

Polymer-Based Catalysts for Toluene Hydrogenation

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ABSTRACT: Crosslinked poly(4-vinylpyridine-co-styrene) was synthesized by radical polymerization. Catalysts having 1 wt % Pd were obtained by impregnation of a copolymer, poly(4-vinylpyridine-co-styrene) with a Pd colloidal dispersion. We modified metal particle sizes by changing the aging period of the colloidal dispersion, with the average size in the range of 2.5–4.3 nm. The most probable structure of the metal cluster attached to the polymers is described. X-ray diffraction, transmission electron microscopy (TEM), and H₂-O₂ titrations were used as characterization techniques. The H₂ consumption during titration was extremely low, and the calculated metal dispersion was between 15 and 25 times lower than those estimated from TEM. This suggests

that the Pd crystals were almost completely covered by the polymer. The vapor-phase hydrogenation of toluene on resins supported Pd catalysts were studied. The catalysts in the hydrogenation of toluene exhibited low activity, and the obtention of significant selectivities to partial hydrogenation products (close to 60 mol %) was remarkable. The results are explained in terms of a significant decrease in the hydrogenation capacity due to the coverage of metal particles by the resin. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 381-385, 2002

Key words: catalysis; metal-organic catalysts; colloids; Pd; toluene hydrogenation; chemisorption

INTRODUCTION

Different attempts have been made to heterogenize homogeneous catalysts.¹⁻⁷ As result of this process, the active site is bound to a heterogeneous surface. The main drawbacks of the use of this type of catalyst are related to the complexity of the (1) synthesis of the organometallic complex (2) synthesis of the functional polymer, and (3) attachment chemistry.

One procedure used to simplify this situation requires a functional polymer that is used for the attachment of a metal precursor salt. After reduction of the supported salt, the polymer-bound zerovalent metal may be obtained. However, due to the relatively low thermal stability of most of polymers used as support, only compounds that may be easily reduced at low temperatures may be used for this purpose. Thus, polymer-bound zerovalent palladium systems are one of the few catalysts that may be used for this procedure. The hydrogenation of nitriles has been reported on Pd-supported Amberlite XAD-4 catalysts,^{8,9} and Teichner et al.¹⁰ reported the hydrogenation of cyclohexene on polyamide-6,6-supported Pd catalysts. The catalytic activity of zerovalent Pd dispersed in hydroxyethylmethacrylate was described by Rempel et al.,¹¹ and Pd supported on polyamide matrices,¹² func-

tional polystyrene matrices,¹³ and sulfonic acid resins have also been reported.¹⁴ However, Pd²⁺ ions exchanged in a styrene-4 vinylpyridine resin could not be reduced to Pd⁰ on hydrogen treatment up to 423 K.¹⁵

Another method to disperse zerovalent metal species involves the obtention of metal colloids by the so-called metal vapor deposition in which metal atoms are evaporated under vacuum and trapped by organic solvents, leading to colloidal dispersions.¹⁶ This method allows one to obtain different metal or bimetallic colloids of zerovalent species that may be impregnated on a given support. Thus, using this method, Cárdenas et al. prepared colloidal particles of Cu,¹⁷ Ni,¹⁸ Pd,¹⁹ and Au-Pd.²⁰ The synthesis of copolymers with metal incorporated from sols or metal clusters, dispersed in monomers has also been reported.²¹⁻²⁴ Warshawsky and Colleagues²⁵⁻²⁷ reported zerovalent metal polymer composites the direct immobilization of palladium salts on functional polymers, followed by the chemical deposition of transition metal or noble metal ions.

These kind of procedures imply considerable simplification over previous methods of the preparation of polymeric zerovalent metal-dispersed catalysts because (1) hydrophobic metal complexes readily swell crosslinked polymeric matrices and (2) they are homogeneously distributed within the matrix. Additionally, the polymeric matrix may not act as an inert support, and if the functional groups are selected properly, they may also have some catalytic affect by modifying the catalytic properties of the active metal,¹³ or the system may be used as bifunctional catalysts.

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The aim of this study was to examine Pd supported on poly(4-vinylpyridine-co-styrene) as a catalyst for toluene hydrogenation under different experimental conditions. Pd-supported catalysts were prepared by the metal vapor deposition method followed by impregnation on the resin.

EXPERIMENTAL

Reagents

4-Vinylpyridine and styrene were purified by distillation. 2,2'-Azo-bis-isobutyronitrile (AIBN) was recrystallized from methanol. Divinylbenzene (DVB) was used without further purification.

Synthesis of the polymeric catalyst

The polymeric matrix used as support was synthesized by radical polymerization, with an equimolar ratio of 4-vinylpyridine and styrene as monomers. DVB (4 mol %) and AIBN (0.5 mol %) as the crosslinking agent and initiator, respectively, were used. The polymerization reaction was carried out at 343 K for 24 h, and a yield higher than 93% of poly(4-vinylpyridine-co-styrene) was obtained. The polymer was completely insoluble in water and in common organic solvents such as methanol, acetone, *N,N*-dimethylformamide, and dichloromethane.

Colloidal dispersion

Palladium colloidal dispersion was obtained by the metal vapor deposition method.¹⁹ The metal atoms were trapped by an organic solvent, acetone, at 77 K. Then, the colloidal dispersion temperature was raised up to room temperature, and the polymeric matrix was impregnated with the appropriate amount of the colloidal dispersion to get catalysts with a Pd loading of 1 wt %. Before the impregnation, the colloidal dispersion was aged at room temperature for different periods to induce changes in metal particle size. Thus, ageing times from 0 to 7 h were used. For the sake of simplicity, dispersions will be referred to hereafter as Pd(*x*)/resin, where *x* is 0, 1, 4, or 7. After impregnation, the samples were dried under vacuum at 343 K for 24 h and treated *in situ* in a H₂ flow at 343 K for 1 h before characterization or catalytic evaluation.

Characterizations

H₂-O₂ titrations were carried out at 343 K in a temperature programmed desorption (TPD)/temperature programmed reduction (TPR) 2900 Micromeritics system with a thermal conductivity detector. Before the chemisorption experiments, the samples were preoxidized in O₂ at 298 K and outgassed in an Ar flow (50

cm³ min) at 343 K for 1 h; then, pulses of H₂ were sent to the sample until complete saturation was reached.

Transmission electron micrographs and electron diffraction patterns were obtained on a Jeol JEM 1200 EXII microscope (Tokyo, Japan). The supported catalysts were ground in an agata mortar and dispersed in ethanol. A drop of each dispersion was placed on a 150-mesh copper grid coated with carbon. To obtain metal particle size, several magnifications were used in both bright and dark fields. For electron diffraction studies, a gold standard (Merck 99.99% pure) was used.

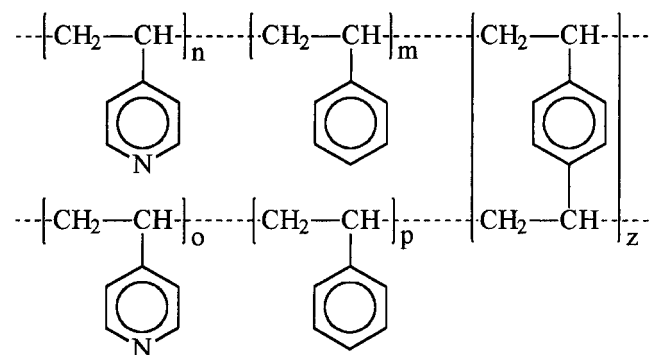
X-ray diffraction (XRD) studies were carried out in a Rigaku powder diffractometer with nickel-filtered CuK_α radiation (Tokyo, Japan).

Catalytic measurements

Catalytic experiments were carried out in a fixed-bed microcatalytic reactor with online Hiden Analytical HAL Quadrupole Mass Spectrometer (MS) Act 200T (Warrington, England). In each experiment, 10 mg of catalyst was prereduced *in situ* in flowing hydrogen (20 cm³/min³) in a programmed mode at 10 K/min up to 343 K and kept at this temperature for 1 h. Then, the sample was cooled down to the reaction temperature in a hydrogen flow. A H₂/toluene = (molar ratio = 60) gas mixture was flowed at 20 cm³/min through the catalytic bed. The catalytic activity was measured continuously by MS after the changes in the signal of the main fragments due to the reactants and different expected products. Blank experiments showed no catalytic activity due to the support in these conditions.

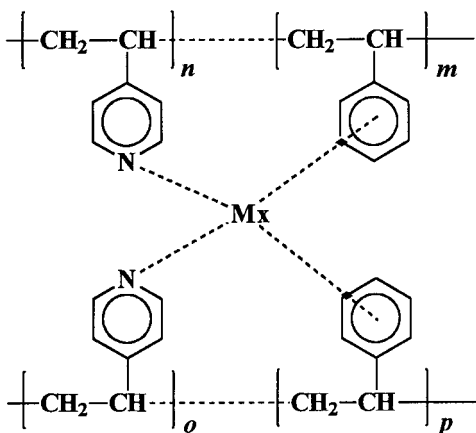
RESULTS AND DISCUSSION

To obtain a polymer matrix as a potential hydrogenation catalyst, we obtained the crosslinked poly(4-vinylpyridine-co-styrene) by radical polymerization with a yield of 93%. The copolymer was completely insoluble in water.



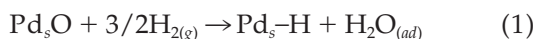
P(Sty-co-4-VPy)

To obtain a colloid dispersion, we impregnated the polymer with palladium by the deposition method. The most probable structure for this is the following:



According to previous results, the metal clusters should be stabilized between the aromatic ring of one monomer and the pyridinic ring of the other.

Selective chemisorption of gases (CO or H₂) is usually used as a method to evaluate metal dispersion and for the estimation of the metal particle size. However, before chemisorption of the probe molecule, the metal surface must be cleaned. This process requires an outgassing procedure at a high temperature, 723–773 K for 2–10 h. Obviously, this method cannot be used when the support may be modified or decomposed during the treatments. For these kind of samples, the method of H₂–O₂ titrations proposed by Benson and Boudart²⁸ may be used. The sample does not require any special treatment. The metal supported catalyst is exposed at room temperature to air or oxygen and outgassed or flashed with an inert gas to remove the physically adsorbed gas, and then the reaction between adsorbed oxygen and hydrogen is carried out. The reaction may be represented by the following equation:



where *s* indicates surface atoms, *g* indicates the gas phase, and *ad* indicates the adsorbed phase. Even though there are some discrepancies in dealing with the adsorption stoichiometries,^{29,30} eq. (1) is generally accepted. From the equation, it can be seen that for each Pd surface atom 3/2 H₂ molecules are required. Therefore, metal dispersion, that is, the ratio surface metal atoms to total metal atoms may be obtained if the metal loading is known. Table I displays the surface Pd atoms, the metal dispersion, and the Pd particle size estimated from titrations and by transmission electron microscopy (TEM). To estimate metal particle size, we must assume that the metal crystals have a given shape. For example, consider a cube, with five of the faces available for chemisorption and the sixth deposited on the support:

$$d = 5/S\rho \quad (2)$$

TABLE I
Pd Surface Atoms, Apparent Metal Dispersion from Titration Data, and Metal Particle Sizes Estimated from Titration and TEM for 1 wt % Pd/Resin Catalysts

Catalyst	At Pd _s /gf Pd × 10 ¹⁹	<i>D</i>	<i>d</i> (nm)	
			Titration	TEM
Pd(0)	0.94	0.016	61	2.3
Pd(1)	1.42	0.024	41	3.0
Pd(4)	1.06	0.018	55	4.1
Pd(7)	1.18	0.020	49	4.2

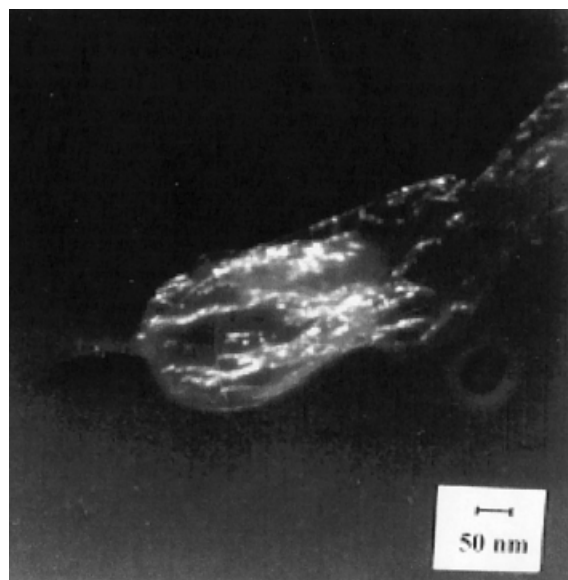
D = metal dispersion = Pd surface atoms/Pd total atoms.

where *d* is metal particle size, *S* is the metallic surface area, and *ρ* is the metal density. The ratio of palladium metal atoms to grams of catalysts was extremely low in all the studies catalysts; therefore, the apparent metal dispersions were also low, and, consequently, the estimated metal particle size was large.

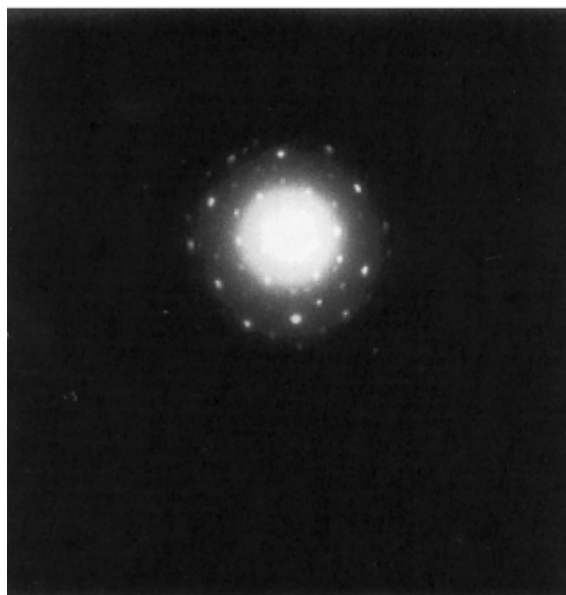
Other methods were used to compare metal particle size. XRD of the catalysts showed no lines due to the metal component, indicating high dispersion of Pd, with a metal particle size smaller than 5.0 nm.

TEM of the catalysts showed a rather narrow particle size distribution, with a slight increase in the average particle with increases the aging time, as expected [see Fig. 1(a,b)]. The average metal particle size was in the range 2.3–4.2 nm, and the predicted dispersion calculated from these values was in the range 0.42–0.24. These values were between 15 and 25 times higher than those obtained from chemisorption data. TEM results are also compiled in Table I. The significant differences observed in the particle size values indicate that even though chemisorption and/or titrations are widely used to estimate metal dispersion and average particle size, real metal particle size values are not predicted in the case of polymeric supports or reducible supports that present the known strong metal support interactions (SMSI) effect³¹ because of most of the metal surface is covered by the support and only a small fraction remains accessible for chemisorption. Similar effects were reported previously by Teichner et al.³² for Pt on polyamide-6,6. In the catalysts studied in this work, it is likely that the coverage of the metal by the resin occurred during impregnation and solvent evaporation of the resin.

Figure 1(c) shows an electron diffraction pattern for one of the studied catalysts. Under the conditions used for electron diffraction studies, an area of approximately 1 μ² was examined; therefore, the diffraction corresponded to all the crystals included in the selected area. The electron diffraction patterns of the Pd/resin catalysts prepared by impregnation of the colloidal Pd dispersion showed both rings and spots, indicating the presence of a reduced quantity of small crystals. When this pattern was indexed, a good agreement with Pd⁰ was obtained.



(a)



(b)

Figure 1 (a) TEM micrograph of the Pd(4)/resin catalyst and (b) electron diffraction pattern of the Pd(4)/resin catalyst.

Catalytic hydrogenation of toluene was performed at 313 and 323 K. The detected compounds were hydrogen, toluene, methycyclohexadiene (MCHD), methycyclohexene (MCHE), methycyclohexane (MCHA), benzene (B), and methane. The reaction was followed by online MS, and no deactivation was detected after 2 h on stream. Figure 2 displays the molar product distribution during toluene hydrogenation at 313 K for one of the studied catalysts. A significant amount of partially hydrogenated products, such as MCHD and MCHE, compounds that are usually difficult to obtain from catalytic hydrogenation, was noticeable.

Table II compiles the activity per site or turnover frequency (TOF), which represents the number of tol-

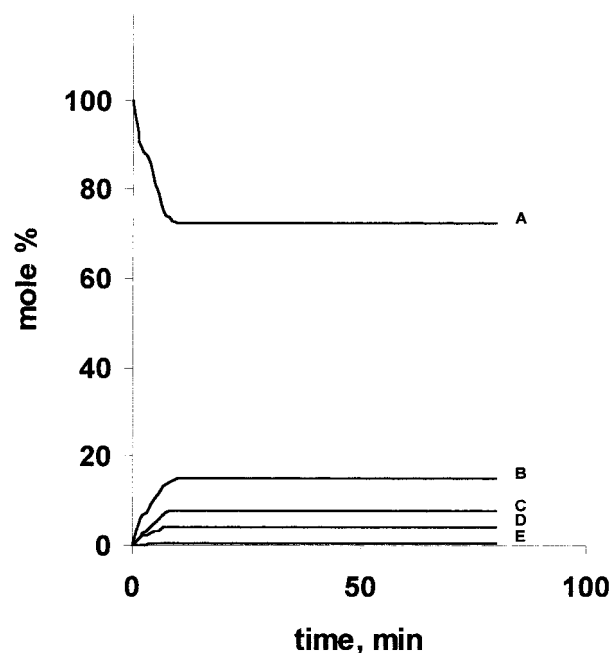


Figure 2 Molar product distribution during toluene hydrogenation at 313 K for the Pd(7)/resin catalyst.

uene molecules converted per second per Pd surface atom, and selectivities to different products for toluene hydrogenation at 413 K on the studied Pd catalysts. TOF did not change significantly for the different catalysts. This behavior was expected because this hydrogenation reaction belongs to a structure-insensitive reaction, according Boudart's classification,^{33,34} and therefore, TOF should not depend on the metal particle size. On the other hand, not well-defined trends in selectivity were observed; however, most of the catalysts exhibited a selectivity to partial hydrogenated compounds (MCHD + MCHE) close to 60 mol %. The presence of B (and methane) as products was also noteworthy. These are hydrogenolysis products, reactions that usually take place at higher temperatures. At a higher reaction temperature, 323 K, the results were similar, but, there was a slight increase in TOF and a decrease in the selectivity to MCHD + MCHE at about 45 mol %. The observed behavior may be explained on the basis of a modification of the active sites, in which Pd crystals were buried into a

TABLE II
TOF, and Selectivity to Different Products for Toluene Hydrogenation at 413 K on 1 wt % Pd/Resin Catalysts

Catalyst	TOF (s ⁻¹)	Selectivity (mol %)			
		MCHD	MCHE	MCHA	B
Pd(0)	3.4	22	44	23	11
Pd(1)	2.5	33	25	36	6
Pd(4)	1.5	13	13	23	51
Pd(7)	1.0	2	54	16	28

polymeric matrix, drastically decreasing the hydrogen uptake, as demonstrated by the chemisorption results. As consequence, they showed only a moderated hydrogenation capacity and, therefore, allowed us to obtain partially hydrogenated products.

CONCLUSIONS

Pd zerovalents supported on polymeric matrices could be obtained by use of the metal vapor deposition method. From the TEM results (TEM and H_2-O_2 titrations), we found that the average particle size was in the range 2.3–4.2 nm, corresponding to estimated dispersion between 0.42 and 0.24. However, H_2-O_2 titrations indicated that all the catalysts exhibited a very limited amount of Pd surface atoms. This behavior was attributed to coverage of the metal crystal by the polymeric support. The catalysts showed low activity in the hydrogenolysis on toluene and significant selectivities to partially hydrogenated products. This behavior was attributed to a decrease in the hydrogenation capacity of the metal component for partial blockage by the support.

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References

1. Sherrington, D. C. *Brit Polym J* 1980, 70, 1.
2. Michalska, Z. M.; Strzelec, K. *React Funct Polym* 2000, 44, 189.
3. Michalska, Z. M.; Strzelec, K.; Sobczak, J. W. *J Mol Catal* 2000, 156, 91.
4. Bayer, E.; Schumann, W. *J Chem Soc Chem Commun* 1986, 949.
5. Bailar, J. C., Jr., *Catal Rev Sci Eng* 1974, 10, 17.
6. Pajares, J. A.; Reyes, P.; Oro, L. A.; Sario, R. *J Mol Catal* 1981, 11, 181.
7. Pittman, C. U. *J Org Chem* 1975, 40, 540.
8. Teresawa, M. *J Organometallic Chem* 1978, 162, 403.
9. Holy, N. L. *J Chem Soc Chem Commun* 1978, 1074.
10. Michel, C.; Hoang-Van, C.; Teichner, S. J. *J Chim Phys* 1978, 75, 814.
11. Hines, L.; O'Driscoll, K. F.; Rempel, G. L. *J Catal* 1975, 38, 435.
12. Harrison, D. P.; Rase, H. F.; *Ind Eng Chem Fundam* 1967, 6, 161.
13. Bar-Sala, G.; Warshawsky, A. *J Polym Sci Part A Polym Chem* 1990, 28, 1303.
14. Tibbitt, J. M.; Bates, B. C.; Katzer, J. R. *J Catal* 1975, 38, 505.
15. Reyes, P.; Borda, G.; Cárdenas, G.; Rivas, B. Unpublished results.
16. Davis, S. C.; Severson, S. J.; Klabunde, K. *J Am Chem Soc* 1981, 103, 3024.
17. Cárdenas, G.; Oliva, R.; Soto, H.; Pantoja, O. *Bol Soc Chil Quim* 1995, 40, 83.
18. Cárdenas, G.; Oliva, R. *Mater Res Bull* 1998, 33, 1599.
19. Cárdenas, G.; Muñoz, C.; Vera, V. *Bol Soc Chil Quim* 1996, 41, 235.
20. Cárdenas, G.; Segura, R. *Mater Res Bull* 2000, 35, 1369.
21. Cárdenas, G.; Salgado, E.; Vera, V. *Macromol Rapid Commun* 1996, 17, 775.
22. Cárdenas, G.; González, M. *Polym Bull* 1996, 37, 175.
23. Cárdenas, G.; Salgado, E.; Carbacho, H. *Polym Bull* 1996, 36, 569.
24. Cárdenas, G.; Acuña, J.; Rodríguez, M.; Carbacho, H. *Polym Bull* 1995, 34, 31.
25. Warshawsky, A.; Upton, D. A. *J Polym Sci Part A: Polym Chem Ed* 1989, 27, 2963.
26. Warshawsky, A.; Upton, D. A. *J Polym Sci Part A: Polym Chem Ed* 1989, 27, 2995.
27. Ferrar, W. T.; O'Brien, D. F.; Warshawsky, A.; Voycheck, C. L. *J Am Chem Soc* 1988, 110, 288.
28. Benson, J. E.; Boudart, M. *J Catal* 1969, 4, 704.
29. Mears, D. E.; Hunsford, R. C. *J Catal* 1967, 9, 125.
30. Wilson, G. R.; Hall, W. K. *J Catal* 1997, 172, 46.
31. Haller, G. L.; Resasco, D. E. *Adv Catal* 1989, 36, 173.
32. Bernard, J. C.; Hoang-Van, C.; Teichner, S. J. *J Chim Phys* 1975, 72, 50.
33. Boudart, M. *Adv Catal* 1969, 20, 153.
34. Reyes, P.; Pecchi, G.; Morales, M.; Fierro, J. L. G. *Appl Catal* 1997, 163, 145.