

EFFECT OF ACTIVE SITE DISTRIBUTION ON LIQUID-PHASE OLEFIN HYDROGENATION OVER POLYMER-SUPPORTED PALLADIUM COMPLEX

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Abstract – Chloromethylated polystyrene beads with different distributions have been prepared and phosphinated. $PdCl_2$ was supported on the phosphinated supports to give polymer-supported Pd complex catalysts with different active site distributions. The effect of active site distribution on catalytic activity was investigated in the hydrogenation of olefins.

Key words: *Polymer-supported Catalyst, Active Site Distribution, Hydrogenation, $PdCl_2$, Cyclohexene*

INTRODUCTION

The effect of active site distribution on catalytic performance in inorganic-supported catalyst has been studied in detail [Lee and Aris, 1985]. The distribution plays an important role in mass and heat transfer in supported catalysts. In some instances the catalytic performance may be optimized through a non-uniform active site profile [Harold and Luss, 1987]. However, few investigations have been reported [Ihm et al., 1989] on the active site distribution in polymer-supported catalysts. Polymer supports have many advantages over inorganic supports; the polymer support is flexible, its chemical modification is easy, its capacity is high, and the active site structure and catalytic properties are similar to those of the analogous homogeneous catalyst. The transport phenomena of substrates in polymer-supported catalysts may be different from that in inorganic-supported catalysts due to the interaction of the polymer with the substrates. In general, the sorption of substrates into a polymer can be an important factor in the overall transport phenomena. Therefore, the selectivity of substrate and/or product might be enhanced by controlling the active site distribution and also by changing the sorption behavior of the support.

The purpose of this work was to prepare polymer-supported catalysts having various active site distributions and to investigate the characteristics of these catalysts in olefin hydrogenation.

EXPERIMENTAL

1. Preparation of Polymer Beads

The preparation conditions for the polymer supports are listed in Table 1. Polymer supports with different distributions of functional groups were prepared as follows. 2PCMS50 was prepared by suspension polymerization with chloromethylstyrene

monomer at 80 °C for 15 hr. 2PCMS50 was prepared by removing the chloromethyl groups on the internal surface of 2PCMS50 via a chemical reaction with $LiAlH_4$ [0.25 M solution, dissolved in tetrahydrofuran (THF)] for 10 minutes under THF reflux. For 2PCMS30/2PS, the crosslinked polystyrene, 2PS, was prepared first as a base polymer. The 2PS support was then swollen at room temperature in a mixture of diluent and monomers having the composition shown in Table 1, and then the 2PCMS30/2PS support was produced by additional suspension polymerization of the 2PS at 60 °C for 12 hr, 70 °C for 12 hr, and 85 °C for 4 hr. The 2PS/2PCMS50 support was prepared via the reverse process i.e. using 2PCMS50 as the base polymer then additional polymerization of 2PS. In this way more functional groups should be located in the inner parts of the polymer bead. The beads obtained were washed with hot water and THF three times followed by an exhaustive extraction with THF in a Soxhlet for 12 hr to remove the remaining impurities. The beads were dried under reduced pressure and stored in a desiccator.

2. Preparation of Catalysts

The phosphinated polymer supports were prepared via reaction of lithium diphenylphosphine with the chloromethyl groups of the poly(chloromethylstyrene-co-divinylbenzene) beads [Tomborski et al., 1962]. Palladium dichloride was then anchored to the phosphinated polymer beads to produce polymer-supported catalyst. The details are as follows.

Excess lithium metal was sliced into pieces to increase its surface area, and then charged into a 500 ml round bottomed flask sealed with rubber septum. Oxygen and moisture were removed from the system by alternate vacuum/nitrogen flushes. THF (250 ml) was transferred into the flask to which chlorodiphenylphosphine (50 ml) was added carefully and stirred slowly at room temperature for 24 hr under a nitrogen atmosphere. The mixture gradually turned to deep red.

The chloromethylated beads were placed in a 500 ml two-necked round bottomed flask fitted with a filter and condenser. THF (250 ml) and lithium diphenylphosphine in THF (100 ml)

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Table 1. Preparation Conditions of polymer supports^a

Supports	Styrene	Divinylbenzene	Chloromethylstyrene	Toluene	Base polymer
2PS ^b	96	4	-	-	-
2PCMS30 ^b	64.4	4	31.6	-	-
2PCMS50 ^b	46	4	50	-	-
2PS/2PCMS50 ^c	19.2	0.8	-	60	2PCMS50(20 g)
2PCMS30/2PS ^c	12.8	0.8	6.4	60	2PS(20 g)
H2PCMS50 ^d					

^aThe unit is ml.^bThe polymer supports were prepared directly by suspension polymerization.^cThe base polymer was soaked in the mixture, and then it was polymerized.^dThe external chloromethyl groups of 2PCMS50 was reduced with LiAlH₄.**Table 2. Swelling properties of polymer supports and catalysts**

Support/Catalyst	Swelling ratio (v/v)	
	in THF	in MeOH
2PCMS30	2.5	1.1
2PCMS30/2PS	3.2	1.1
2PS/2PCMS50	3.1	1.1
H2PCMS50	3.5	1.1
2PCMS30-P-Pd	2.1	1.2
2PCMS30/2PS-P-Pd	2.5	1.2
2PS/2PCMS50-P-Pd	2.0	1.2
H2PCMS50-P-Pd	2.2	1.1

were added to the flask and refluxed for 3 days under nitrogen atmosphere. The beads were separated from the solution and washed several times sequentially with THF, benzene and hexane under a nitrogen atmosphere. The resulting polymer beads were dried with a hot nitrogen stream to remove solvents and stored in a glove box. The color of the phosphinated bead was red/orange.

The mixture of phosphinated polymer beads (3 g), palladium dichloride (1 g), triphenylphosphine (1 g), and toluene (200 ml) was refluxed for 3 days under nitrogen. The solvent was decanted off and the residual polymer was extracted with THF until the yellow color of the extracted solvent disappeared. The beads were then dried under vacuum for one day, and stored in a desiccator.

3. Hydrogenation Reaction

Hydrogenation of each olefin (cyclohexene or styrene) over polymer-supported catalysts was carried out in THF or methanol. The catalyst (0.03 g) and solvent were introduced into a 25 ml flask via a septum-sealed side-arm. The vessel was evacuated and flushed with hydrogen several times and then continuously with hydrogen for 5 minutes to ensure a complete hydrogen atmosphere. The flask was attached to the reaction system equipped with a gas burette, a vent, and a thermostated water bath. The reaction mixture was stirred by a magnetic stirrer. After 60 min, the stirring was stopped and substrate was introduced into the vessel. Hydrogenation started when stirring recommenced. The stirring was so rapid that external mass transfer limitation could be neglected. The volume of hydrogen uptake at ambient pressure was measured by the gas buret.

4. FTIR Measurement

The infrared spectra were recorded on Bomem MB-102 infrared spectrometer using KBr pellets. The gelular beads were swollen in THF, crushed mechanically, dried at 100°C for 30

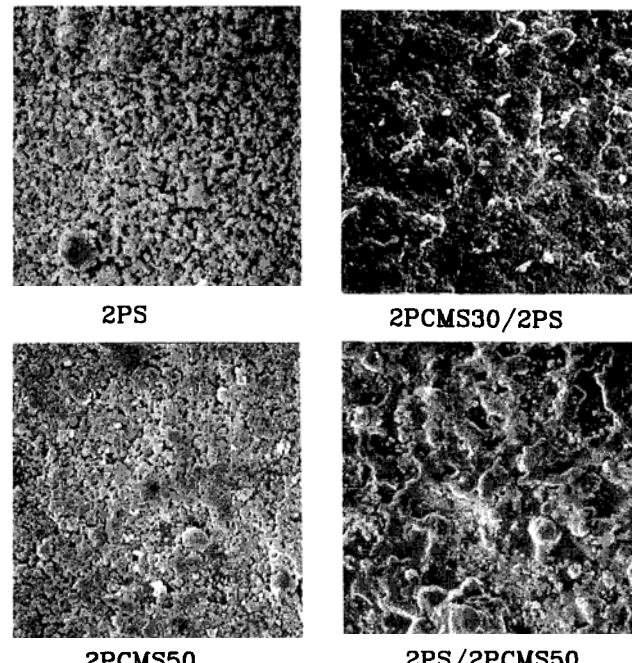


Fig. 1. SEM photographs of surfaces of polymer beads (magnification $\times 15,000$).

minutes, and then mixed with KBr.

RESULTS AND DISCUSSION

The surfaces of polymer bead are shown in the SEM photographs in Fig. 1. It can be seen that the surfaces of 2PCMS 30/2PS and 2PS/2PCMS50 are covered with a lightly crosslinked copolymer. In the preparation of 2PCMS30/2PS and 2PS/2PCMS50, most of monomers exist on the surface of the base polymer (2PS or 2PCMS50) and they may form a crosslinked polymer layer on the surface during suspension polymerization.

As shown in Fig. 2, the characteristic band of the chloromethyl group at 1260 cm^{-1} (C-Cl stretching vibration) has disappeared on phosphination [Egawa et al., 1990]. This implies that most of the chloromethyl groups in the gelular support have been substituted by the phosphine ligand. On anchoring palladium dichloride onto the phosphinated polymer bead, the characteristic peak of Pd-Cl stretching vibration appears at 352 cm^{-1} [Mani et al., 1990].

Due to the different preparation methods, the active sites

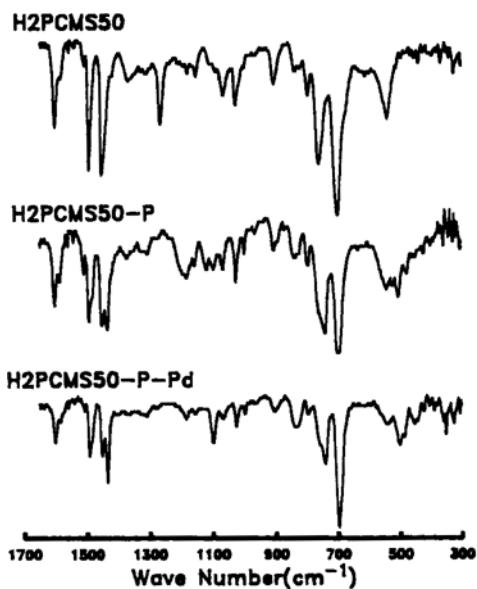


Fig. 2. FTIR spectra of polymer supports and catalyst.

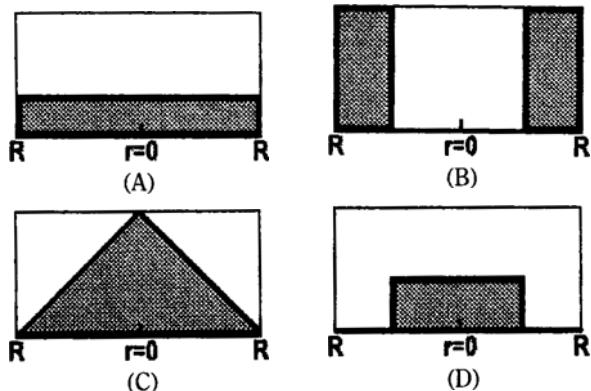


Fig. 3. Schematic diagrams of Pd distributions.

(A) 2PCMS30-P-Pd, (B) 2PCMS30/2PS-P-Pd,
(C) HPCMS50-P-Pd, (D) 2PS/2PCMS50-P-Pd

may be distributed somewhat differently within the catalysts as follows: 2PCMS30-P-Pd is likely to have a uniform distribution; for 2PCMS30/2PS-P-Pd, the active sites are likely to be more concentrated in the exterior layer of the catalyst; the concentration of active sites in HPCMS50-P-Pd is likely to increase from the surface to the center of catalyst; and for 2PS/2PCMS50-P-Pd, the active sites of supported species can be buried inside the catalyst. It might be considered from the experimental conditions that the distributions can be depicted schematically as shown in Fig. 3.

The catalytic activity of supported species can be affected greatly by the swelling properties of the polymer-supported catalyst [Roucis and Ekerdt, 1984]. As shown in Table 2, the swelling was highly dependent on the nature of the organic solvent used. Since THF is good solvent for polystyrene-based supports, the gelular polystyrene-based support and catalyst were significantly swollen in THF but little swollen in methanol which is not compatible with polystyrene. By anchoring palladium dichloride on the polymer support, the swelling ratio in methanol slightly increased, while it decreased in THF.

Table 3. Initial hydrogenation rates (mmol/g-catalyst · min)

Catalyst	Styrene		Cyclohexene	
	in MeOH	in THF	in MeOH	in THF
2PCMS30-P-Pd	0.29	0.11	0.12	
2PCMS30/2PS-P-Pd	1.20	0.30	0.53	
2PS/2PCMS50-P-Pd	0.98	0.32	0.12	
H2PCM50-P-Pd	0.35	0.33	0.10	

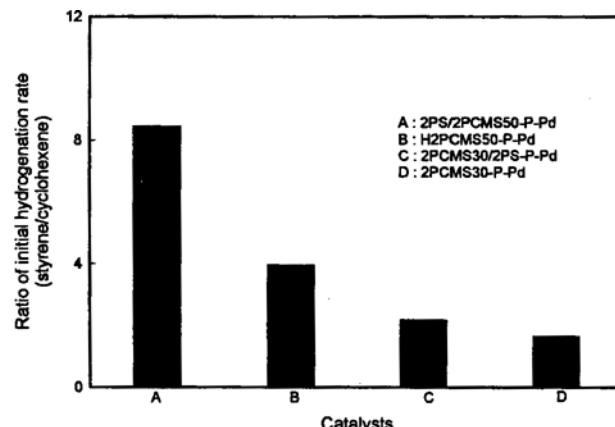


Fig. 4. Ratio of initial hydrogenation rates over various catalysts.

Generally the hydrogenation of olefins over palladium complexes is favored in polar solvents such as alcohols [Mani et al., 1990]. When hydrogenation is carried out over a polystyrene-based catalyst using an alcohol as solvent, the diffusional limitation of substrates can become important because the polymer is only poorly solvated. The hydrogenation rate of cyclohexene over 2PCMS30-P-Pd or 2PCMS30/PS-P-Pd in methanol is higher than that in THF but the reaction rate over 2PS/2PCMS50-P-Pd or H2PCM50-P-Pd in methanol is lower than that in THF, as shown in Table 3. Where there is no diffusion limitation, the hydrogenation rate of the olefin is higher in methanol than that in THF [Jo et al., 1996]. Therefore, it can be seen that the catalytic activity of 2PS/2PCMS50-P-Pd or H2PCM50-P-Pd, where the active species are more concentrated inside the resins, is significantly influenced by diffusional limitation through external polymer layer. The external polymer layer may therefore behave as an inert polymer membrane. When the catalyst beads contact with a good solvent such as THF, it will be highly swollen and diffusion limitation of the substrate through the polymer layer will be reduced. When the catalyst beads contact a poor solvent such as methanol, the polymer layer will be poorly swollen and diffusional limitation is likely to become important. Accordingly the observed catalytic activity is higher in THF than in methanol, though the intrinsic catalytic activity is higher in methanol, bearing in mind its dielectric constant [Jo et al., 1996].

As shown in Fig. 4, the ratio of initial hydrogenation rate of styrene to that of cyclohexene over 2PS/2PCMS50-P-Pd is higher than that over the other catalysts. The exterior layer of cross-linked polystyrene is more compatible with styrene than cyclohexene, and the permeability of styrene through this layer is likely to be higher than that of cyclohexene [van Krevelen, 1976]. Therefore, the ratio of hydrogenation rate of styrene to that of cyclohexene might be enhanced by the exterior poly-

styrene layer. The exterior polymer layer of these catalysts also seems to act as polymer membrane. A control of active site distributions should be important for enhancing the activity and selectivity of polymer-supported catalysts and for preparing the optimum catalyst.

REFERENCES

Egawa, W., Nonaka, T. and Tsukamoto, K., "Studies on Selective Adsorption Resin XXVII. Preparation and Properties of Macroreticular Chelating Resins Containing Amidoxime Groups from Chloromethylstyrene-Divinylbenzene Copolymer Bead", *Polym. J.*, **22**, 120 (1990).

Harold, M. P. and Luss, D., "Impact of the Catalytic Activity Profile on Observed Multiplicity Features: CO Oxidation on Pt/Al₂O₃", *Ind. Eng. Chem. Res.*, **26**, 1616 (1987).

Ihm, S. K., Ahn, J. H., Widdecke, H., Strup, K. and Klein, J., "Diffusional Aspects for the Chlorination of the Sulfonated Poly(Styrene-co-Divinylbenzene) Resin Beads", *J. Appl. Polym. Sci.*, **37**, 109 (1989).

Jo, Y. D., Park, K. S., Ahn, J. H. and Ihm, S. K., "Mechanistic Study of Hydrogenation of Cyclohexene Catalyzed by Polymer-supported Palladium(II) Complex in Various Solvents", *React. and Funct. Polym.*, **29**, 91 (1996).

Lee, S. Y. and Aris, R., "The Distribution of Active Ingredients in Supported Catalysts Prepared By Impregnation", *Catal. Rev. Sci. Eng.*, **27**, 207 (1985).

Mani, R., Mahadevan, V. and Srinivasan, M., "Studies on the Hydrogenation of Olefins Using Polymer-Bound Palladium (II) Species", *British Polym. J.*, **22**, 177 (1990).

Roucis, J. B. and Ekerdt, J. G., "The Influence of Intraparticle Mass Transfer on the Activity of a Gel-Form Polymer-Bound Transition Metal Catalysts", *J. Catal.*, **86**, 32 (1984).

Tomborski, C., Ford, F. E., Lehn, W. L., Moore, G. J. and Seloski, E. J., "Synthesis of Organolithium Compounds of Some Group IV and V Elements", *J. Org. Chem.*, **27**, 619 (1962).

van Krevelen, D. W., "Properties of Polymer", Elsevier, New York, 1976.