1-Pd, elution analysis was carried out as follows. Resin 1-Pd beads (19.6 mL in water, containing 200 μg -atom palladium) were placed in a column, and the palladium in the beads was eluted with 600 mL of a 3% solution of ethylenediaminetetraacetic acid disodium salt (EDTA, 2Na) under argon for 13 h. The elution patterns are shown in Fig. 5. The amount of the palladium ion in the eluate was measured by the 2-nitroso-1-naphthol method [12]. The following procedure was repeated three times for complete removal of palladium ion. A mixture of Resin 1-Pd beads (4.9 mL in water) and 3% EDTA, 2Na aqueous solution (200 mL) was stirred under argon at 60°C for 24 h, and the amount of the palladium ion desorbed was determined from the Pd concentration in the decanted aqueous solution. After three treatments, 94% of the Pd had been removed from the resin.

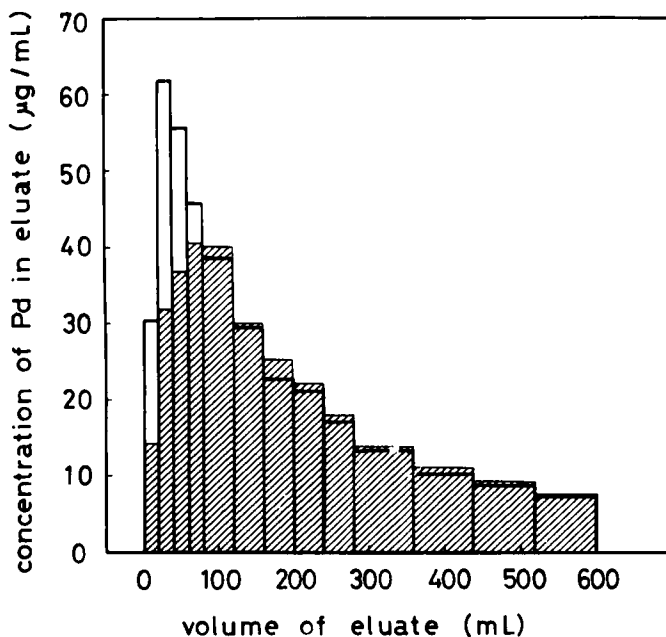


FIG. 5. Removal of Pd ion by elution with 3% EDTA.2Na aqueous solution from Pd-charged Resin 1 before (thick-lined histogram) and after (hatched thin-lined histogram) refluxing in methanol-water for activation.

Particle Size Distribution of Palladium Metal in the Catalyst

Sections of a Resin 1-Pd bead were observed with an electron microscope from the outer surface of the bead to about $5.5 \mu\text{m}$ inside (Fig. 6). From the surface to about $4.5 \mu\text{m}$ inside the bead, very finely dispersed metal particles were observed. From the surface to $1 \mu\text{m}$ inside, there were metal particles with diameters of $10\text{-}60 \text{ \AA}$. From 1 to $4.5 \mu\text{m}$ inside, there were particles of $10\text{-}30 \text{ \AA}$ diameter. No metal particles were seen beyond $4.5 \mu\text{m}$ inside. The number of metal particles decreased gradually from the surface to the inside of the bead. After removal of 94% of palladium by treatment with EDTA.2Na, Resin 1-Pd showed the same distribution of metal particles as the original Resin 1-Pd. The particle size distributions are shown in Fig. 7.

Characterization of the Catalyst by X-Ray Microanalysis

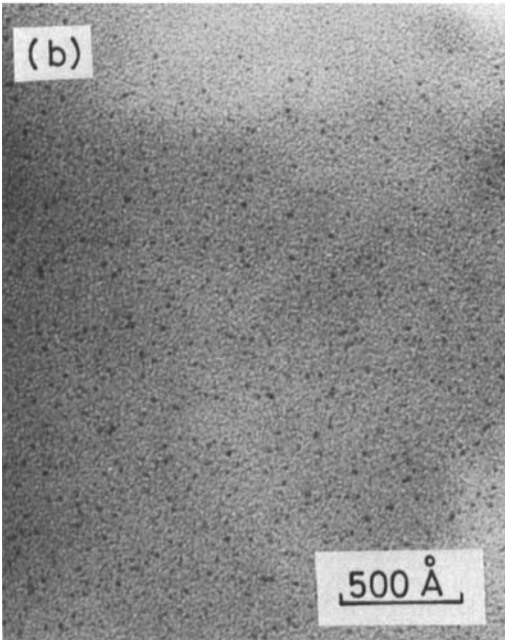
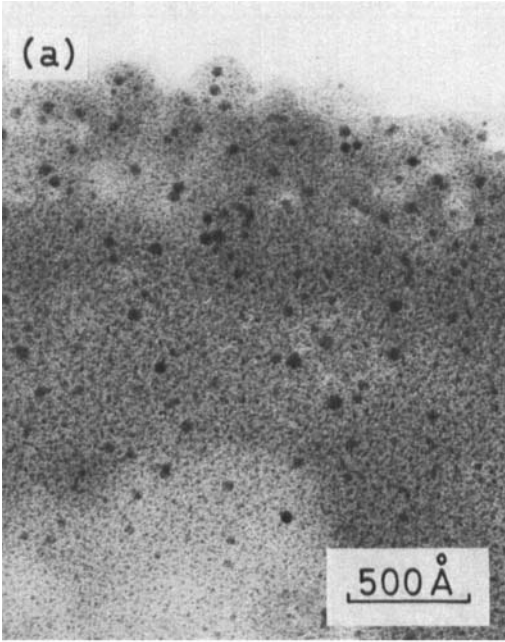
The surface and sections of Resin 1-Pd beads were examined with an x-ray microanalyzer. The iminodiacetic acid groups in Resin 1-Pd should form sodium salts under our conditions. The characteristic x-rays due to sodium and palladium (NaK_{α} , 1.04 keV; PdL_{α} , 2.84 keV; PdL_{β} , 2.99 keV) were observed on the surface of the beads, as shown in Fig. 8. From line analyses of sections of the bead, it is clear that palladium exists only in the surface layer and that sodium is equally distributed through the bead.

A similar analysis was carried out for Resin 1-Pd after removal of palladium ion (94%) by treatment with EDTA.2Na (Fig. 9). The amount of palladium is too small to be detected although sodium is found from the surface to the inside.

Catalytic Hydrogenation of Dienes

Resin 1-Pd is an active catalyst for hydrogenation of cyclopentadiene under mild conditions; typical curves for hydrogen uptake are shown in Fig. 10. The rate of hydrogen uptake is nearly constant until cyclopentadiene disappears from the reaction mixture, and then the rate decreases suddenly. The quantity v_1 was defined as the initial rate of hydrogenation of the diene, and v_2 as the rate of subsequent hydrogenation of the monoene after the diene disappeared from the reaction mixture. The ratio v_1/v_2 is a measure of the selectivity of catalysts as well as of the selectivity in yields of cyclopentene at 100% conversion of cyclopentadiene. Generally a catalyst with a large v_1/v_2 value is superior in selectivity to a catalyst with a small v_1/v_2 value.

As shown in Table 1, cyclopentadiene was hydrogenated to cyclopentene in 97.1% selectivity at 100% conversion of cyclopentadiene under 1 atm hydrogen in methanol at 30°C. When palladium-on-charcoal was used as the catalyst, the yield of cyclopentene at 100% conversion of cyclopentadiene was only 88.4%. However, the catalytic activity per g-atom of palladium for Resin 1-Pd was only 0.019 times that of palladium-on-charcoal. Resin 1-Pd also showed high selectivity in the hydrogenation of 1,3-cyclooctadiene or 1,5-cyclooctadiene to cyclooctene. The catalytic activity and selectivity of Resin 1-Pd did not change after removal of Pd ion (94%) by treatment of Resin 1-Pd with EDTA.2Na solution; neither did addition of N-benzyliminodiacetic acid disodium salt to Resin 1-Pd in methanol.



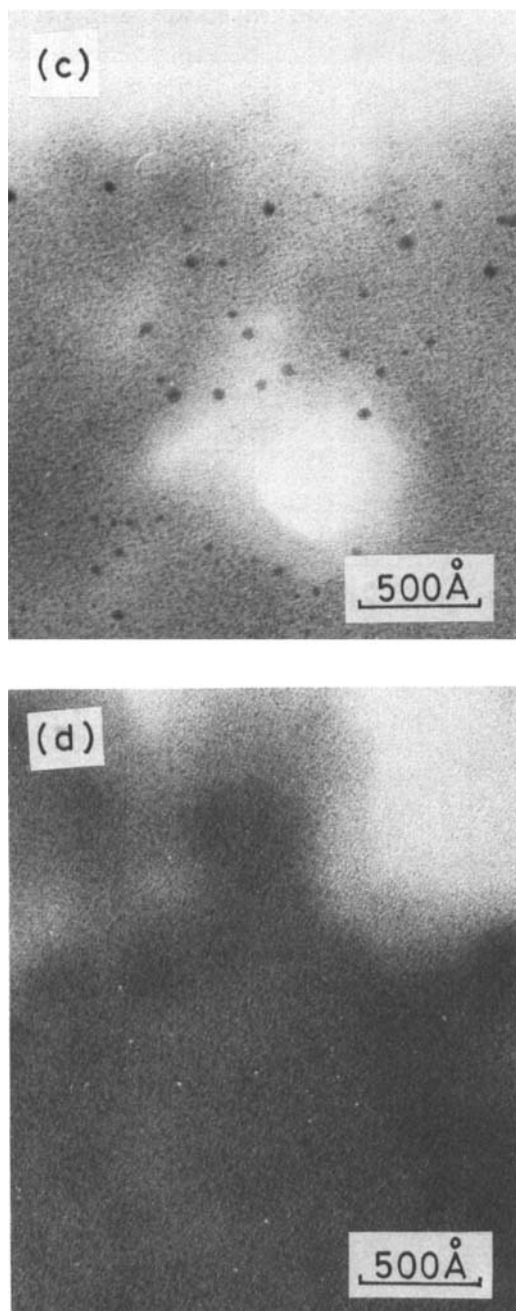


FIG. 6. Electron micrographs of colloidal Pd in original Resin 1-Pd (a) near the surface of beads and (b) $2\ \mu\text{m}$ from the surface, and those in EDTA,2Na-treated Resin 1-Pd (c) near the surface and (d) $2\ \mu\text{m}$ from the surface (see text for details).

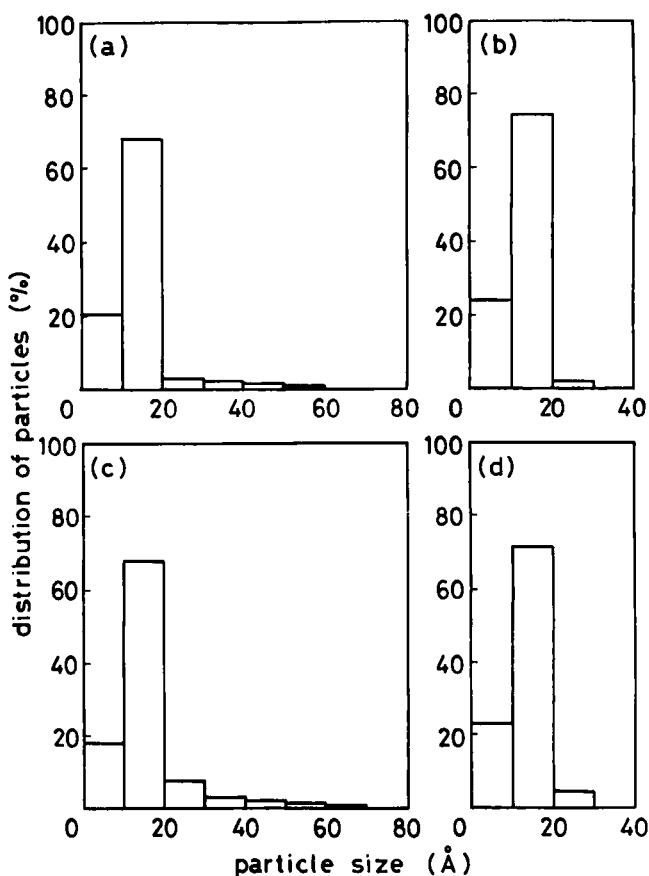


FIG. 7. Particle size distributions of colloidal palladium in original Resin 1-Pd (a) near the surface of beads and (b) 2 μm from the surface, and those in EDTA.2Na-treated Resin 1-Pd (c) near the surface and (d) 2 μm from the surface. These histograms were obtained from the corresponding electron micrographs of Fig. 6.

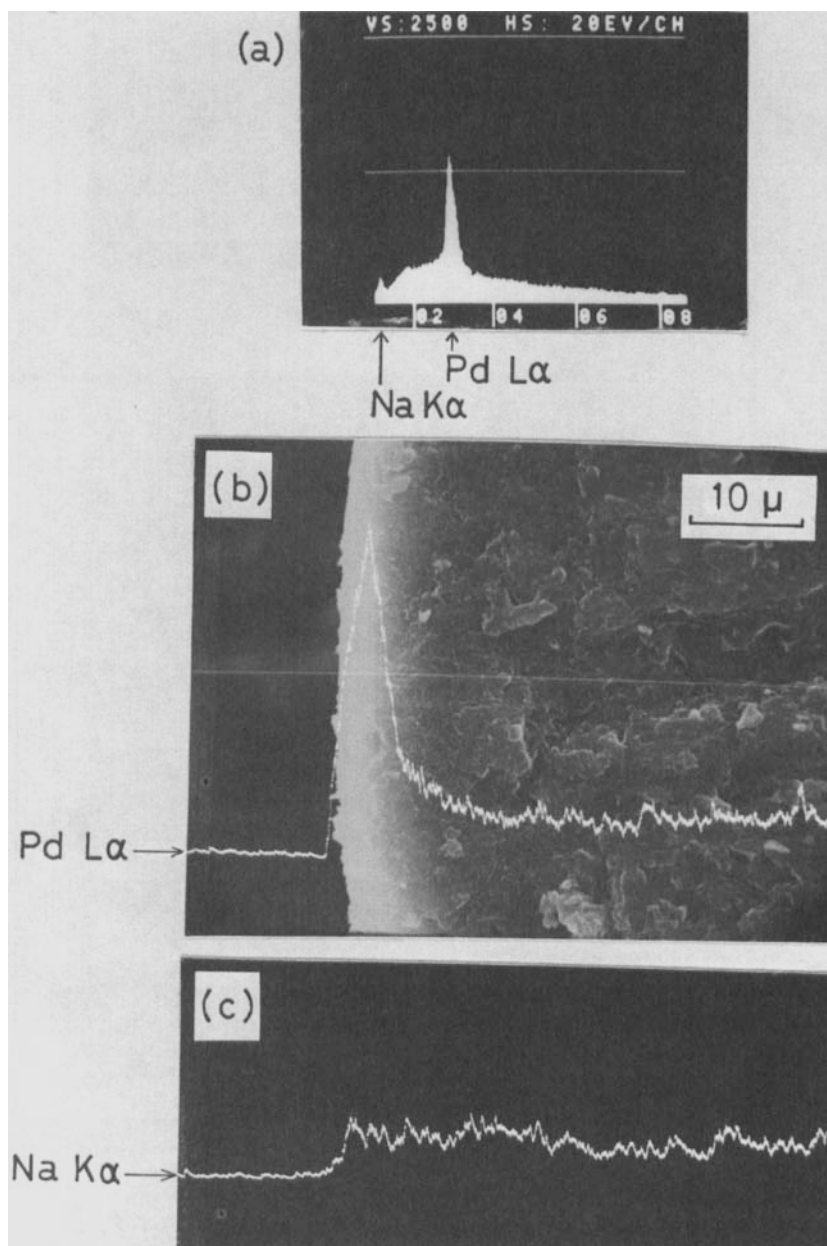


FIG. 8. X-ray microanalyses of original Resin 1-Pd; (a) x-ray spectrum of the surface of the bead, (b) secondary electron image and line profile for $\text{PdL}\alpha$ of the cross section of the bead, and (c) line profile for $\text{NaK}\alpha$ of the same cross section with b.

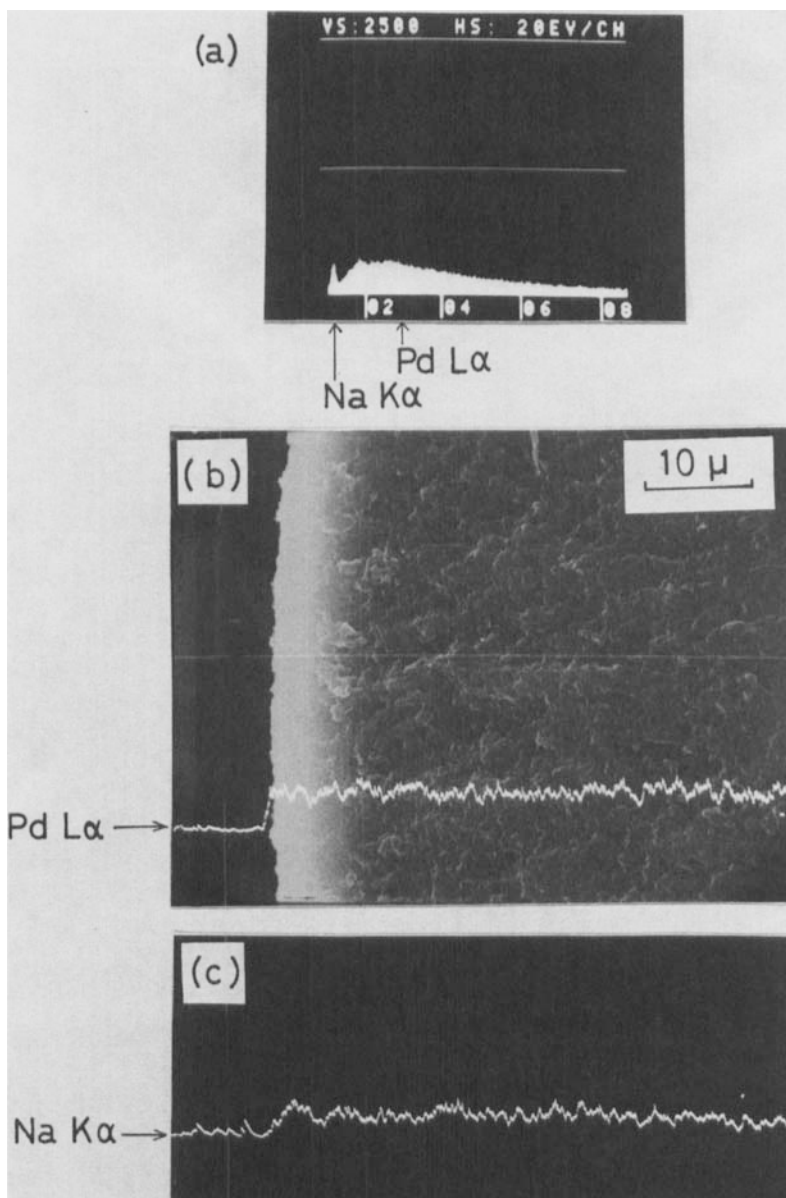


FIG. 9. X-ray microanalyses of EDTA.2Na-treated Resin 1-Pd (94% of charged Pd was removed from the original Resin 1-Pd as Pd ion by the treatment); (a) x-ray spectrum of the surface of the bead, (b) secondary electron image and line profile for PdL α of the cross section of the bead, and (c) line profile for NaK α of the same cross section with b.

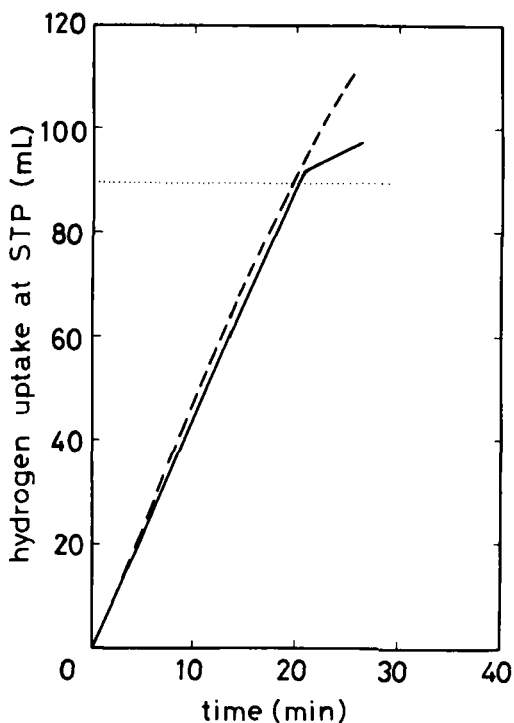


FIG. 10. Hydrogenation of cyclopentadiene (0.2 mol/L) with Resin 1-Pd (charged Pd, 50 $\mu\text{g-atom}$, —) and 5% Pd on charcoal (charged Pd, 1.0 $\mu\text{g-atom}$, ---) as catalysts in 20 mL methanol under 580 torr of hydrogen at 30°C. The dotted line shows the amount of hydrogen uptake equimolar to that of cyclopentadiene.

Hydrogenations of cyclopentadiene were carried out in various solvents at 30°C under 1 atm hydrogen (Table 2). The highest activity and selectivity were observed in methanol.

DISCUSSION

Formation of Colloidal Palladium Supported on the Chelate Resin and Its Catalytic Active Species

The preparation process of Resin 1-Pd is represented schematically as follows.

TABLE 1. Hydrogenation of Dienes^a

Diene ^b	Catalyst	$v_1 \times 10^2,$	v_1/v_2	Selectivity, ^c %
		$\frac{\text{mol H}_2}{\text{g-atom Pd}\cdot\text{s}}$		
CPD	Resin 1-Pd	6.7	4.9	97.1
"	Resin 1-Pd/NBIDA ^d	6.9	4.7	96.7
"	Resin 1-Pd-EDTA.2Na ^e	6.5	4.7	96.8
"	Pd/C (5%) ^f	360	1.4	88.4
"	Pd/C/NBIDA ^g	370	2.9	93.2
1,3-COD	Resin 1-Pd	20	75	98.9
"	Resin 1-Pd-EDTA.2Na ^e	22	79	99.1
1,5-COD	Resin 1-Pd	5.8	27	95.4
"	Resin 1-Pd-EDTA.2Na ^e	5.2	24	94.8

^a30°C; H₂, 580 torr; solvent, methanol; [diene] = 0.2 mol/L.

^bCPD = cyclopentadiene, COD = cyclooctadiene.

^cYield of monoene at 100% conversion of diene.

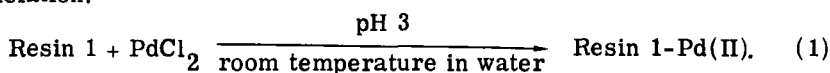
^dResin 1-Pd (Pd, 50 μg-atom) in the presence of N-benzylimino-diacetic acid disodium salt (NBIDA) (100 μmol) in methanol (20 mL).

^eResin 1-Pd after the removal of Pd ion (94%) by treatment with EDTA.2Na.

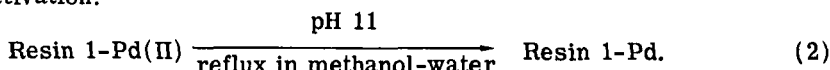
^fPalladium-on-charcoal (5%).

^gPalladium-on-charcoal (5%) (Pd, 1 μg-atom) in the presence of NBIDA (75 μmol) in methanol (20 mL).

Chelation:



Activation:



The observation by electron microscopy of small metal particles 10-60 Å in diameter indicates the reduction of palladium ion by methanol in the activation process. In a previous report it was shown that base is necessary for this reduction [7]. High pH in the

TABLE 2. Hydrogenation of Cyclopentadiene in Various Solvents^a

Solvent	Initial rate $\times 10^2$, H ₂ mol/ (g-atom Pd·s)	Selectivity, ^b %	E _T (30), ^c kcal/mol
Methanol	6.7	97.1	55.5
Ethanol	4.0	94.8	51.9
Dimethylsulfoxide	0.03	-	45.0
N,N-Dimethylformamide	3.7	95.6	43.8
Methyl ethyl ketone	2.3	95.1	41.3
Ethyl acetate	2.9	93.6	38.1
Benzene	2.2	94.7	34.5
Hexane	0.31	-	30.9

^a30°C; H₂ pressure = (760 torr - vapor pressure of solvent);

[cyclopentadiene] = 0.2 mol/L.

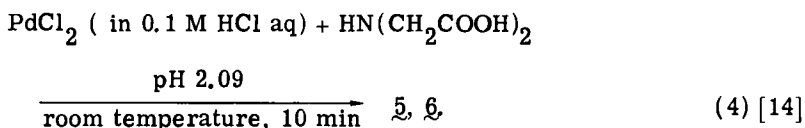
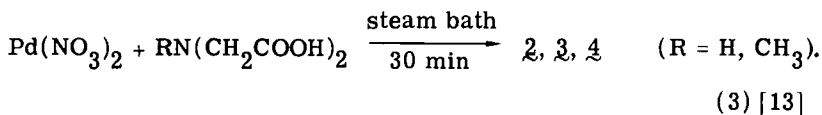
^bYield of cyclopentene at 100% conversion of cyclopentadiene.

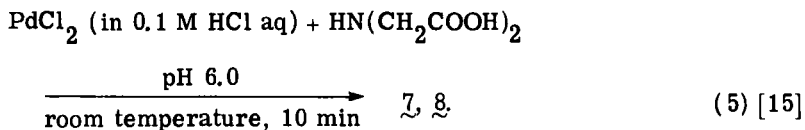
^cFrom Ref. 20.

activation process for preparation of Resin 1-Pd means that hydroxide ion is the base.

The detection of large amounts of palladium ion in the eluate of EDTA.2Na solution demonstrates that Resin 1-Pd still contains a large amount of palladium ion after activation. The elution patterns of palladium ion before and after refluxing in methanol-water are somewhat different. This suggests differences between the states of palladium in the two beads.

Smith [13] (Eq. 3) and Gonzalez-Vilchez [14, 15] (Eqs. 4 and 5) reported the formation of several kinds of complexes of palladium(II) ion with iminodiacetic acid derivatives.





The structures proposed in these studies are shown in Fig. 11. The type of coordination in these complexes depends on the preparation method. In Complexes 2, 5, and 7, one equivalent of iminodiacetic acid coordinates with a mole of palladium atom, and in Complexes 3, 4, 6, and 8, two equivalents of iminodiacetic acid do. The iminodiacetic acid coordinates via an N atom monodentately in Complexes 5 and 7, via N and O atoms bidentately (3, 4, 6, 8), or via N and O atoms tridentately (2).

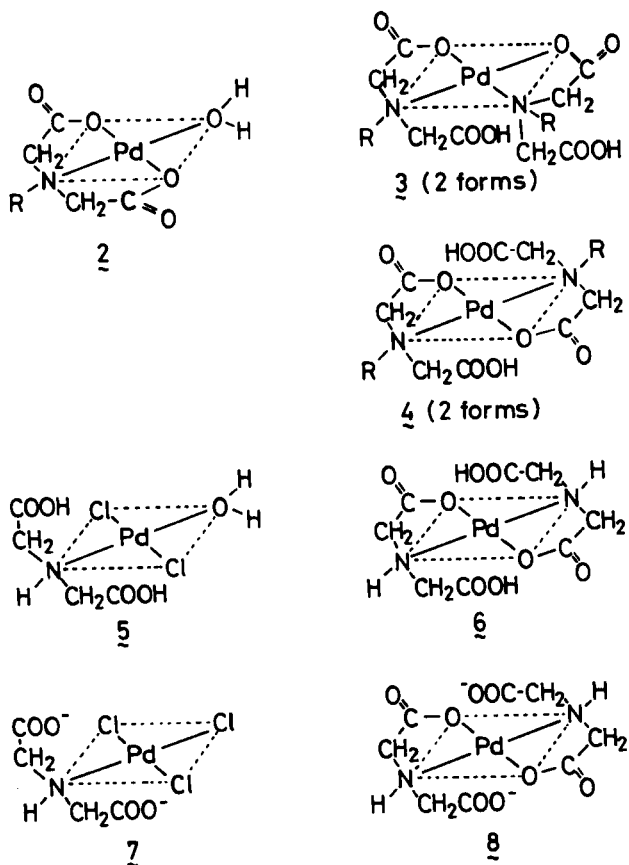


FIG. 11. Pd(II) complexes with iminodiacetic acid group(s).

Resin 1-Pd(II) complex is considered to contain a mixture of these complexes. When Resin 1-Pd was treated with an EDTA.2Na solution, the loosely coordinated palladium ionlike Complexes $\bar{5}$ and $\bar{7}$ should be released preferentially. Decrease of the eluted palladium after refluxing (Fig. 5) suggests that the relatively loose complexes in Resin 1-Pd(II) are converted to more tight complexes or metal particles by the activation procedure. The fraction of the complexes undergoing such transformation is estimated to be 7% from the difference in the amount of palladium in the elution volume 0-80 mL for the sample before and after refluxing. Therefore, the amount of palladium metal reduced by refluxing is considered to be less than 7%. On the other hand, the relatively tight complexes in Resin 1-Pd(II) are believed not to change in the activation process because the elution pattern in the volume 80-600 mL did not change after activation.

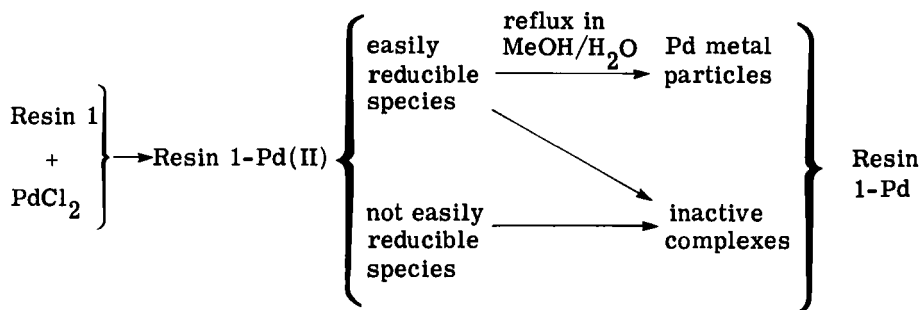
Resin 1-Pd, from which 94% of palladium was removed by triple treatment with an EDTA.2Na solution at 60°C for a day, had the same catalytic properties as the original one. This suggests that the metal particles in Resin 1-Pd are the main active species. If a very small quantity of ionic palladium complexes with high activity exists as another possible species, it should possess coordinative unsaturation for the catalytic reaction. This unsaturation should be removed by coordination with added N-benzyliminodiacetic acid. As shown in Table 1, however, the properties of Resin 1-Pd did not change even in the presence of 2 equivalents of the disodium salt of N-benzyliminodiacetic acid. This suggests that such active complexes are not present and that only palladium metal particles are the active species.

From these results, Scheme 1 is proposed for the preparation of the catalyst. In Scheme 1 the route from "easily reducible species" to "inactive complexes" is rationalized by two reasons: 1) the activity of the catalyst varied considerably according to the conditions for activation, and 2) the catalyst preheated at low pH was not active even after refluxing at high pH. Since the chelated structure is stable, it is presumed that "easily reducible species" in Scheme 1 has mainly monodentate structures such as $\bar{5}$ or $\bar{7}$. The changes in Scheme 1 are completed within 3 h on the basis of the correlation of refluxing time with catalytic activity (Fig. 4).

Amount and Distribution of Metal Particles

The three elutions of Resin 1-Pd with EDTA.2Na removed 94% of the palladium in the resin. Extrapolation of this result suggests that an additional 1% of the palladium might be eluted by further treatments. Thus the total amount of elutable palladium ion in Resin 1-Pd is estimated at 95%, while the residual 5% is considered to exist as metal particles. When the activity per g-atom of palladium is calculated from the actual amount of metal particles, the activity of Resin 1-Pd is about one-third that of palladium-on-charcoal.

Electron microscopy revealed metal particles only in the outer



SCHEME 1.

4.5 μm of the resin bead. X-ray microanalysis showed that not only metal particles but also ionic species of palladium exist only near the surface. These facts are explained by the considerations 1) that the rate of complex formation of palladium ion is greater than that of diffusion into the resin beads, and 2) that the amount of iminodiacetic acid groups in the resin is in large excess (75-fold) of the amount of palladium ion. The density of palladium decreases with depth from the surface. These considerations also explain why metal particles over 30 \AA in diameter are not present below 2 μm from the surface since a low ratio of metal-to-support generally gives fine and well-dispersed metal particles in supported noble-metal catalysts [16].

Selectivity in the Hydrogenation of Cyclopentadiene to Cyclopentene

The state of metal particles is related to catalytic activity and selectivity in two ways. One is the effect of the iminodiacetic acid groups. It is shown in Table 1 that the yield of cyclopentene at 100% conversion of cyclopentadiene catalyzed by palladium-on-charcoal increases from 88.4 to 93.2% by carrying out the reaction in the presence of excess N-benzyliminodiacetic acid (75 equivalents based on Pd). This fact suggests that the iminodiacetic acid groups contribute to the good selectivity of Resin 1-Pd. This effect of the iminodiacetic acid groups may depend on the size of the metal particle. It is thought that the number of active sites not affected by iminodiacetic acid groups increases with increasing size of the metal particles, since the iminodiacetic acid groups are fixed on the resin. This may cause a decrease in selectivity. Because the initial rate of hydrogenation of cyclopentadiene catalyzed by palladium-on-charcoal is not changed by addition of N-benzyliminodiacetic acid, the interaction of metal with iminodiacetic acid groups is so weak that it scarcely affects the reaction of cyclopentadiene, which can strongly coordinate to the active sites of metal. The selective hydrogenation of alkynes to alkenes catalyzed by Lindlar

catalyst modified with quinoline [17] is a well-known example of an increase of selectivity in the presence of foreign substances on a metallic surface.

The other aspect of the relation between the state of the metal particles and catalytic activity is the dependence of reactivity on the size of the metal particles. Since the particles size of palladium metal is very small in Resin 1-Pd, the active site should have some properties of the metal complex, which would result in the difference of the coordinating ability of cyclopentadiene and cyclopentene. Carturan et al. [18] observed a particle-size dependence in the hydrogenation of 1-hexene catalyzed by a catalyst prepared from "metal organic glass" and $[\text{Pd}(\text{C}_3\text{H}_5)_2]$, and the selective hydrogenation of 1,5-cyclooctadiene to cyclooctene was catalyzed by small particles (2-20 Å) of Pd prepared in a similar way [19].

Hydrogenation Behavior of the Catalyst

As shown in Fig. 10 and Table 1, cyclopentene is scarcely hydrogenated when cyclopentadiene is present. After cyclopentadiene is completely hydrogenated, cyclopentene begins to be hydrogenated at about one-fifth of the initial rate for cyclopentadiene. Therefore cyclopentadiene is considered to coordinate to the active species of the catalyst preferentially to cyclopentene.

A good correlation between $E_T(30)$ value [20] of the solvent and the hydrogenation rate is observed, as shown in Table 2. This solvent effect on the rate may reflect the degree of swelling of the resin and the polarity near the active site in each solvent. When dimethylsulfoxide (DMSO) was used as a solvent, a very low rate of hydrogenation was observed compared with that expected from the $E_T(30)$ value of the solvent. This effect of DMSO on the catalytic activity of Resin 1-Pd may be caused by the strong coordinating ability of DMSO to the active site, as a similar effect has been reported in the hydrogenation of dienes by a polymer-anchored palladium complex catalyst [21].

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