Hydrogenation Catalysis of Nanosized Palladium Supported by Polymer/Silica Disupporter. II. Effects of the Characteristics of the Catalyst on Hydrogenation

Yinfeng Liu, Aiming Huang, Jing Chen, Lai Chen, Jiadong Hua

Department of Polymer Materials, Shanghai University, Shanghai 201800, China

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ABSTRACT: A series of nanosized palladium catalysts supported by silica and polymers, prepared by the complex transformation method, were used for catalytic hydrogenation of nitrobenzene. It was found that both the thickness of the polymer layer and the size of the palladium particles would affect the catalysis. The results indicated that the reaction rate would be optimal when a polymer supporter formed a single layer on the silica surface. The catalytic activity of the catalyst would not simply increase with the decrease of the size of palladium particles. The effects of other conditions on the catalytic properties, such as the order during preparation of the catalyst, solvent, and the pH values, were also discussed. © 2003 Wiley Periodicals, Inc. J Appl Polym Sci 89: 3661–3665, 2003

Key words: palladium; catalysts; complex transformation; hydrogenation; catalysis

INTRODUCTION

Polymer–metal complex used as catalysts has been studied for more than 30 years. It has been indicated that there are macromolecular effects in catalytic systems because the polymer ligands modify the electronic structure of the center metal to yield higher activity and higher selectivity for catalytic reactions than that of their smaller molecule complex analogs.[1] An interesting phenomenon reported in previous studies is that the polymer–metal complex catalysts have always been activated by hydrogen before being used for either hydrogenation or oxidation.[2–4] We now consider that the activation process is a complex transformation process of coordinated metal ions to the nanosized metal cluster. One of the reasons for the higher activity of such catalysts is that the size of the metal cluster is nanoscale.

Nanosized catalysts, characterized by their quantum effect and surface effect as well as their superfine particle size effect, possess high activity for catalytic reaction.[5] By the complex transformation method, a polymer–metal complex could be a precursor to yield stable nanoparticles of metal compounds with uniform distribution of size.[6] The polymer could perform three actions: dispersion, protection, and stabilization. In the previous study, a series of nanosized palladium catalysts supported by polymer/silica were prepared and characterized.[7] Here the catalytic property was evaluated by the hydrogenation of nitrobenzene to determine the size effects of the catalyst and the reaction conditions on the catalytic activity.

EXPERIMENTAL

Preparation of nanometer palladium catalyst supported by polymer/silica

Poly(4-vinyl pyridine) (PVP, self synthesized according to Liu et al.[8]), polyvinyl alcohol (PVA, chemically pure, purchased from Guangzhou Medical Chemical Reagent Company), and poly(acrylic acid) (PAA, self synthesized) were employed as polymer supporters. The polymerization of 20 g acrylic acid (analytical reagent grade, purchased from Shanghai Chemical Reagent Company) was initiated by 0.5 g benzoyl peroxide in 80 g toluene at 75°C for 10 h, to give a white precipitate. The precipitate was filtered, washed by toluene, and dried at 30°C for 24 h in a vacuum dryer, to obtain PAA.

The polymer–palladium complexes supported by silica were prepared through method A and method B, respectively. Method A prepared a polymer/aerosol powder in advance and then coordinated the polymer ligands with palladium dichloride, whereas method B carried out the coordination process first and then covered the polymer complex on aerosol powder. Nanosized palladium catalysts supported by

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Correspondence to: Y. Liu (Liuyf@sh163.net).

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TABLE I
IR Absorption of the Ligand Groups Along with the Polymer Chain Before and After Coordination with Palladium and After Activation by Hydrogen

Polymer supporter	Ligands	Before coordination (cm^{-1})	After coordination (cm^{-1})	After activation (cm^{-1})
PVP	C═N	1598.9	1615.0	1607
	C—N	1414	1425	1419
PVA	C—O	1091	1100	1095
	O—H	3447.4	3418.6	3427
PAA	C—O	1720	1692, 1601	1700

polymer/silica were then obtained by the complex transformation method. The catalyst turned from yellow to black after activation by hydrogen, which indicated that the palladium ion was reduced to palladium atom. The process was described in detail in a previous study.[7] The structure and the morphology of the catalysts were determined by IR, SEM, and TEM, respectively.

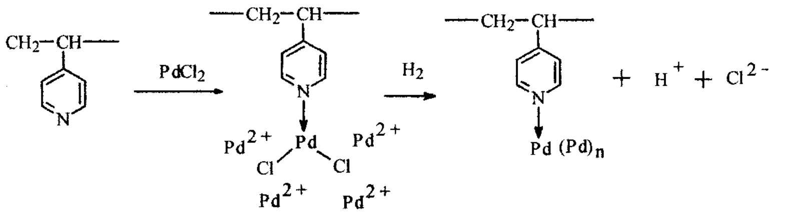
Catalytic hydrogenation of nitrobenzene

The catalyst, accurately weighed to contain 0.1 mmol of palladium, was mixed with 1.0 mL of nitrobenzene (~ 10 mmol). The mixture was then placed into a closed reactor. Until the catalyst deposited under the liquid, hydrogen was not inducted into the reactor. The catalytic reaction was then carried out under 1 atom of hydrogen at room temperature with and without alcohol solvent. The activity of the catalyst was evaluated by the uptake rate of hydrogen. The effect on the catalysis of pH adjusted by 0.1*M* NaOH or 0.1*M* HCl was also considered.

RESULTS AND DISCUSSION

The structure of the catalyst taken

The IR absorption of the ligand groups along with the polymer chain is shown in Table I. It may be seen that the absorption peak of each ligand group is different between the states before and after being reacted with palladium dichloride, indicating the formation of a coordination bond between the ligand groups and palladium ions. Because the absorption peaks after activation by hydrogen differ from the states before activation, and even from before coordination, it may be suggested that a coordination bond still exists after activation, which was formed between the polymer ligands and palladium atoms. The procedure of the nanosized palladium catalyst may be schematically represented as follows:



(1)

Effect of the polymer layer covered on silica

Because the size of the aerosol particles would decrease after being covered with polymer, because of the transformation of the hydrophilic surface of silica to a hydrophobic one, the thickness would not be measured directly through the morphology of silica determined by optical microscopy. The average thickness of the polymer layer covered on silica D_p has to be evaluated by the ratio R_w of the amounts of the polymer and the aerosol. The results are shown in Figure 1, where the results related to chitosan were from Huang et al.[5] The mean square gyration diameter D of the polymer may be estimated by the molecular weight M and the unperturbed molecular dimension A by the following equation[9]:

$$D = \left(\frac{2A^2M}{3}\right)^{1/2} \tag{2}$$

Because data on the unperturbed molecular dimension of some polymers cannot be found in polymer handbooks, this procedure offers a new measurement to determine this parameter by the critical thickness at the optimum reaction rate with eq. (2).

It may be found that the thickness of the layer significantly affected the catalysis, as shown in Figure 2. When the catalysis rate reached the maximum

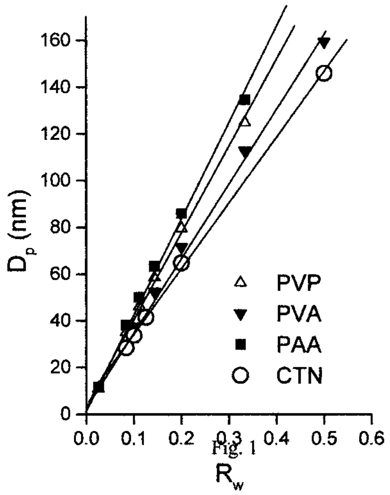


Figure 1 Relationship between the weight ratio of polymer to silica and the thickness of the polymer layer covered on silica.

TABLE II
Comparison of the Root Mean Square Gyration Diameter of the Polymers and the Thickness of Polymer Layer at Optimum Reaction Rate

Polymer	PVP	PVA	PAA
Unperturbed molecular dimension *A* (nm)	0.0793	0.0950	0.0750
Molecular weight (*M*)	4.8×10^4	8.8×10^4	2.6×10^4
Root mean square gyration diameter *D* (nm)	35	23	24
Thickness of polymer layer at optimum reaction rate D_p (nm)	30	25	25

value, the polymer layer thickness tended toward matching the root mean square gyration diameter (Table II).

When the amount of polymer was not sufficient to form a single layer on the silica surface, a portion of the palladium ions would directly adsorb on the silica surface. After reduction conversion, these palladium ions would gravitate to uncontrolled particles with broad distribution, which easily aggregated during the catalytic hydrogenation, thus decreasing the activity of the catalyst.

When the thickness of the polymer layer exceeded that of a single layer, the palladium particles were mainly embedded in the polymer network and seldom interacted with the silica surface. The thicker the polymer layer was, the greater the number of palladium particles were under the layer surface; thus it took a longer time for the substrate to disperse into the layer to reach the inner catalyst particles. At a given content of palladium, the greater the number of particles located in the deep layer, the slower the catalytic reaction rate would be.

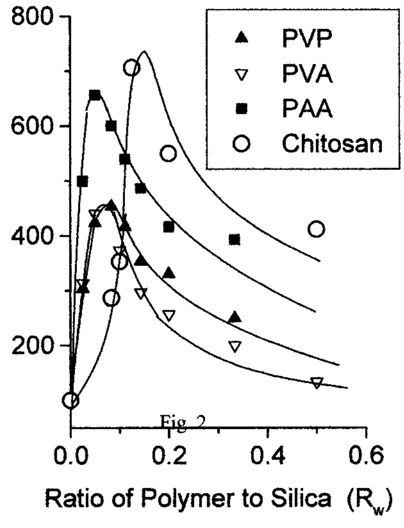


Figure 2 Effect of the weight ratio of polymer to silica on the catalysis. Conditions: palladium, 0.1 mmol; H_2, 1 atm; nitrobenzene, 10 mmol, in 9 mL alcohol; room temperature; pH = 7.

If the polymer could just cover the silica with a single layer, the palladium particles predominantly remained on the surface layer but adsorbed less on the silica surface so that the catalytic rate could reach optimum value.[5]

Effect of the particle size

The size of the palladium particles, which varied with the molar ratio of the ligand to palladium ions in the complex, was determined by TEM. The results are plotted in Figure 3, where it may be seen that the average diameter of palladium particles would rapidly decrease with increases in the molar ratio of ligand to palladium (R_m) and then decrease to <30 nm as R_m was >50.

The relationship between the catalytic hydrogenation rate for nitrobenzene and the molar ratio of ligand

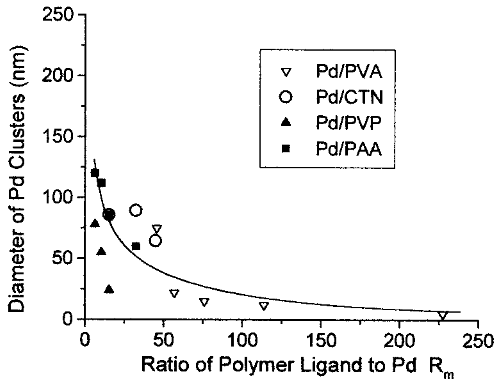


Figure 3 Relationship between the ratio of polymer ligand groups to palladium and the mean size of palladium particles.

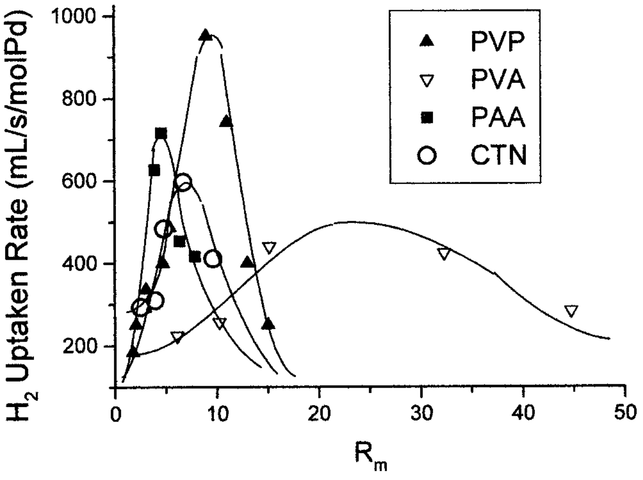


Figure 4 Effect of the molar ratio R_m of ligand to palladium on catalysis. Conditions: palladium, 0.1 mmol; H_2, 1 atm; nitrobenzene, 10 mmol, in 9 mL alcohol; room temperature; pH = 7.

to palladium of the catalyst is shown in Figure 4. It may be seen that the catalysis activity was not a monotonic function of the molar ratio R_m. It shows a bell shape with a maximum value in the curve, which implies that the catalytic activity did not simply increase with a decrease in the size of the palladium particles. It may easily be understood that the increase in catalytic activity is directly related to the diminution in the size of the particles. Increases in both the degree of dispersion and surface area with greater surface defects would improve the adsorption capability of the substrate onto the catalyst surface. Further reducing the size will lead to more product being absorbed onto the catalyst surface and, moreover, lead to a change in the electronic structure. Baetzold[10] reported that in the hybrid orbital the component ratio of *s* to *p* and to the *d* orbital would be changed by a variation in the size of the metal cluster. The *d* orbital component would appear to increase at the first period and then decrease with a decrease in the size of the cluster. In fact, catalytic hydrogenation depends on the *d* orbital of the center metal to admit electrons of the unsaturated substrate interacting with the hydrogen proton.[11]

Thus the catalysis activity would reach the optimum value as the content of the *d* orbital in the hybrid orbital of the catalyst reaches a maximum at an appropriate size of metal cluster. In the present experiments, the highest activity of the catalyst occurred at the molar ratio of ligand to palladium of about 10, whereas the size of the palladium cluster was about 50 to 80 nm for PVA, PAA, and chitosan.

Other factors

The optimum catalysis of different polymer supporters yielded different values, with the order as PVP > PAA > CTN > PVA (Fig. 4). Although all these polymers cannot be dissolved in nitrobenzene, they can be swollen in alcohol, especially PVP and PAA, thereby allowing the substrate nitrobenzene to disperse into the polymer layer to interact with the palladium cluster. It may be seen that the alcohol solvent facilitates the hydrogenation reaction (Fig. 5). These results correspond with those of our previous research.[12]

In the presence of alcohol, the catalytic reaction was carried out at different pH values adjusted to 1, 7, and 14, respectively (Fig. 5). It was found that an acidic solution was favorable for this reaction because the product aniline could be desorbed from the catalyst through an acid–base action.

The palladium particles supported by polymer/SiO_2 prepared by different methods possess different catalysis activity. The catalyst prepared by method B (where the polymer was first coordinated with palladium and then covered onto silica) could reach higher activity than that by method A (where the polymer was first covered onto silica and then coordinated with palladium) (Fig. 6).

Because coordination is a time-dependent process, for method A, the polymer first covered on silica cannot be coordinated with all the palladium ions in time. Thus a portion of the palladium ions would reach the inner layer to be absorbed directly onto silica, which would not be effective for catalysis; moreover, the palladium ions would not be distributed uniformly in the polymer layer. A portion of the palladium ions would remain primarily near the polymer surface, which after conversion to a palladium cluster would not be stable because of the lack of polymer network confinement near the surface. These phenomena would result in low catalysis activity. Repeated experiments showed that the catalyst prepared by

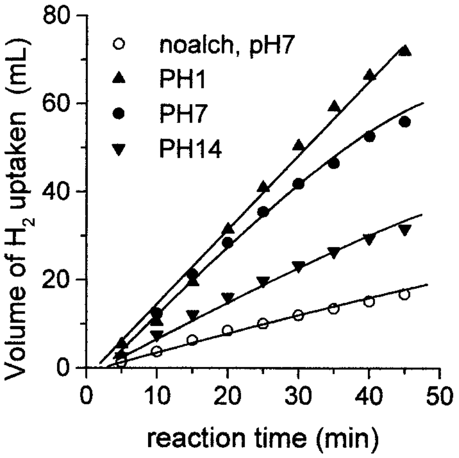


Figure 5 Effect of solvent and pH on catalysis. Conditions: palladium 0.1, mmol; H_2, 1 atm; nitrobenzene, 10 mmol, in 9 mL alcohol; room temperature; supporter, PVP/SiO_2; R_w = 5.0, R_m = 4.7.

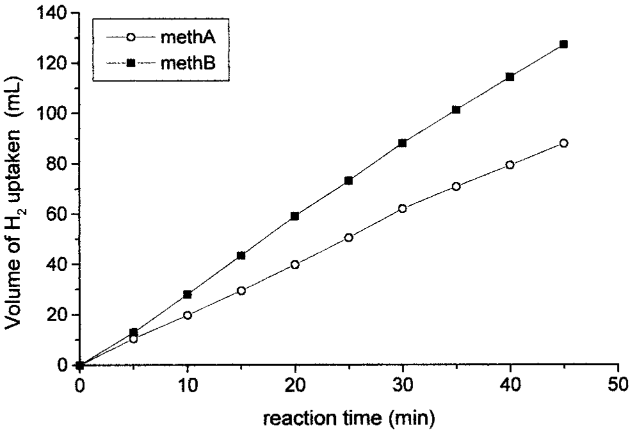


Figure 6 Effect of different methods for catalyst preparation on catalysis. Conditions: palladium, 0.1 mmol; H_2, 1 atm; nitrobenzene, 10 mmol, in 9 mL alcohol; room temperature; supporter, PAA/SiO_2; $R_w = 5.0$, $R_m = 6.0$.

method B has more stable catalysis action (hardly decreased when the catalyst was repeated 10 times) than that by method A (decreased by half when repeated three times), which implied that palladium in the catalyst prepared by method A was easily spent during the reactions.

CONCLUSIONS

A nanosized palladium catalyst was successfully synthesized by the complex transformation method. The catalysis activity reached the optimum value when the polymer could form just a single layer overlapped on the silica supporter. The size of the palladium particles, which depended on the molar ratio of the polymer ligand to palladium, would be decreased as the ratio increased. For nitrobenzene hydrogenation, the catalysis was not as good when the particle size was smaller, although it reached the highest value at about 50–80 nm.

The catalyst prepared by method B, in which the polymer was first coordinated with palladium and then covered on silica, was better than that prepared by method A, in which the coordination step was preceded by covering on silica. Solvent alcohol was helpful for the swelling of polymers, in PVP and PAA, and improved the substrate diffusion into the polymer layer to make contact with the palladium cluster; therefore, it could facilitate the catalytic hydrogenation for nitrobenzene. The pH value that favors the product aniline desorbed from the catalyst center could enhance the catalytic reaction.

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