Synthesis and Property of Nanosized Palladium Catalysts Protected by Chitosan/Silica

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ABSTRACT: A chitosan (CTN)/silica-supported nanosized palladium catalyst was obtained from a silica-supported chitosan palladium complex through a complex transition method. An adsorption model was employed to simplify the structure of the di-supporter. It was indicated that when the polymer coil adsorbed on the silica surface with even a monolayer the catalytic activity would reach an optimum value, and different situations of the, nanosized palladium particles would cause a different catalysis. The molar ratio of the chitosan structure unit to the palladium would affect the metal's size, which therefore influenced its catalytic activity. The experimental results corresponded with the inferences. © 2002 Wiley Periodicals, Inc. J Appl Polym Sci 85: 989–994, 2002

Key words: catalysts; palladium; chitosan; silica; nanotechnology

INTRODUCTION

Recently a great amount of scientific and technological research has been devoted to the nanomaterial, which is one of the most important parts of nanotechnology. Nanomaterial has its specialty rules of chemical and physical properties due to its mesocosm scale between the microcosm and the macrocosm. The nanosized metal catalyst, which has a large special area, high surface energy, and much surface defect causing high catalytic activity, has recently drawn much attention to its high performance. However, a suspension of nanosized catalyst is unstable, which is easy to aggregate to form precipitate from the catalytic systems resulting in a decrease of catalytic activity.[1]

To prevent coagulation and precipitation of the metal nanoparticles, a "protective colloid or poly-mer" is required during the formation of nanosized metal catalysts. The "protective supported materials" includes inorganic material and organic polymers. The organic polymer supporter is much more efficient than inorganic ones. In the past several years, many polymer–metal complex catalysts have been widely investigated in which polymer ligands, such as chitosan (CTN), poly-acrylamide, polymethacrylic acid, polyacids, poly-4-vinylpyridine (P-4VP), polyvinyl alcohol (PVA), etc., were used to coordinated with transition metals, such as Ru, Rh, Pd, Pt, to form complex catalysts.[2,3]

However, in the heterogeneous catalysis systems, only the surface of the catalyst is the reactive site. So the polymer supporter will not show its most availability in heterogeneous systems. Some superfine particles are then employed to increase the surface area, therefore improving the catalytic activities. In this kind of catalyst, both the ratios of superfines to polymer and of polymer to metal are important for the catalytic activities, whereas there have been few reports on that case.

Table I   The Synthesis Conditions of Samples

Sample	The Weight of Chitosan (g)	The Weight of Silica (g)	The Volume of 0.1 $MPdCl_2$ (mL)
1	0.333	0.667	3.0
2	0.333	0.667	5.0
3	0.333	0.667	7.0
4	0.333	0.667	11.0
5	0.333	0.667	13.0
6	0.167	0.833	5.5
7	0.110	0.890	3.7
8	0.091	0.909	3.0
9	0.077	0.923	2.5

In the present study, we prepared a series of silica/polymer-supported nanosized palladium catalysts with various ratios of silica to polymer (w/w) and of polymer ligand to palladium (molar ratio). The average sizes of the supporter and the nanocatalyst metal were determined by optical and electron microscopes. The catalytic activity was examined by the catalytic hydrogenation for nitrobenzene. The influence of the size of palladium and of the thickness of polymer layer adsorbed on the silica surface were discussed.

EXPERIMENTAL

A series of silica/chitosan-supported nanosized palladium catalysts were prepared by the complex transition method,[4] which involved two steps—first, the synthesis of polymer–metal ion complex with a silica supporter, and then the transition of the complex to the metal particles.

Synthesis of the Silica-Supported Chitosan-Pd (II) Complex

The silica-supported polymer–metal complex was synthesized with different ratios of silica to polymer and of polymer ligand to metal. As an example, Pd—CTN/SiO_2 at the weight ratio of silica to polymer being 5 and the mol ratio of the polymer structure unit to the metal ion being 5 is described as follows. A certain amount of chitosan was dissolved in an aqueous solution containing 2% acetic acid to form a 3 wt % CTN solution; 10 mL of CTN solution was coprecipitated with 1.5 g silica by a large amount of acetone to give a shell-core supporter CTN/SiO_2, which was then dried at 353 K for 12 h; 1.0 g of CTN/SiO_2 and 2.0 mL of 0.1 M palladium (II) chloride solution were added

to a flask, and the pH value of the whole system was then adjusted to 1–2 by 1.0 M hydrogen chloride. After refluxing the mixed system for 12 h, a complex of the silica-supported chitosan–palladium ion complex [Pd(II)—CTN/SiO_2] was obtained, which was then washed by ethanol, and dried at 353 K for 12 h. The prepared conditions of the samples are listed in Table I.

Characterization of Silica Supported Chitosan-Pd(II) Complex

The complexes were determined by infrared spectroscopy (FTIR-1600 system, Perkin-Elmer). The specific absorption peaks of infrared spectra of Pd(II)—CTN/SiO_2 and CTN/SiO_2 listed in Table II showed that the vibration absorption of the functional groups within the complex differed from that of the pure polymer. This indicates that a coordination bond between the amide group and the palladium ion has formed.

Synthesis and Characterization of a Di-Surpported Nanosized Pd Catalyst

The above complex samples were reduced to silica/chitosan di-supported metal catalysts by hydrogen in alcohol solution. This process was called the preactive step. The morphology and the size of the supporters and of the metal particles were

Table II   IR Data of CTN/SiO_2 and Pd(II)–CTN/SiO_2 Complex

Sample	CTN/SiO_2	Pd(II)–CTN/SiO_2
C—N (cm^{-1})	1082.9	1093.9
N—H (cm^{-1})	3444.0	3423.1
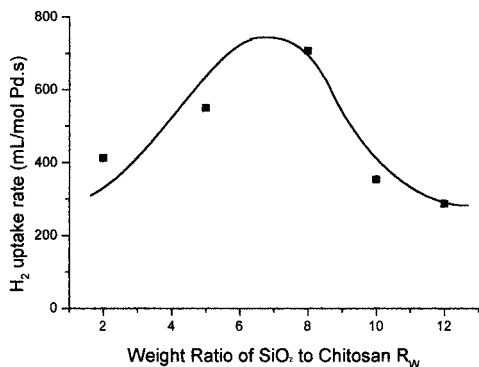
Figure 1 The effect of the ratio of silica to polymer on the catalysis.

Figure 2 The model of di-supported palladium catalyst: (a) polymer layers on silica surface; (b) three positions of Pd particles: I—adsorbed on the outer surface; II—scattered in the polymer networks; III—adsorbed on the inner surface.

determined by optical microscopy (BEX-60 system OM, JVC), scanning electron microscopy (HHS-2X SEM, Japanese) and transmission electron microscopy (H-800 TEM, Hitachi).

Catalytic Hydrogenation

The catalytic hydrogenation for nitrobenzene (10 mmol) was carried out with self-made hydrogenation apparatus in 9.0 mL of ethanol at room temperature and 1 atm of hydrogen pressure. For comparing the catalytic activities, each sample used in the catalytic system containing 0.1 mmol of Pd. The hydrogen uptaken rate was used as the parameter to compare the relative activity of each sample.

RESULTS AND DISCUSSION

Effect of the Ratio of Silica to Polymer on Catalysis

The catalytic activity was varied with the ratio of silica to polymer. Figure 1 shows the result. It was found that the catalytic rate increased initially to an optimum value and then declined.

The thickness of the polymer layers covering the silica surface affect the catalysis. We suggest a simple structure model of the di-supporter.

The surface of a silica is hypothesized to be uniform, and the possibility of a polymer coil a polymer coil adsorbed on any site of the surface to be equivalent. When all the surface sites of a silica are occupied by polymer coils, the other polymer coil will then adsorbed on the first polymer layer by Van der Waals force [Fig. 2(a)]. Thus, the thickness of the polymer layers can be evaluated by the ratio of silica to polymer.
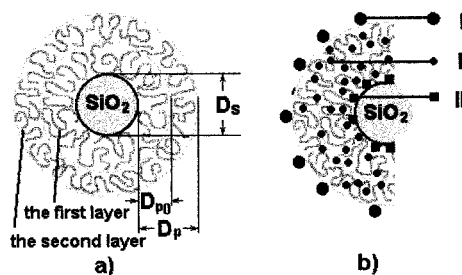
Let the diameter of a silica particle be D_s, the thickness of polymer layer on the silica surface be D_p, we can write:

$$V_s = \frac{1}{6} \cdot \pi D_s^3 \qquad (1)$$

$$V_p = \frac{1}{6} \cdot \pi[(D_s + D_p)^3 - D_s^3] \qquad (2)$$

where V_s is the volume of a silica particle, V_p is the volume of a polymer chain. Then, the weight ratio can be expressed as

$$\frac{W_p}{W_s} = \frac{V_s \cdot \rho_s}{V_p \cdot \rho_p} \qquad (3)$$

where, W_p and W_s are the weight of polymer and of the silica respectively. ρ_s is the silica density and ρ_p is the density of the polymer.

So the thickness of the polymer layer should be:

$$D_p = 0.5 \cdot D_s\left[\left(\frac{W_p \cdot \rho_s}{W_s \cdot \rho_p} + 1\right)^{\frac{1}{3}-1}\right] \qquad (4)$$

According to eq. (4), we can evaluated the D_p with the weight ratio of silica to chitosan (CTN). The evaluated data are listed in Table III, from

Table III   The Thickness of CTN

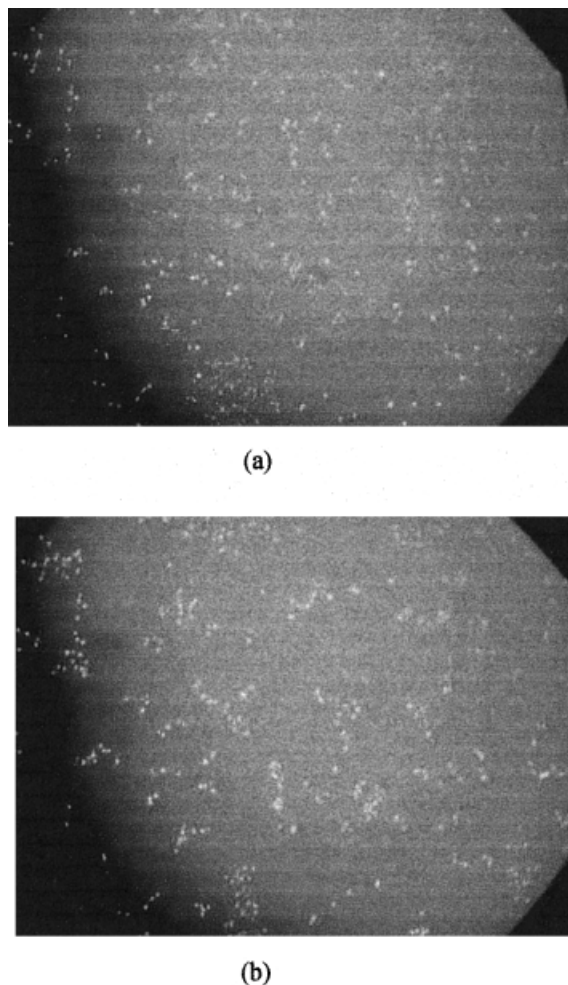| Value of the ratio	2	5	8	10	12
Thickness evaluated (nm)	159.3	112.8	71.5	52.4	37.4

Figure 3 The optical micrograph of the silica particle (a) and of a CTN/silica particle (b).

which it could be found that the value of D_p is in the range of 37.4 to 159.3 nm accompied by the weight ratio of silica to CTN from 12 to 2. The optical microscopy (Fig. 3) gave a 161.2 nm at the ratio being 2, which corresponded to the evaluated values. Therefore, we can transfer Figure 1 to Figure 4 in which the catalytic rate is varied with the thickness of the polymer layer.

It could be demonstrated that the thickness of the polymer layer corresponding to the optimum rate is the thickness of monolayer of polymers adsorbed on the silica surface. The gyration radius (S_O) of a polymer coil is related to the molecular unperturbed dimension A and the average molecular weight M by eq. (5):

$$S_0 = A\left(\frac{\bar{M}}{6}\right)^{0.5} \tag{5}$$

The value of A of chitosan is approximate, and the average molecular weight is about; the value of gyration radius could be calculated to be about 24 nm, which coincide to the half of the thickness of polymer layer. It implies that when the polymer adsorbed on the surface of silica forms a monolayer the catalytic rate would reach the optimum value.

Palladium particles supported by silica/polymer may have three different positions [(Fig. 2 (b)]. I is that on the other surface, which may directly contact to the substrate that leads the catalytic reaction immediately. But this type of nanosized palladium is not restricted by polymer chain, so it tends to aggregate each other to loss its activity. II is restricted in the polymer network that the reaction rate depends on for the diffusion rate. The thicker the layer, the less active the catalyst. III adsorbed onto the silica surface lies on the innermost surface of the polymer layer, which is the least active for catalysis because the substrate must take a long time to penetrate in the polymer layer. This indicates that the highest efficiency mode is the metal restricted by a polymer monolayer on the silica surface.

The Size of Palladium Particle

The average size of palladium particles with different molar ratios of CTN to palladium was measured by SEM (Fig. 5). Table IV shows the results of palladium particle's size and its catalytic activity.

From Table IV, it could be found that the palladium particle's size increased with decreasing the mol ratio of the polymer ligand to palladium. Within a polymer network, the number of palladium atoms increases with decreasing of the mol ratio of the polymer ligand to palladium. So the size of the palladium particle increased. Figure 6
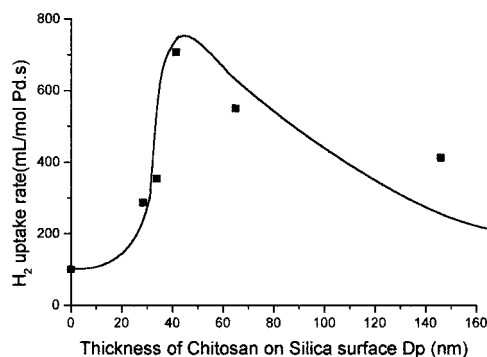

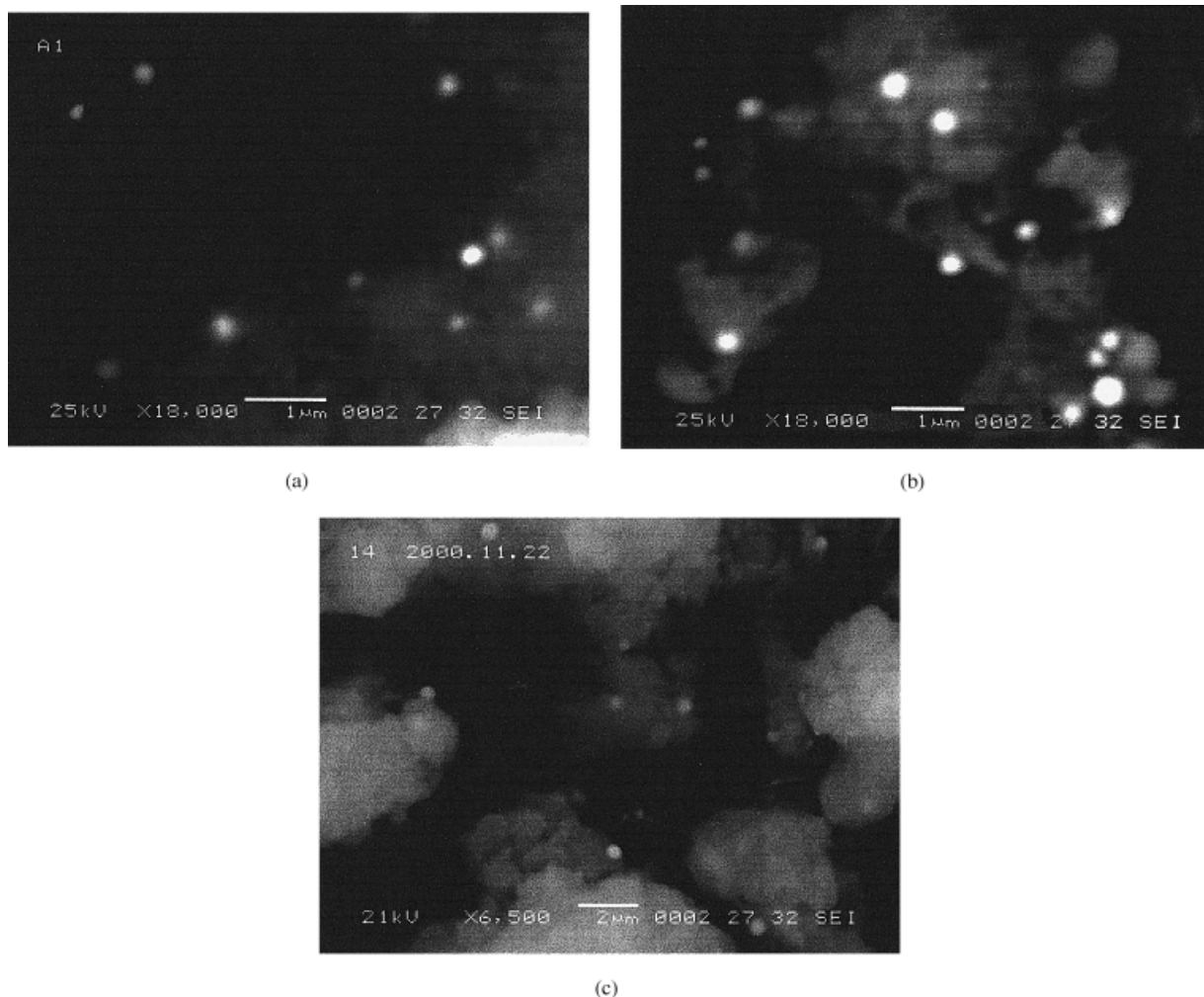**Figure 4** The effect of the D_p on the catalysis.

Figure 5 The SEM picture of palladium with different mole ratios of CTN to palladium N:Pd ratios are (a) 9.65:1; (b) 6.73:1; (c) 4.82:1.

shows the number of palladium atoms varying with the mol ratio of the polymer ligand to palladium in a certain network.

The different sizes of the palladium particles would result in different catalytic activity. This implies that the catalytic activity increases with decreasing the size of palladium at first, and will decline after a critical size. The activity increases with decreasing of size of the palladium particle.

However, the possibility of side reactions would then increase, and meanwhile, the selectivity of the catalytic center would decrease.

CONCLUSION

The experimental results show that the catalytic activity of a palladium–chitosan/silica system can

Table IV   The Size and the Catalytic Activity of Palladium

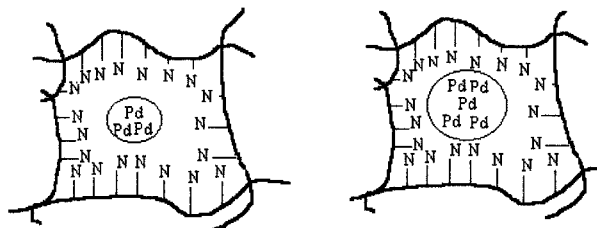| R_m	Size of Palladium (nm)	H_2 Uptake Rate V_{max} (mL/molPds)
9.65	64.7	411.67
6.73	89.6	596.67
4.82	186.0	483.33

Figure 6 The member of the palladium atom with the different mol ratio of the polymer ligand to palladium in a single network.

be modified by adjusting the weight ratio of silica to polymer and mol ratio of the polymer ligand to palladium. The change of the weight ratio of silica to polymer and mol ratio of the polymer to metal, in fact, could result in the change of the reaction space and the palladium particle's size, which should affect the catalytic activity and selectivity significantly. When the CTN is adsorbed on the surface of silica and form a complete monolayer ($D_p \approx 2S$), the catalyst's catalytic activity was maximum. This is especially important because variations in catalytic activities are often accompanied by variations in catalytic selectivity.[5]

The adjustment of palladium particle size by changing the ratios both of silica to polymer (w/w) and polymer ligand to palladium (molar ratio) can prepare the catalysts that have high catalytic activity.

REFERENCES

1. Hidefani, N. L. J Mol Sci 1999, 15, 3.
2. Feldheim, D. L.; Boldy, C. J.; Sebring, P. J Electro Chem Soc, 1995, 142, 32.
3. Hirai, H.; Yakura, N.; Seta, Y. React Functl Polym 1998, 37, 121.
4. Sang, L. Y.; Qian, W.; Zhang, Y.; Yuan, R.; Shi, W.; Min, W.; Wang, J.; Cheng, L.; Peng, P.; Hua, X. J Polym Bull. (in Chinese) 1918, 3: 11.
5. Rylander, P. N. In Catalytic Hydrogenation Over Platinum Metals; Academic Press: New York, 1967.