Selective Hydrogenation of Cyclopentadiene to Cyclopentene Using Colloidal Palladium Supported on Chelate Resin

Hidefumi Hirai,* Shigeru Komatsuzaki, and Naoki Toshima
Department of Industrial Chemistry, Faculty of Engineering, The University of Tokyo, Hongo, Bunkyo-ku, Tokyo 113

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Cyclopentadiene was hydrogenated to cyclopentene selectively by using colloidal palladium supported on chelate resin with iminodiacetic acid moieties as a catalyst. The catalyst, containing metal particles of 1—6 nm in diameter, was prepared by reduction of the palladium(II)-chelate resin complex with methanol. Cyclopentene was produced in 97.1% yield at 100% conversion of cyclopentadiene at 30 °C under 1 atm of hydrogen. This value in yield was also achieved on repeated uses of the catalyst. The hydrogenation rate was correlated to the polarity parameter, $E_T(30)$ values, of the solvents used in the reaction, except in the case of dimethyl sulfoxide. The hydrogenation rates of cyclopentadiene (R_D) and cyclopentene (R_E) were expressed as $R_D=k_D[H_2][\text{catalyst}]$ and $R_E=k_E[H_2][\text{cyclopentene}][\text{catalyst}]$, respectively, where k_D and k_E are the rate constants. The equilibrium constant for complex formation between cyclopentadiene and the catalyst, K_D, was estimated to be over 400 times larger than that between cyclopentene and the catalyst, K_E. A mechanism, including the coordination of olefins to the catalyst and the subsequent hydrogenation of the coordinated complexes, was proposed.

Much attention has been paid for heterogenized transition-metal complex catalysts, since recovering and reusing of catalysts are indispensable in practical use of expensive noble metals.[1-4] The heterogenized homogeneous catalysts on organic or inorganic supports often have efficient catalytic properties of homogeneous analogs. Furthermore, the heterogenized catalysts sometimes have advantages in catalyst stability and reaction selectivity. Metal complexes in the heterogenized catalysts have various structures, *e.g.*, chelated structures, dimeric structures, and metal cluster structures, according to the preparative conditions.

We have already shown that finely dispersed colloidal transition metals were obtained by reduction of metal salts with alcohols in the presence of vinyl polymer with polar groups.[5-7] The particle sizes of these colloidal metals were below several nm in diameter, and were distributed in narrow ranges. Some of them exhibited specific selectivities as hydrogenation catalysts for olefins.[8,9] Chini[10] has pointed out that large metal carbonyl clusters could be applied to the chemistry of small metal particles (0.5—3 nm). Finely dispersed colloidal metals supported on polymers could be regarded as macromolecular complexes of metal clusters. Recently, we have reported on the preparation and the characterization of colloidal palladium catalysts supported on chelate resins with iminodiacetic acid moieties.[11] The chelate resin-supported catalysts were composed of small palladium metal particles and palladium complexes with iminodiacetic acid moieties. The sizes of metal particles were distributed from 1 to 6 nm and mainly from 1 to 2 nm. The metal particles in the resin-supported catalyst had catalytic activities for selective hydrogenation of diene to monoenes. The selective hydrogenation of cyclopentadiene is a significant process for utilization of the C_5 fraction of naphtha cracking products.[12,13] Furthermore, cyclopentadiene is one of the simplest dienes as a substrate for partial hydrogenation, since cyclopentadiene and cyclopentene have no isomers, respectively.

In the present paper the selective hydrogenation of cyclopentadiene to cyclopentene using the resin-supported colloidal palladium will be reported in detail with attention to the swelling effect of the polymer matrix on the catalytic properties.

Experimental

Materials. A chelate resin with iminodiacetic acid moieties attached to a styrene-divinylbenzene copolymer matrix, Diaion CR10 (Mitsubishi Chemical Ind. Co. Ltd., the size of the resin bead ranged from 0.3 to 1.2 mm in diameter in the swelled state) was used as a supporting polymer. The resin-supported colloidal palladium was prepared as follows: Palladium(II) chloride (Kojima Chemical Co. Ltd.) and the chelate resin were kept under stirring in water (pH 3) at room temperature for 1 h to form the palladium complex of the chelate resin, and the resulting complex was kept under refluxing in methanol-water (1:1)(pH 11) for 6 h as described previously.[11] The catalyst was preserved in methanol. One cubic centimeter of the resin-supported Pd catalyst swelled in methanol contained 18.5 μg-atom of palladium. The charged molar ratio of iminodiacetic acid moiety to palladium atom was 75.

Cyclopentadiene was obtained by pyrolysis of dicyclopentadiene (Yoneyama Chemical Co. Ltd.), and was purified by distillation under argon before use. Cyclopentene and cyclopentane were obtained from Tokyo Chemical Ind. Co. Ltd. and were distilled under argon.

Commercial guaranteed reagent grade methanol was used after distillation under argon. Ethanol, benzene, hexane, ethyl methyl ketone, ethyl acetate, *N*,*N*-dimethylformamide, and dimethyl sulfoxide at guaranteed reagent grade were used after removal of oxygen. *N*-Benzyliminodiacetic acid was obtained from Aldrich Chemical Co. Inc. Five percent Pd on charcoal was obtained from Nippon Engelhard Ltd.

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

Hydrogenation in Methanol. The measured volume (0—2.69 cm^3) of resin-supported Pd catalyst in methanol was put in a 100 cm^3 flask which was attached to the shaker with thermostat (Tokyo Rikakikai Co. Ltd.). After the atmosphere in the flask was replaced with hydrogen, methanol [$(20-x-y)\,cm^3$] was added into the flask and the flask was shaken for 1 h. A methanol solution (x cm^3) of cyclopentadiene or cyclopentene (2 mol/dm^3 each) and a methanol solution (y cm^3) of cyclopentane (2 mol/dm^3) were added into the flask, and the flask was shaken vigorously to start the reaction keeping the total pressure in the flask at 1 atm.

The rates of the hydrogenations were determined by the initial rates of the hydrogen uptake.

For the discussion on kinetics, the initial rates with the fresh catalysts were used. The dependence of the rate on hydrogen partial pressure was measured by using the mixed gases of hydrogen and nitrogen. The mixed gases were prepared by adding each gas into a high pressure vessel of stainless steel in different fixed ratios.

Hydrogenation in Other Solvents. Resin-supported Pd catalyst ($2.69\,cm^3$) separated from methanol was washed with a solvent which should be used for the hydrogenation reaction, and kept in the solvent for more than 1 h. After removal of the solvent, the flask containing the catalyst was mounted in the thermostated shaker. The atmosphere in the flask was replaced with hydrogen, and the solvent ($19.7\,cm^3$) was added. After the flask was shaken for 1 h, cyclopentadiene ($0.33\,cm^3$, 4 mmol) was added into the flask, which was shaken vigorously to start the reaction keeping the total pressure at 1 atm.

Analysis of the Products. The products were analyzed with GLPC by using a glass capillary column of Silicone OV-101 ($0.28\,mm\phi \times 30\,m$) at 20 °C with a flame ionization detector. In the present paper, the selectivity (S%) is defined by the yield of cyclopentene at the point of complete disappearance of cyclopentadiene in the reaction mixtures.

Reaction in Gas-phase Using a Closed Circulation System. Resin-supported Pd catalyst ($2.69\,cm^3$) separated from methanol was supported with glass wool in a reactor. Hydrogen, cyclopentadiene, and methanol were introduced into a circulation system from respective vessels by means of the pressure difference. All parts of the reactor system were composed of either Pyrex glass or Teflon, and the volume of the reaction circuit was $940\,cm^3$. The reaction was started by connecting the circulation system with the reactor. Gaseous mixtures in the reactor were analyzed periodically with GLPC.

Results

Hydrogenation of Cyclopentadiene in Methanol. Selective hydrogneation of cyclopentadiene to cyclopentene took place by using resin-supported Pd catalyst in methanol at 30 °C under an atmospheric pressure of hydrogen. The volume of hydrogen taken up increased proportionally to the reaction time up to the amount equimolar with cyclopentadiene as indicated in Fig. 1 (No. 1). As shown in the preceding paper,[11)] the active species of resin-supported Pd catalyst is metallic palladium. The amount of the metallic palladium is 5% of the charged amount of palladium, *i.e.*, 0.93 μg-atom Pd per $1\,cm^3$ of the resin catalyst. Hydrogenation rates were represented as rates of hydrogen uptake divided by the amount of metallic palladium in the catalyst. The hydrogenation rate decreases to about one-fifth of the initial rate after the conversion of cyclopentadiene reaches 100% as shown in Fig. 1. This decrease of the rate facilitates the isolation of cyclopentene in a high yield because of the minimum subsequent hydrogenation of cyclopentene. The composition of the products was followed by gas chromatographic analyses. The results are presented by circles in Fig. 2. Cyclopentene was obtained in 97.1% yield at complete conversion of cyclopentadiene by using the fresh resin-supported Pd catalyst.

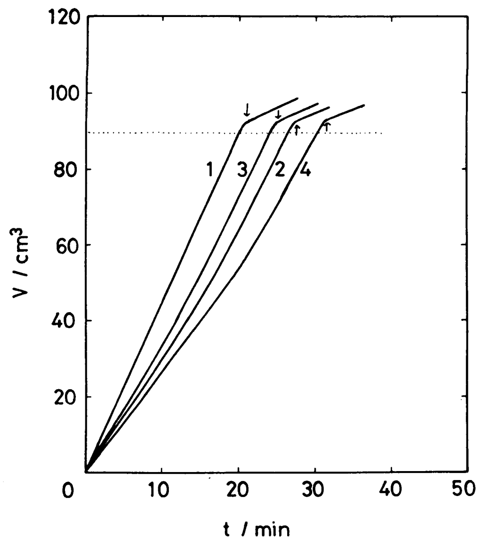

Fig. 1. Hydrogen uptakes (V) against reaction time in the hydrogenation of cyclopentadiene with the fresh (1), reused (2, 3), and pretreated (4) resin-supported Pd catalyst at 30 °C under an atmospheric hydrogen pressure. The dotted line shows the amount equimolar with cyclopentadiene. The arrows represent the points at which 100% conversion of cyclopentadiene was achieved.

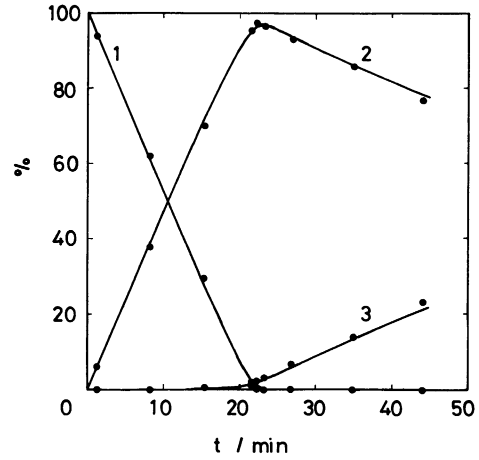

Fig. 2. Experimental and calculated composition (%) of the substrate and products in the hydrogenation of cyclopentadiene. Circles show the experimental values of composition of cyclopentadiene, cyclopentene, and cyclopentane under the conditions [metallic Pd]=0.125 (mol/dm^3), initial concentration of cyclopentadiene=0.2 (mol/dm^3), and $[H_2]=0.003$ (mol/dm^3). The curves are calculated for cyclopentadiene (1), cyclopentene (2), and cyclopentane (3) by assuming $k_2=440$ ($dm^3/mol\ s$), $k_4=1000$ ($dm^3/mol\ s$), $m=200$ (dm^3/mol) and $n=0.5$ (dm^3/mol).

The catalyst can be separated from the reaction mixtures and can be used again as a catalyst. The initial rate of hydrogen uptake and the selectivity for cyclopentene by using fresh and recovered resin-supported Pd catalysts are summarized in Table 1 as well as those with reference catalysts. When palladium on charcoal is used as a catalyst, cyclopentene is obtained in 88.4% yield. The addition of 75-fold molar amount of *N*-benzyliminodiacetic acid disodium salt to the palladium on charcoal results in 93.2% yield of cyclopen-

Table 1. Hydrogenation of cyclopentadiene[a]

Run	Catalyst	$r/10^{-1}\,\mathrm{s}^{-1}$[b]	S (%)[c]
1	Fresh resin-supported Pd	13.4	97.1
2	Recovered resin-supported Pd from run 1	8.2	97.3
3	Recovered resin-supported Pd from run 2	9.4	96.7
4	Resin-supported Pd pretreated with cyclopentane[d]	7.2	96.6
5	Resin-supported Pd stored in methanol[e]	13.4	96.7
6	Resin-supported Pd stored in water[e]	13.6	97.0
7	Commercial Pd on charcoal (5%)	36.0	88.4
8	Pd on charcoal with NBIDA[f]	37.1	93.2
9	Recovered Pd on charcoal from Run 8[g]	—	88.9

a) Conditions: 30 °C; H_2, 580 Torr; solvent, methanol; [cyclopentadiene]=0.20 mol/dm^3. b) The initial rate of hydrogen uptake (mol/s) per one g-atom of metallic Pd in the catalyst. c) The selectivity; the yield of cyclopentene at 100% conversion of cyclopentadiene. d) Resin-supported Pd pretreated with methanol containing cyclopentane (0.2 mol/dm^3) for 1 h. e) Under air for 30 d. f) Five percent palladium on charcoal (2.13 mg containing 1 μg-atom of Pd) was used in the presence of *N*-benzyliminodiacetic acid disodium salt (NBIDA) (75 μmol) in methanol (20 cm^3). g) Palladium on charcoal recovered from the reaction mixture in run 8 by decantation was used. Since some of the catalyst was lost in the decantation procedure, the catalytic activity per Pd g-atom was not known exactly.

Table 2. Hydrogenation of cyclopentadiene in various solvents[a]

Solvent	$r/10^{-1}\,\mathrm{s}^{-1}$[b]	S (%)[c]	$E_T(30)/\mathrm{kcal_{th}\,mol^{-1}}$[d]
Methanol	13.4	97.1	55.5
Ethanol	8.0	94.8	51.9
Dimethyl sulfoxide	0.06	—	45.0
N,N-Dimethylformamide	7.4	95.6	43.8
Ethyl methyl ketone	4.6	95.1	41.3
Ethyl acetate	5.8	93.6	38.1
Benzene	4.4	94.7	34.5
Hexane	0.62	—	30.9

a) Conditions: 30 °C; H_2 pressure=760 Torr—(vapor pressure of solvent media); catalyst, resin-supported Pd catalyst (2.69 cm^3); solvent, 20 cm^3; [cyclopentadiene]=0.2 mol/dm^3. b) The initial rate of hydrogen uptake (mol/s) per one g-atom of metallic Pd in the catalyst. c) The yield of cyclopentene at 100% conversion of cyclopentadiene. d) From Ref. 22.

tene (run 8). This value is slightly inferior to that with resin-supported Pd, but the yield is reduced to 88.9% by a repeated use of the catalyst (run 9).

After the reaction, the catalyst was separated from the reaction mixture, washed with methanol several times, kept in fresh methanol for 1 h, and then reused. The initial rate (run 2 in Table 1) with the reused resin-supported Pd catalyst is two-thirds of that with the fresh catalyst. But the rate gradually increased with reaction time and recovered to the original value near the hydrogen-uptake equimolar with the charged cyclopentadiene (run 2 in Fig. 1). The yield of cyclopentene at complete conversion of cyclopentadiene is the same as that with the fresh catalyst. When the reused resin-supported Pd catalyst is used again (run 3), the catalytic behavior is similar to that of run 2. To compare with this result, the fresh resin-supported Pd catalyst was kept in methanol containing cyclopentane (0.2 mol/dm^3) for 1 h, washed with methanol and then used as a catalyst. The results were similar to those of the catalyst in the repeated use, as shown at run 4 in Table 1 and Fig. 1.

When resin-supported Pd catalyst was stored in methanol or water under air for 30 d, no difference in the catalytic behavior was observed as shown at runs 5 and 6 in Table 1.

Hydrogenation of Cyclopentadiene in Various Solvents. Hydrogenations of cyclopentadiene in the presence of the resin-supported Pd catalyst were carried out in various solvents at 30 °C under an atmospheric pressure of hydrogen. The results are shown in Table 2 and Fig. 3. The highest activity and selectivity are achieved in methanol among the solvents examined. The hydrogen uptake curves in Fig. 3 are almost linear up to the point where the hydrogen-uptake is equimolar with the charged cyclopentadiene, and the slopes decrease gradually after the equimolar points. The decreasing extents of the rates near the equimolar points are different from each other. When methanol was used as a solvent, the decreasing extent is largest.

Kinetics for Hydrogenation of Cyclopentadiene in Methanol. The dependences of the initial rate on the concentration of cyclopentadiene, the amount of the catalyst, and the pressure of hydrogen were investigated.

Dependence upon Concentration of Cyclopentadiene: The rates of hydrogen uptake are plotted against the concentration (below 0.4 mol/dm^3) of cyclopentadiene in methanol with open circles in Fig. 4. The rate somewhat decreases with increase of the cyclopentadiene concentration. The initial rates were also measured under the condition that the sum of the respective concentrations of cyclopentadiene and cyclopentane was a constant value, 0.4 mol/dm^3, by adding

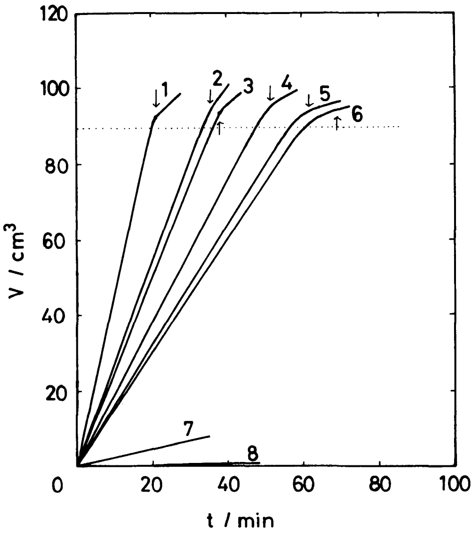

Fig. 3. Hydrogen uptakes (V) against reaction time in the hydrogenation of cyclopentadiene with the resin-supported Pd catalyst at 30 °C under an atmospheric hydrogen pressure in methanol (1), ethanol (2), *N,N*-dimethylformamide (3), ethyl acetate (4), ethyl methyl ketone (5), benzene (6), hexane (7), and dimethyl sulfoxide (8). The dotted line shows the amount equimolar with cyclopentadiene. The arrows represent the points at which 100% conversion of cyclopentadiene was achieved.

the appropriate amount of cyclopentane simultaneously at the addition of cyclopentadiene. The results are shown with closed circles in Fig. 4. The dependence of the rates upon the concentration of cyclopentadiene was essentially zero order.

Dependence upon Pressure of Hydrogen: The initial rates of hydrogenation of cyclopentadiene in methanol were measured under partial pressure of hydrogen below 580 Torr (1 Torr≈133.322 Pa). Dependence of the rate upon hydrogen pressure was the first order.

Dependence upon Amount of Catalyst: From the results with various amounts of the catalyst below 1.61 cm³ in 20 cm³ of methanol, dependence of the rate upon the amount of the catalyst was the first order.

Kinetic Expression: The kinetic experiments indicate that the rate of hydrogenation of cyclopentadiene, R_D, can be represented by the following Eq. 1, where k_D is a rate constant.

$$R_D = k_D[H_2][\text{catalyst}] \quad (1)$$

The constant k_D was determined at different temperature. The relationship of k_D with temperature is indicated in the Arrhenius plot in Fig. 5. The activation energy is calculated to be 8.0 kcal$_{th}$/mol (1 cal$_{th}$≈ 4.184 J) for the hydrogenation of cyclopentadiene.

Kinetics for the Hydrogenation of Cyclopentene in Methanol. Initial rates of the hydrogenation of cyclopentene catalyzed by resin-supported Pd were measured in methanol. Dependence of the rate upon the concentration of cyclopentene, the amount of the catalyst, and the partial pressure of hydrogen were determined.

Results under various cyclopentene concentrations below 0.4 mol/dm³ are shown with open circles in Fig. 6. The initial rates of hydrogenation were also measured under the condition that the sum of the respective concentrations of cyclopentene and cyclopentane was a constant value, 0.4 mol/dm³, by adding the appropriate amount of cyclopentane simultaneously at the addition of cyclopentene. These results are shown with closed circles in Fig. 6, indicating that the dependence upon the cyclopentene concentration is the first order. The hydrogenation rates were measured under various hydrogen pressures below 580 Torr, and the dependence upon the hydrogen pressure was the first order. The rates with various amounts of the catalyst below 1.61 cm³ in 20 cm³ of methanol were measured, and the dependence of the rate upon the amount of the catalyst was the first order.

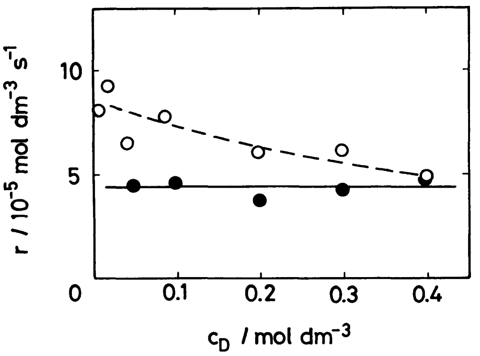

Fig. 4. Dependence of hydrogen uptake rate (r) on cyclopentadiene concentration (c_D) in methanol (20 cm³) at 30 °C under 580 Torr of hydrogen with the resin-supported Pd catalyst (metallic Pd, 1 μg-atom) without (○) and with addition (●) of cyclopentane ([cyclopentadiene]+[cyclopentane]=0.4 mol/dm³).

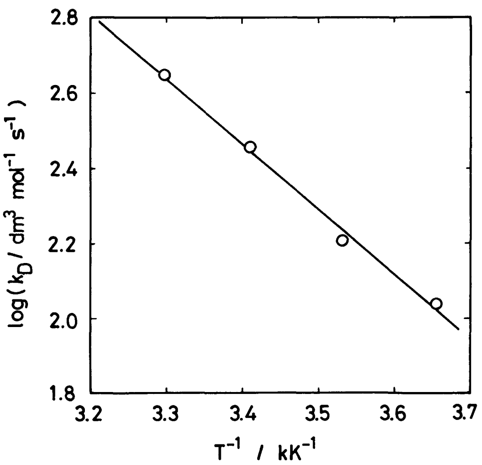

Fig. 5. Arrhenius plot for the rate constant in hydrogenation of cyclopentadiene in methanol.

These kinetic experiments indicate that the rate of hydrogenation of cyclopentene, R_E, can be represented by Eq. 2, where k_E is a rate constant.

$$R_E = k_E[H_2][\text{cyclopentene}][\text{catalyst}] \quad (2)$$

Hydrogenation in Gas-phase. Hydrogenations of cyclopentadiene in gas-phase were carried out using a closed circulation system. When the methanol-swelled resin-supported Pd catalyst containing 2.5 μg-atom of metallic palladium was used, the hydrogena-

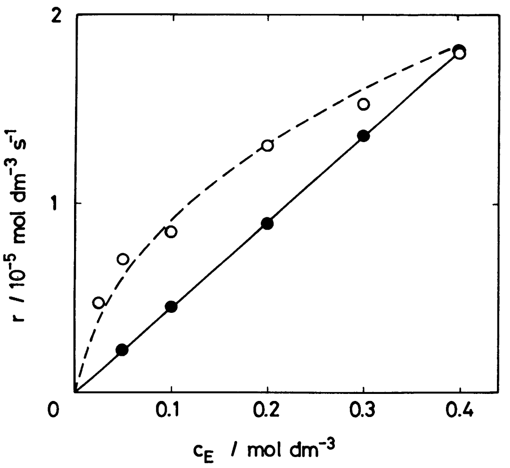

Fig. 6. Dependence of hydrogen uptake rate (r) on cyclopentene concentration (c_E) in methanol (20 cm^3) at 30 °C under 580 Torr of hydrogen with the resin-supported Pd catalyst (metallic Pd, 1 µg-atom) without (○) and with addition (●) of cyclopentane ([cyclopentene]+[cyclopentane]=0.4 mol/dm^3).

tion proceeded at 25 °C under 280, 70, and 70 Torr of initial partial pressures of hydrogen, cyclopentadiene, and methanol, respectively. After 104 min, the conversion of cyclopentadiene was 14% and the selectivity to cyclopentene was 96%. When the reaction was carried out at 50 °C, the hydrogenation was faster than that at 25 °C by the factor of 9 and the selectivity to cyclopentene at 14% conversion of cyclopentadiene was 90%. When the same gaseous mixture was circulated over the non-swelled resin-supported Pd catalyst (dried at 50 °C for 5 min under vacuum), no hydrogenation products were detected even after 100 min at 50 °C.

Discussion

Kinetics of Hydrogenation of Cyclopentadiene and Cyclopentene. When cyclopentadiene and cyclopentene are hydrogenated independently over the resin-supported Pd catalyst, Eqs. 1 and 2 represent the initial rates of each reaction. For example, the initial rate for cyclopentene is about one tenth of that for cyclopentadiene at 0.1 mol/dm^3 of the substrates. When cyclopentadiene is present, however, cyclopentene is not hydrogenated so fast. Thus, cyclopentadiene reacts predominantly and the highly selective hydrogenation of cyclopentadiene to cyclopentene takes place as shown in Table 1 and Fig. 2. In this case, the rate for cyclopentadiene does not change with the reaction time, but the hydrogenation of cyclopentene is suppressed to a very low rate. Indeed, at the reaction time of 10 min in Fig. 2 the hydrogenation rate of cyclopentadiene is almost the same as the initial rate, but that of cyclopentene is nearly equal to zero, although each concentration of cyclopentadiene and cyclopentene is about 0.1 mol/dm^3 at this point. This fact suggests that the coordination process of the substrate to the active species of the catalyst is important for the hydrogenation of cyclopentadiene and cyclopentene. Therefore, Eqs. 3—6 are proposed as a scheme, which includes the coordination processes, *i.e.*, the substrate forms an intermediate with the catalyst at first by coordination and then the intermediate reacts with hydrogen to give the product.

$$\text{cyclopentadiene} + \text{catalyst} \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} \text{cyclopentadiene} - \text{catalyst} \tag{3}$$

$$\text{cyclopentadiene} - \text{catalyst} + \mathrm{H_2} \xrightarrow{k_2} \text{cyclopentene} + \text{catalyst} \tag{4}$$

$$\text{cyclopentene} + \text{catalyst} \underset{k_{-3}}{\overset{k_3}{\rightleftharpoons}} \text{cyclopentene} - \text{catalyst} \tag{5}$$

$$\text{cyclopentene} - \text{catalyst} + \mathrm{H_2} \xrightarrow{k_4} \text{cyclopentane} + \text{catalyst} \tag{6}$$

Similar schemes have been proposed for the hydrogenations of alkynes and alkenes using palladium metal catalysts on vitreous supports.[14] Since the active species, the small Pd metal particle, is fixed to the cross-linked polymer matrix, it is assumed that the active species do not affect each other.[15] So the amount of metallic Pd per unit volume of solvent can be used as the catalyst concentration in kinetic studies. The total concentrations of the catalyst, C, cyclopentadiene, D, and cyclopentene, E, are defined in the following equations, respectively:

$$[\mathrm{C}] = [\text{catalyst}] + [\text{cyclopentadiene} - \text{catalyst}] + [\text{cyclopentene} - \text{catalyst}], \tag{7}$$

$$[\mathrm{D}] = [\text{cyclopentadiene}] + [\text{cyclopentadiene} - \text{catalyst}], \tag{8}$$

$$[\mathrm{E}] = [\text{cyclopentene}] + [\text{cyclopentene} - \text{catalyst}]. \tag{9}$$

Assuming the steady state (d[cyclopentadiene—catalyst]/dt=0, d[cyclopentene—catalyst]/dt=0) and the negligibly small concentration of the catalyst compared with substrates, Eqs. 10—12 are derived from Eqs. 3—9:

$$-\frac{\mathrm{d[D]}}{\mathrm{d}t} = [\mathrm{C}][\mathrm{H_2}]\frac{\dfrac{k_1k_2[\mathrm{D}]}{k_{-1}+k_2[\mathrm{H_2}]}}{1+\dfrac{k_1[\mathrm{D}]}{k_{-1}+k_2[\mathrm{H_2}]}+\dfrac{k_3[\mathrm{E}]}{k_{-3}+k_4[\mathrm{H_2}]}}, \tag{10}$$

$$\frac{\mathrm{d[E]}}{\mathrm{d}t} = [\mathrm{C}][\mathrm{H_2}]\frac{\dfrac{k_1k_2[\mathrm{D}]}{k_{-1}+k_2[\mathrm{H_2}]}-\dfrac{k_3k_4[\mathrm{E}]}{k_{-3}+k_4[\mathrm{H_2}]}}{1+\dfrac{k_1[\mathrm{D}]}{k_{-1}+k_2[\mathrm{H_2}]}+\dfrac{k_3[\mathrm{E}]}{k_{-3}+k_4[\mathrm{H_2}]}}, \tag{11}$$

$$\frac{\mathrm{d[A]}}{\mathrm{d}t} = [\mathrm{C}][\mathrm{H_2}]\frac{\dfrac{k_3k_4[\mathrm{E}]}{k_{-3}+k_4[\mathrm{H_2}]}}{1+\dfrac{k_1[\mathrm{D}]}{k_{-1}+k_2[\mathrm{H_2}]}+\dfrac{k_3[\mathrm{E}]}{k_{-3}+k_4[\mathrm{H_2}]}}, \tag{12}$$

where [A] is the concentration of cyclopentane.

When [E] equals to zero in Eq. 10,

$$-\frac{\mathrm{d[D]}}{\mathrm{d}t} = \frac{k_1k_2[\mathrm{D}][\mathrm{C}][\mathrm{H_2}]}{k_1[\mathrm{D}]+k_{-1}+k_2[\mathrm{H_2}]}. \tag{13}$$

And when [D] equals to zero in Eq. 11,

$$\frac{\mathrm{d[E]}}{\mathrm{d}t} = \frac{-k_3k_4[\mathrm{E}][\mathrm{C}][\mathrm{H_2}]}{k_3[\mathrm{E}]+k_{-3}+k_4[\mathrm{H_2}]}. \tag{14}$$

The initial rate for the hydrogenation of cyclopentadiene alone is expressed by Eq. 13. Since cyclopentadiene has large coordinating ability owing to its conjugated double bond,[16] it can be postulated for Eq. 13 that $k_1[\mathrm{D}]$ is much larger than $(k_{-1}+k_2[\mathrm{H_2}])$. Then Eq. 13 is simplified to Eq. 15:

$$-\frac{d[\mathrm{D}]}{dt} = k_2[\mathrm{C}][\mathrm{H_2}]. \qquad (15)$$

Eq. 15 agrees with the experimental result represented by Eq. 1. The rate constant k_2 $(=k_\mathrm{D})$ is calculated to be 440 ($\mathrm{dm^3/mol\,s}$) from the experimental results. The activation energy (8.0 $\mathrm{kcal_{th}/mol}$) obtained from the Arrhenius plot for k_D in the present reaction is comparable with that in the hydrogenation of 1,3-cyclooctadiene with polymer-bound palladium(II) complex catalyst.[17]

The initial rate for the hydrogenation of cyclopentene alone is expressed by Eq. 14 in the above scheme. It is necessary that k_{-3} is large enough comparing with $(k_3[\mathrm{E}]+k_4[\mathrm{H_2}])$ for Eq. 14 to be simplified to the experimental expression, Eq. 2. This will be discussed in the next section.

Selectivity in the Hydrogenation of Cyclopentadiene to Cyclopentene. The amounts of cyclopentadiene and cyclopentene at a certain reaction time in the hydrogenation of cyclopentadiene can be calculated by integrating Eqs. 10 and 11 numerically. Equations 10 and 11 can be rewritten by using factors m and n as following expressions:

$$-\frac{d[\mathrm{D}]}{dt} = [\mathrm{C}][\mathrm{H_2}]\frac{k_2m[\mathrm{D}]}{1+m[\mathrm{D}]+n[\mathrm{E}]}, \qquad (16)$$

$$\frac{d[\mathrm{E}]}{dt} = [\mathrm{C}][\mathrm{H_2}]\frac{k_2m[\mathrm{D}]-k_4n[\mathrm{E}]}{1+m[\mathrm{D}]+n[\mathrm{E}]}, \qquad (17)$$

where

$$m = \frac{k_1}{k_{-1}+k_2[\mathrm{H_2}]},\ n = \frac{k_3}{k_{-3}+k_4[\mathrm{H_2}]}. \qquad (18)$$

The simultaneous differential Eqs. 16 and 17 were solved numerically with a Runge-Kutta method[18] by substituting various values into the factors m, n, and k_4, respectively. When $m=200$ ($\mathrm{dm^3/mol}$), $n\leq 0.5$ ($\mathrm{dm^3/mol}$), and $k_4\geq 1000$ ($\mathrm{dm^3/mol\,s}$) were assumed, the best agreement of the calculated result with the experimental one was obtained. The compositions of each product were calculated by assuming $m=200$ ($\mathrm{dm^3/mol}$), $k_2=440$ ($\mathrm{dm^3/mol\,s}$), $n=0.5$ ($\mathrm{dm^3/mol}$), and $k_4=1000$ ($\mathrm{dm^3/mol\,s}$), and are drawn as curves in Fig. 2. The experimental data are plotted with circles in Fig. 2. K_D and K_E are defined as equilibrium constants of Eqs. 3 and 5, respectively, *i.e.*, $k_1/k_{-1}=K_\mathrm{D}$, and $k_3/k_{-3}=K_\mathrm{E}$. Since $m=200$ ($\mathrm{dm^3/mol}$) and $1/m=(1/K_\mathrm{D})+(k_2[\mathrm{H_2}]/k_1)$ (from definition), we have obtained $K_\mathrm{D}\geq 200$ ($\mathrm{dm^3/mol}$).

In order to make the theoretical expression (Eq. 14) in good agreement with the experimental expression (Eq. 2) within experimental errors, it is necessary that k_{-3} is at least 5 times larger than the sum of $k_3[\mathrm{E}]$ and $k_4[\mathrm{H_2}]$. From the experimental conditions, the concentration of cyclopentene [E] is less than 0.4 ($\mathrm{mol/dm^3}$) and that of hydrogen $[\mathrm{H_2}]$ equals to 0.003 ($\mathrm{mol/dm^3}$) from the solubility of hydrogen in methanol.[19] These experimental data and the value of k_4 ($\geq 1000\,\mathrm{dm^3/mol\,s}$) lead the conclusion that $K_\mathrm{E}\leq 0.5$ ($\mathrm{dm^3/mol}$) and $k_{-3}\geq 15$ ($\mathrm{s^{-1}}$). Thus, since $K_\mathrm{D}\geq 200$, K_D is at least 400 times larger than K_E. On the other hand, k_2 is less than a half of k_4 since $k_2=440$ and $k_4\geq 1000$. Therefore, the large $K_\mathrm{D}/K_\mathrm{E}$ ratio is considered to cause the high selectivity for the hydrogenation of cyclopentadiene to cyclopentene.

Since particle size of palladium metal is very small in the present Pd catalyst,[11] the state of active species is supposed to have some properties of metal complexes or metal clusters.[10,20] This would result in the large $K_\mathrm{D}/K_\mathrm{E}$ ratio for cyclopentadiene and cyclopentene. Since the selectivity with palladium on charcoal increases with the addition of *N*-benzyliminodiacetic acid disodium salt, the iminodiacetic acid moiety in the resin-supported Pd catalyst possibly causes the increase of the selectivity. The increase of selectivity in the successive catalytic reaction by the presence of foreign substances is known, *e.g.*, in the case of Lindlar catalyst modified by quinoline.[21] The iminodiacetic acid moiety in the resin is not lost in repeated uses of the resin-supported Pd catalyst, though *N*-benzyliminodiacetic acid disodium salt is gradually removed in repeated uses of the palladium-on-charcoal catalyst modified with *N*-benzyliminodiacetic acid disodium salt. So the effect of iminodiacetic acid moiety can be emphasized in the repeated uses of the resin-supported catalyst.

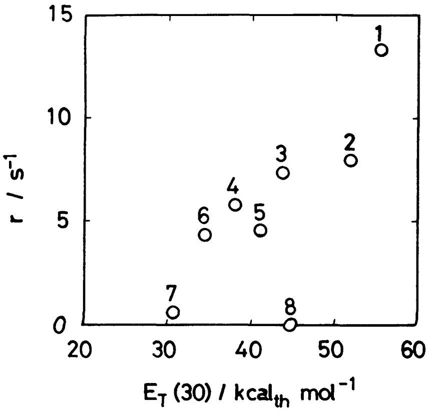

Fig. 7. Correlation of the hydrogenation rate (r) with $E_\mathrm{T}(30)$ value of the solvent: 1, methanol; 2, ethanol; 3, *N*,*N*-dimethylformamide; 4, ethyl acetate; 5, ethyl methyl ketone; 6, benzene; 7, hexane; 8, dimethyl sulfoxide. r is the rate of molar hydrogen uptake in a second per molar metallic Pd as catalyst.

Behavior of the Catalyst in Various Reaction Conditions. The hydrogenation rates of cyclopentadiene in various solvents are plotted against the E_T (30) value[22] in Fig. 7. A considerable correlation between the E_T (30) value and the hydrogenation rate is observed, suggesting that the polarity of the solvent affects the rate of hydrogenation. This solvent effect on the rate is supposed to be based on the swelling degree of the resin and on the so-called polar effect which is generally observed in the catalytic hydrogenation of olefins.[23] When dimethyl sulfoxide was used as a solvent, a very low rate was observed compared with that expected from the E_T (30) value. This inhibitory effect of dimethyl sulfoxide on the catalytic activity may be caused by strong coordinating ability of the solvent to the active species, as the similar effect has been reported in the hydrogenation reaction of dienes by a polymer-bound palladium(II) complex catalyst.17) In the kinetic measurement the rate in methanol somewhat decreased with the increasing concentration of cyclopentane which was added to make the sum of the concentrations of the substrate and cyclopentane constant. This result may be ascribed to the polarity change of the reaction field by adding cyclopentane, since a very low rate was observed in hexane in contrast with a high rate in methanol. To eliminate the effect of solvent polarity change from kinetic results, the rates were measured in the presence of appropriate amount of cyclopentane as mentioned in the rate dependence on the concentration of cyclopentadiene (Fig. 4).

When the resin-supported Pd catalyst was reused after recovering by filtration from the reaction mixture, the lower initial rate was observed than that with a fresh catalyst. This is probably due to the contact of the catalyst with hydrophobic compounds such as cyclopentane before the start of the reaction, since a similar behavior was observed in the reaction by the catalyst pretreated with methanol containing cyclopentane for 1 h. From the elemental analyses of carbon and nitrogen in the supporting resin, about two-thirds of benzene rings in the resin are considered to have iminodiacetic acid moieties. So the resin consists of the hydrophobic parts like styrene residues and the hydrophilic parts like iminodiacetic acid moieties. The hydrophobicity of the cyclic C_5 compound increases in the order: cyclopentadiene$<$cyclopentene$<$cyclopentane.24) Therefore, when more hydrophobic compound like cyclopentane contacts with the resin-supported Pd catalyst, some cyclopentane would interact with the hydrophobic parts and would remain in the region even after washing with methanol. The hydrophobic parts may surround the active site of the catalyst. Thus in the repeated use, cyclopentadiene might be prevented to approach to the active species of the catalyst by cyclopentene and cyclopentane fixed in the matrix. But, in the steady state of the hydrogenation of cyclopentadiene, the active species is also surrounded by the appropriate amount of cyclopentadiene corresponding to its concentration in the solution. Therefore, it should take a time for the environmental conditions of the active species to achieve the steady state.

The results using a closed circulation reactor indicate that the swelling of the resin with methanol is necessary for resin-supported Pd catalyst to function effectively. In the dry state the resin is shrunk to prevent the substrate from approaching to the active species. When the catalyst was used in the swelled state under the existence of methanol vapor in the gas-phase, the selective hydrogenation of cyclopentadiene was observed to proceed by using a closed circulation reactor.

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