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A POLYION COMPLEX-SUPPORTED PALLADIUM CATALYST FOR SELECTIVE HYDROGENATION OF CONJUGATED DIOLEFINS TO MONOOLEFINS

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A colloidal palladium supported on the polyion complex composed of polyacrylic acid and polyethylene imine catalyzes highly selective hydrogenation of conjugated diolefins to monoolefins at 30°C under an atmospheric hydrogen pressure.

The complex prepared from palladium(II) chloride and styrene-divinylbenzene copolymer with iminodiacetic acid groups was found to catalyze the selective hydrogenation of conjugated diolefins to monoolefins at 30°C under an atmospheric hydrogen pressure.1) We now wish to report that the colloidal metal of palladium supported on a polyion complex composed of polyacrylic acid and polyethylene imine functions highly selective hydrogenation of conjugated diolefins to monoolefins at 30°C under an atmospheric hydrogen pressure.

An orange-colored solution of $PdCl_2 \cdot 2H_2O$ (0.2, 0.5, or 2 mmol), 1 N NaOH (40 mmol), and polyacrylic acid (degree of polymerization 2600; 40 mmol as monomeric unit) in methanol (100 ml)-water (100 ml) was refluxed under nitrogen for 6 hr. The solution became dark brown and the palladium(II) chloride was reduced to the colloidal metal of palladium dispersed in polyacrylic acid. A trace of black precipitate formed during refluxing was removed by filtration. The filtrate containing the sodium salt of polyacrylic acid with colloidal palladium (PAA-Pd-Na) in methanol-water solution was added to an aqueous solution (100 ml) of polyethylene imine (degree of polymerization 1100; 40 mmol as monomeric unit) and the solution was stirred for 30 min. Thereafter, the value of pH of the solution was adjusted to about 4 by adding 1 N HCl aqueous solution (about 40 ml) to precipitate a polyion complex containing colloidal palladium. The gray precipitate was washed with methanol, dried at 30°C in vacuo for 3 hr and ground, resulting in fine particles of the polyion complex-supported palladium catalyst (PAA-Pd-PEI) in a yield of 98～100% based on polyacrylic acid or polyethylene imine.

A methanol solution of polyacrylic acid with colloidal palladium (PAA-Pd-H) was also prepared as follows. The methanol-water solution of sodium salt of polyacrylic acid with colloidal palladium which was obtained by refluxing as described above was passed through a 20×2.5 cm column of cation exchange resin, Amberlite IR-120 (H) (Rohm and Haas), and was washed with water until the washing was no longer acidic. The obtained polyacrylic acid with colloidal palladium solution was evaporated

Table I. Rates of Hydrogenation of Various Substrates by PAA-Pd-PEI Catalyst: r[a] = 80; Pd = 0.125 mmol[4]; substrate concentration, 0.2 M; solvent, MeOH; total reaction mixture, 50 ml; temp., 30 ± 0.05°C; H_2 pressure = 760 mmHg - vapour pressure of solvent media.

Substrate	Initial hydrogen uptake in ml/min at s.t.p.	Reaction time (min)	Products (%)
Cyclopentadiene	15.7	16	Cyclopentene (98.5) Cyclopentane (1.5)
Cyclohexa-1,3-diene	13.8	13	Cyclohexene (78.5) Cyclohexane (trace) Benzene (21.5)
Cycloocta-1,3-diene	22.3	14	Cyclooctene (99.6) Cyclooctane (0.4)
Cyclopentene	0.49		
Cyclohexene	0.12		
Cyclooctene	0.14		
Hexa-2,4-diene[b]	22.4	16	trans-Hex-2-ene (46.4) cis-Hex-2-ene (15.5) trans-Hex-3-ene (32.8) cis-Hex-3-ene (4.3) Hexane (1.0)
Methylsorbate	15.4	75	Methyl-2-hexenoate (81.0) Methyl-3-hexenoate (10.4) Methyl-4-hexenoate (7.5) Methylcaproate (1.1)
Hex-1-ene	1.86		
Dec-1-ene	1.04		
trans-Hex-2-ene	0.18		
2-Methylbut-2-ene	0.12		
Cycloocta-1,5-diene[c]	1.55	210	Cycloocta-1,5-diene (15.9) Cyclooctene (81.3) Cyclooctane (2.8)
Cyclohepta-1,3,5-triene	1.10		

a) r is the molar ratio of the monomeric residue in polyacrylic acid or polyethylene imine to $PdCl_2 \cdot 2H_2O$.

b) Trans-trans, 70 % and trans-cis, 30 %.

c) Substrate concentration, 0.1 M.

at 50°C under a reduced pressure and dissolved in methanol.

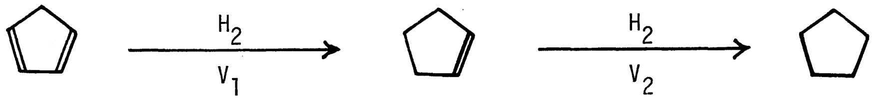
Hydrogenation of substrates under an atmospheric pressure was carried out by using the apparatus and the procedure described in the previous paper,$^{2)}$ and the reaction products were analyzed by glpc.$^{2)}$

The reduction of palladium(II) chloride to the colloidal palladium on the refluxing of the methanol-water solution may proceeds by a similar mechanism to the reduction of rhodium(III) chloride to a colloidal rhodium dispersed in polyvinyl alcohol in methanol - water solution.$^{3)}$

Some polyolefins and monoolefins were hydrogenated in methanol at 30°C under an atmospheric hydrogen pressure by the PAA-Pd-PEI catalyst. As shown in Table I, conjugated cyclic and linear diolefins are very easily hydrogenated. On the other hand, monoolefins, even terminal olefins such as hex-1-ene, and dec-1-ene are very slowly hydrogenated. For example, the rates of hydrogenation of cycloocta-1,3-diene, cyclohexa-1,3-diene, and cyclopentadiene relative to those of corresponding monoolefins become more than 150, 110, and 32 times, respectively. However, a conjugated triene, cyclohepta-1,3,5-triene was difficult to be hydrogenated. Migration of C = C double bonds of olefins was also observed during hydrogenation. For example, hex-1-ene yielded trans-hex-2-ene (31.7 %), cis-hex-2-ene (24.2 %), trans-hex-3-ene (4.1 %) and cis-hex-3-ene (2.8 %) with hexane (37.2 %) at a reaction time of 140 min under the conditions as given in Table I.

The high catalytic activity of the PAA-Pd-PEI catalyst for the hydrogenation of conjugated diolefins enabled the selective hydrogenation of these substrates to monoolefins. The results of hydrogenation of some conjugated diolefins catalyzed by the PAA-Pd-PEI catalyst are shown in Table I. The products in the table were obtained at a reaction time, when the equivalent mole of hydrogen to the charged diolefin was absorbed and the hydrogenation rate began to decrease, besides the case of cyclohexa-1,3-diene.$^{5)}$ As shown in Table I, the conjugated dienes can be hydrogenated to the corresponding monoolefins with high selectivities by use of the PAA-Pd-PEI catalyst. In the case of cyclohexa-1,3-diene, disproportionation of the diene to benzene and cyclohexene is also observed during the course of hydrogenation. Such disproportionation of cyclohexa-1,3-diene has been observed for palladium metal catalysts.$^{6)}$

The effects of the molar ratio (r) of the monomeric residue of polyacrylic acid or polyethylene imine to $PdCl_2 \cdot 2H_2O$ on the catalytic activity and the selectivity of the PAA-Pd-PEI catalyst were examined for the hydrogenation of cyclopentadiene producing cyclopentene as denoted in Eq. (1),



(1)

where v_1 and v_2 respectively mean the initial hydrogen uptake for the hydrogenation of cyclopentadiene and the rate of the subsequent hydrogenation of the produced cyclopentene. The rates of the hydrogenation of the diene and the monoolefin were nearly constant throughout the reaction time. As shown in Table II, with the increasing value of r, the rate of hydrogenation of cyclopentene is much more suppressed than that of hydrogenation of cyclopentadiene. Therefore, the selectivity toward cyclopentene can be improved by using the catalyst with a large value of r.

The polyethylene imine used in this study contains primary, secondary, and tertiary amines in a molar ratio of 1 : 2 : 1. The effects of addition of monomeric amines such as n-butylamine, diethylamine, and triethylamine, in place of polyethylene imine on the catalytic behavior of the PAA-Pd-H catalyst for the hydrogenation as denoted in Eq. (1) were investigated. The effect of addition of diethylamine on the catalytic behavior of an active carbon-supported palladium catalyst (Kojima Chemical Co., Ltd.; Pd/C) and of a cross-linked polyacrylic acid-supported palladium catalyst (IRC-84-Pd-H[7]) was also examined. These results are summarized in Table III. The PAA-Pd-H catalyst without amine is active for the hydrogenation of cyclopentene as well as that of cyclopentadiene. The added amines markedly improve the catalytic activity of the colloidal palladium catalyst for the hydrogenation of cyclopentadiene, but inhibit the catalytic activity for that of cyclopentene. Diethylamine is the most effective among the amines used. In the case of the solid catalyst such as the Pd / C and the IRC-84-Pd-H catalysts, no remarkable effect of diethylamine on the value of v_1 / v_2 was observed. Both values of v_1 / v_2 for the Pd / C and the IRC-84-Pd-H catalysts without amine

Table II. Effect of Molar Ratio (r) of Monomeric Residue in Polymer / Pd on Hydrogenation Rate of Cyclopentadiene and Selectivity of Cyclopentene with PAA-Pd-PEI Catalyst: Pd, 0.125 mmol; substrate concentration, 0.2 M, solvent, MeOH.[a)]

r	v_1 ml / min	v_1 / v_2	Selectivity[b)] %
20	19.0	17	96.6
80	15.7	32	98.5
200	15.0	45	98.5

a) Other conditions are given in Table I.

b) Yield of cyclopentene at 100 % conversion of cyclopentadiene.

were found to be nearly 1.5. A comparison of the values of v_1 / v_2 obtained for the PAA-Pd-H-amine catalyst with that for the PAA-Pd-PEI catalyst at r = 200 given in Table III indicates clearly that the polymeric amine, polyethylene imine, added to the polyacrylic acid with colloidal palladium is much more effective than monomeric amines for increasing the value of v_1 / v_2 and the selectivity toward cyclopentene. This desirable effect of polymeric amine may be ascribed to the suppressed mobility of amino groups in polymer chain forming the polyion complex with polyacrylic acid and/or to the heterogeneous state of the palladium supported by the polyion complex.

The PAA-Pd-PEI catalyst exhibits more improved selectivity toward monoolefins for the hydrogenation of the conjugated diolefins than the Chelex 100-Pd-Na complex.$^{1)}$ Though the Chelex 100-Pd-Na complex shows an excellent selectivity for the hydrogenation of cycloocta-1,3-diene to cyclooctene$^{1)}$, the

Table III. Effects of Addition of Amines on Hydrogenation Rate of Cyclopentadiene and Selectivity of Cyclopentene with Various Catalyst: substrate concentration, 0.2 M; solvent, MeOH.$^{a)}$

Catalyst (r) (Pd, mmol)	Amine (mmol)	v_1 ml / min	v_1 / v_2	Selectivity$^{b)}$ %
PAA-Pd-H (200) (0.025)	——	12.7	1.4	95.5
	n-$CH_3(CH_2)_3NH_2$ (5.0)	24.6	19.0	97.2
	$(CH_3CH_2)_2NH$ (5.0)	17.7	24.0	98.0
	$(CH_3CH_2)_3N$ (5.0)	19.8	15.0	97.1
Pd / C (0.0625)	$(CH_3CH_2)_2NH$ (12.5)	18.8	6.5	95.4
IRC-84-Pd-H (70) (0.125)	$(CH_3CH_2)_2NH$ (8.75)	15.1	3.4	98.0
Chelex 100-Pd-Na (70) (0.125)	——	13.5	3.9	97.3

a) Other conditions are given in Table I.

b) Yield of cyclopentene at 100 % conversion of cyclopentadiene.

complex gives a smaller value of v_1 / v_2 and a selectivity toward cyclopentene for the hydrogenation of cyclopentadiene than the PAA-Pd-PEI catalyst as shown in Table III.

The particles of the polyion complex supported-palladium catalyst can be easily recovered by filtration and reused without any appreciable loss in the catalytic activity and the selectivity toward monoolefins. On the other hand, the homogeneous PAA-Pd-H-amine catalysts are troublesome to be recovered from the reaction mixture. In the case of the solid catalysts such as the Pd / C and the IRC-84-Pd-H with diethylamine, it was difficult to recover the catalysts from the reaction mixture without appreciable loss of the added amine.

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References and Notes

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2) Y. Nakamura and H. Hirai, Chemistry Letters, 1974, 645.
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4) Palladium content in the PAA-Pd-PEI catalyst was calculated from the charged quantity since no appreciable loss of palladium was found in the course of preparation of the catalyst.
5) In the case of cyclohexa-1,3-diene, the products in Table I were obtained when the hydrogen uptake approached to 57 mole- % of charged diene and the hydrogenation rate began to decrease.
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7) The IRC-84-Pd-H catalyst was prepared from sodium salt of the IRC-84-Pd catalyst which was obtained by refluxing of sodium salt form of cross-linked polyacrylic acid (Amberlite IRC-84, Rohm and Haas) partly displaced with Pd(II) ion in methanol-water solution.

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