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# HIGHLY ACTIVE POLYMER-SUPPORTED Pd COMPLEX. A NEW SYNTHETIC METHOD AND ITS USE IN SELECTIVE HYDROGENATION OF OLEFINS AND ACETYLENES

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The palladium chloride complex supported on polymeric diphenylbenzyl phosphine is very active for both hydrogenation of olefins and acetylenes, and isomerization of double bonds. This high activity is probably due to the formation of the coordinatively unsaturated palladium.

Recently, several attempts of fixation of soluble transition metal complexes on solid supports and of its use for heterogeneous reaction have been made.[1)] However, the polymer-supported catalyst concerning palladium has not appeared with the exception of Bailar work.[1a)] Bailar bound palladium benzonitrile complex with polymeric diphenylbenzyl phosphine. The resulting polymer was a selective hydrogenation catalyst for the reduction of polyolefins to monoolefins and was much more active than the $PdCl_2(PPh_3)_2$-$SnCl_2$ catalyst. In this letter, we wish to communicate a new convenient synthetic method of polymer-supported Pd complex catalyst. This complex prepared from the reaction of $PdCl_2$ with polymeric diphenylbenzyl phosphine promotes many olefin hydrogenations and double bond migration reactions under mild conditions. In comparison with the Bailar catalyst, this catalyst is more active for both reactions.

The preparation of the polymer complex is as follows. A mixture of $PdCl_2$ (1.51 g, 8.5 mmol), polymeric diphenylbenzyl phosphine (2.50 g, 8.5 mmol as diphenylbenzyl phosphine group) and benzene (10 ml) was stirred at 80°C for 2 hr. To the gel solution containing brown $PdCl_2$-particle was added ethanol (20 ml) to dissolve $PdCl_2$ and the mixture was further stirred under reflux for 24 hr and cooled. Yellow-green resin particle was suspended in brown solution. The precipitated polymer-supported complex was collected by filtration and washed with ethanol until the filtrate was colorless. All the above procedures were operated under an atmosphere of nitrogen.

Anal. Found: C 53.88: H 4.04; Cl 12.48; P 7.62%

Calcd. for $\mathrm{P}\cdot(PdCl_2)$: C 52.61; H 4.01; Cl 14.82; P 6.47%

The infrared spectrum showed trans Pd-chloride stretching at 351 $cm^{-1}$.[2)] The binding energies of the palladium $3d_{3/2}$, $3d_{5/2}$ and chlorine 2p level were determined for this polymer complex and other palladium compounds with X-ray photoelectron spectroscopy (ESCA) (Table I). This complex has slightly higher Pd(3d) binding energies than $PdCl_2(PPh_3)_2$ and $PdCl_2$, and the Cl(2p) binding energy is similar to that of $PdCl_2$ with bridged chlorine ligands.

Table I. Palladium 3d and halogen binding energies (in eV)[a]

| Complex | Pd | | Cl 2p |
|---|---|---|---|
| | $3d_{3/2}$ | $3d_{5/2}$ | |
| $PSP\cdot PdCl_2$[b] | 344.0 | 338.6 | 199.1 |
| $AFR\cdot PSP\cdot PdCl_2$[c] | 343.8 | 338.5 | 199.2 |
| Bailar catalyst | 343.5 | 338.2 | 198.8 |
| $PdCl_2(PPh_3)_2$ | 343.6 | 338.3 | 198.6 |
| $PdCl_2$ | 343.6 | 338.1 | 199.3 |

a The $E_b$ values are referenced to the carbon 1s (285.0 eV).

b Our polymer complex. c After using olefin hydrogenation.

No ESR signal of $Pd^+$ ion was observed. The ESCA and ESR spectra showed that the valence state of the metal ion was diamagnetic Pd(II). In addition, the IR, ESCA, and ESR spectra of the recovered complex did not vary after olefin hydrogenation.

The hydrogenation procedure is as follows. The polymer complex was added to a reaction flask and the system was alternately evacuated and flushed with hydrogen five times. The hydrogen pressure was set near 1 atm, and a solvent was added through a side-arm entry port to the reaction flask. The mixture was then stirred for 30 min, and a substrate was added. The stirring was begun anew. The volume of hydrogen uptake at constant pressure was measured. The reaction products were analysed by glpc with 3 m column of apiezon grease L or BMEE.

Without pretreatment of the catalyst with hydrogen, the reaction showed an induction period, suggesting that the Pd-hydride species may be a real active catalyst.

Some representative rates of initial hydrogen uptake for the hydrogenation of alkenes and alkynes at 25°C under an atmospheric hydrogen pressure are given in Tables II and III.

Table II. Hydrogenation rates of olefins and acetylenes[a]

| Substrate | Initial rate (ml/min) | Substrate | Initial rate (ml/min) |
|---|---|---|---|
| Styrene | 8.10 | Allyl chloride | 2.52 |
| 1-Heptene | 3.94 | Acrolein | 1.90 |
| 2-Heptene | 0.59 | Methyl acrylate | 5.60 |
| 1-Dodecene | 2.83 | 1,5-Cyclooctadiene | 0.93 |
| Cyclohexene | 0.84 | 1,3-Cyclooctadiene | 5.26 |
| Cyclooctene | 0.07 | Isoprene | 9.60 |
| Allyl alcohol | 5.72 | 1-Hexyne | 2.98 |
| Allylbenzene | 5.10 | Phenylacetylene | 3.53 |

a Using polymer-Pd complex; $3.19 \times 10^{-3}$ mol/l, 0.335 mol/l substrate, 1 atm of hydrogen at 25° in [13-(volume of substrate)] ml of benzene-ethanol(1:1).

Table III. Effect of solvent on styrene hydrogenation[a]

| Solvent | Initial rate (ml/min) | Solvent | Initial rate (ml/min) |
|---|---|---|---|
| DMF | 8.04 | Ethyl acetate | 2.08 |
| Ethanol | 7.74 | Methylene chloride | 1.68 |
| THF | 6.13 | Acetic acid | 1.45 |
| Acetone | 6.10 | Cyclohexane | 0.22 |
| Benzene | 2.84 | Nitromethane | 0.10 |
| Chloroform | 2.45 | DMSO | 0.09 |

a Using polymer-Pd complex; $3.19 \times 10^{-3}$ mol/l, 0.67 mol/l styrene, 1 atm of hydrogen at 25° in 12 ml of solvent.

This polymer complex was an effective catalyst for the reduction of the C=C bond and the C≡C bond, but not active for that of phenyl, carbonyl, and cyano groups. It is noteworthy that this catalyst displayed good selectivity for the reduction of dienes and alkynes to monoolefins. The small hydrogenation rates of both cyclohexene and cyclooctene indicate that the reaction using this catalyst was affected by the molecular size of the olefins. The rate was also greatly affected by change in solvent. It can be said that the solvents with the moderate coordinating ability to metal such as ethanol, THF, DMF, and acetone are the most desirable, while cyclohexane and DMSO having the weak or strong coordinating ability are extremely unfavorable.

The product distribution in the hydrogenation of 1,5-cyclooctadiene was monitored by glpc at interval of time (Fig.1, 1,3-cyclooctadiene was not detected). The result of 1,3-cyclooctadiene hydrogenation was such as shown in Fig.2.

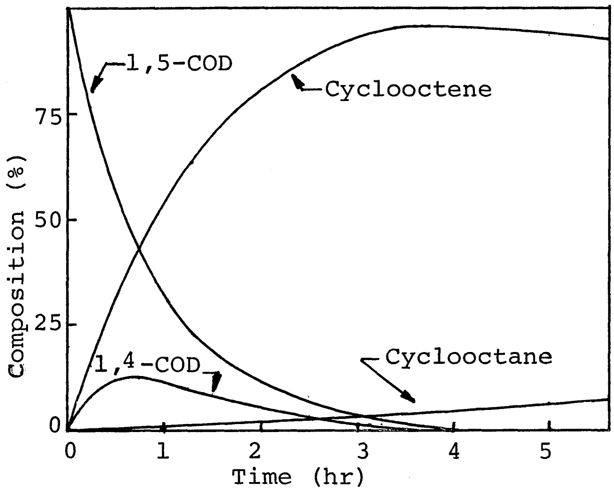


Fig.1. Hydrogenation of 1,5-COD in benzene-ethanol(1:1) under 1 atm of hydrogen at 25°.

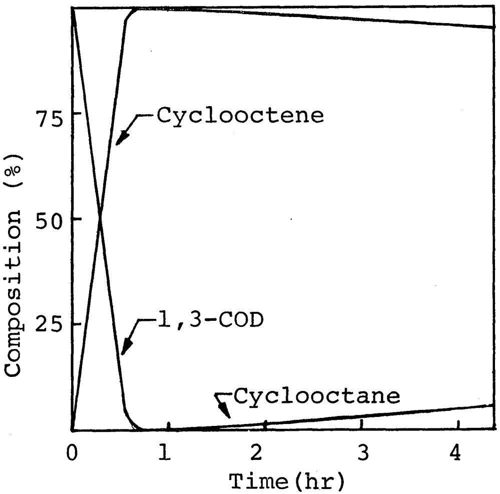
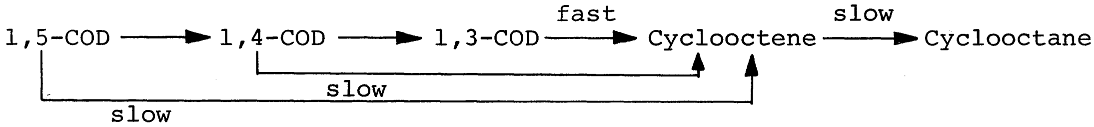


Fig.2. Hydrogenation of 1,3-COD in benzene-ethanol(1:1) under 1 atm of hydrogen at 25°.

The above results reveal that the reduction of 1,5-cyclooctadiene occured with accompanying isomerization of non-conjugated dienes to conjugated diene as follows.



Similarly, the reduction of allylbenzene was found to proceed through β-methylstyrene isomer. Under the reaction conditions used, no isomerization was observed in the absence of hydrogen gas.

In attempt to clarify the difference between the catalytic behavior of this catalyst and that of Bailar one, we prepared the Bailar catalyst by the reaction of $PdCl_2(NCPh)_2$ with the same polymer as used above in acetone. The major differences can be pointed out: (1) The former is much superior to the latter in hydrogenation activity. The rate of styrene hydrogenation was ten times as fast as that of the latter in benzene-ethanol(1:1) under the same Pd concentration. All non-alcoholic solvents necessitated the use of high pressure of hydrogen in the case of the latter, while the former had sufficient activity in acetone, THF, or DMF in addition to alcohol solvents under the ambient pressure. (2) The former accelerates the double bond migration. Therefore, using the former non-cojugated diene was isomerized to conjugated diene, which was further hydrogenated to monoene. On the other hand, using the latter the double bonds of non-conjugated diene were directly reduced to give monoene. It seems that Pd(3d) binding energies of two polymer catalysts reflect the above differences.

In comparison with monomeric-analog $PdCl_2(PPh_3)_2$,[3] this polymer catalyst is much more active for hydrogenations. $PdCl_2(PPh_3)_2$ did not show the reaction activity under 1 atm hydrogen. Other notable difference is that the monomeric catalyst reduced non-conjugated dienes at a greater rate than the conjugated ones, and the opposite result was obtained in this catalyst. The remarkable increase in activity by use of polymer support may be mainly due to the formation of the coordinatively unsaturated palladium,[4] although the change of palladium electronic state should not be neglected.

The preliminary kinetic study was also carried out. The rate equation for styrene as a representative example is as follows.

$$\text{Rate} = k[H_2]\cdot[\text{Cat.}] \text{ , where } k_{25^\circ} = 2.42\text{x}10^3 \text{ l/mol}\cdot\text{min}$$

The polymer catalyst can be reused without any appreciable loss in activity.

The details of the catalyst nature and hydrogenation mechanism are under investigation.

## REFERENCES and NOTES

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2) D. Adams, "Metal-Ligand and Related Vibrations: A Critical Survey of the Infrared and Raman Spectra of Metallic and Organometallic Compounds" 1st ed., Edward Arnold, London (1967) p 74-75.

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4) Addition of $SnCl_2$ (only two mole equivalent to palladium) depressed perfectly hydrogenation.

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