

A Simple Preparation Route to Palladium Nanoparticles Catalyst from Decomposition of Supported [Pd(lysine·HCl)(Cl)₂] Complex

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Abstract: The supported palladium nanoparticles catalyst with uniform-sized Pd particles distribution and without nitrogen or chlorine atoms present in catalyst was prepared by calcination of the supported [Pd(lysine·HCl)(Cl)₂] complex as precursor and characterized by TEM. Moreover the supported [Pd(lysine·HCl)(Cl)₂] complex was from cation exchanging [Pd(lysine·HCl)(Cl)₂] complex with inorganic support. The hydrogenation characteristic of supported Pd nanoparticles catalyst was evaluated by using benzoic acid.

Keywords: Nanostructure, heat treatment, electron microscopy, microstructure.

1. INTRODUCTION

Catalytic hydrogenation is one of the key processes in fine chemicals production. Palladium is a very important metal catalyst in the field of organic and inorganic synthesis for the past three decades [1]. Palladium metal with nanometer-scale dimension is of particular interest due to its catalytic ability, thus the synthesis technology of Pd nanoparticles with uniform-size is very important and attractive in the research area. Several literature reports are related to the development of supported metal nanoparticles on solid supports. These reports include adsorption/impregnation [2-10], immobilization on surfaces functionalized with appropriate ligands [11-13], coprecipitation [2,14], sol-gel [2,15], vapor-phase deposition of organometallic complexes [16], microemulsion [17], diffusion of preformed nanoparticles into the pores *via* sonication [18], and fabrication of nanoparticles *via* electron beam lithography [19,20]. In PdCl₂ or [Pd(NH₃)₄]²⁺ adsorption/impregnation method, the reduction in a relatively low temperature must be carried out by chemical reducer after adsorption/impregnation, i.e. hydrazine, alcohol, NaBH₄ etc. Because of the adsorption action of support or metal Pd, the nitrogen or chlorine atoms produced during preparation will remain in catalyst, which will make the catalytic activity of bifunctional catalyst decrease [9,10]. N. Nishimiya [21] *et al.* synthesized Pd nanoparticles by high temperature calcination and reduction technology. The main results were that the nitrogen or chlorine atoms were taken out from the catalyst and the Pd nanoparticles size was only 10-15 nm.

Generally, the cost of ligand in the organometallic complex is high. In the present work, the supported Pd nanoparticles catalysts with uniform-sized Pd particles distribution and without nitrogen or chlorine atoms present in catalysts were directly prepared by means of calcination of supported palladium complex. The ligand of the palladium complex was a lysine salt which is easily decomposed at a relatively

low temperature and contains a free -NH₃⁺ cation. The free -NH₃⁺ cation can exchange with inorganic support and can be immobilized on the support. The supported Pd nanoparticles catalyst prepared was characterized by TEM. Hydrogenation activities were evaluated by using benzoic acid to give cyclohexane carboxylic acid.

2. EXPERIMENTAL

2.1. Materials

All the chemicals were obtained from Tianjin Reagent Company in P. R. China and used as such without further purification. Zeolite NaY with S_{BET} = 766 m²/g, and Si/Al = 2.86 was from Wenzhou Catalyst Factory in P. R. China. The commercially available Pd metal was obtained from Chinese Jinchuan Colored Metal Company.

2.2. Preparation of Palladium Complex [Pd(lysine·HCl)(Cl)₂] [22]

H₂PdCl₄ solution was prepared by adding 2.1093 g commercial palladium metal (99.99%) and 20 mL HCl (33%) in 100 mL three-necked flask with cooling water bath at room temperature, slow dropping 10 mL H₂O₂ solution (30%) under vigorous stirring, and controlling the mixture temperature below 30°C until all palladium metal was dissolved. Finally, the solution was diluted to 100 mL.

The preparation of [Pd(lysine·HCl)(Cl)₂] complex was shown as follows: 10.0 mL the H₂PdCl₄ (Pd 21.09 mg/mL) solution prepared above was diluted to 30 mL in a 100 mL three-necked flask. Several drops of 0.1 M NaOH solution was added until reaching pH ~ 4-5. The lysine·HCl which was 0.3661 g (1.989 mmol) was introduced into the prepared solution, and the mixture was stirred vigorously at 60-70 °C for 2 h.

2.3. Supported [Pd(lysine·HCl)(Cl)₂] Complex

In a typical synthesis, 2.0 g NaY, 120 mL deionised water were added into 250 mL three-necked flask, the mixture was stirred vigorously and heated to 60 °C in water bath for 1 h. Several drops of 0.1 M HCl solution was added until reaching pH ~ 5. [Pd(lysine·HCl)(Cl)₂] complex (13 mL)

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prepared above was introduced into the mixture, and the mixture was maintained at 60 °C under vigorous stirring for 4 h. The mixture was cooled to room temperature. Finally, the solid was filtered, and washed with deionised water until Cl⁻ was not determined. Then, it was dried at 80 °C for 10 h, and grinded to 80 μm. It was noted as PdL-NaY.

2.4. Preparation of Palladium Nanoparticles Catalyst

The PdL-NaY product was placed in muffle furnace and slowly heated up to 120 °C for 24 h, 300 °C for 2 h and 500 °C for 2 h in air (temperature ramp: 5 °C/min), respectively. 2.0 g products prepared above were maintained at 60 °C under stirring for 2 h in 100 mL 2 % NaCl solution. The mixtures were cooled to room temperature. The solids were filtered, and washed with deionised water until Cl⁻ was not determined. The products were dried at 120 °C in oven for 2 h, and were not reduced in H₂ before hydrogenation reaction. They were noted as Nano-1, Nano-2, Nano-3, respectively.

2.5. Catalytic Test Reaction

The liquid-phase hydrogenation of reactant benzoic acid (99% purity) was investigated in a 1 L stainless autoclave equipped with a pressure regulator, which ensured that the reactions proceeded at a constant hydrogen pressure. The mass of catalyst was 4 g. The mass of reactant benzoic acid was 100 g, and the solvent ethanol was 80 mL. The mixture was pressed and vented three times with N₂ and H₂ respectively, and the pressure was set to 1.0-1.4 Mpa. The reaction commenced by starting the stirring, and the autoclave was heated to 120-140 °C (temperature ramp 5 °C/min). After

reaction for 4 h, the autoclave was cooled to room temperature, and was depressurized and replaced three times by N₂. The catalyst was filtered, and the organic phase was analyzed with Shimadzu 9A gas chromatography which was equipped with a polyglycol capillary column (30 m) and a flame ionization detector (FID). The catalytic activities were characterized by reaction conversion and the cyclohexane carboxylic acid selectivity.

2.6. Sample Characterization

The Pd contents of the samples were determined by inductively coupled plasma (ICP) atomic emission spectrometry. TEM images were recorded with a Tecnai G² 20 S-T WIN transmission electron microscope. The samples suspended in ethanol were mounted on carbon-coated copper grids and then the solvent was evaporated.

3. RESULTS AND DISCUSSION

3.1. Supported [Pd(lysine·HCl)(Cl)₂] Complex

Our former work [22] has shown that N (from α-NH₂ group) and O (from -OH group in -COOH) atoms in lysine·HCl can form coordination bonds with Pd atom from H₂PdCl₄ solution, which constitutes the five-membered chelating ring complex. There is a free -NH₃⁺ cation remained in [Pd(lysine·HCl)(Cl)₂] complex. Therefore, the [Pd(lysine·HCl)(Cl)₂] complex can exchange with the other cations in support, e.g. Na⁺, NH₄⁺, Ca²⁺ etc., and may be supported in the inorganic support by way of the interaction of ionic bonds [23]. In present research work, the [Pd(lysine·HCl)(Cl)₂] complex exchanged with Na⁺ in NaY,

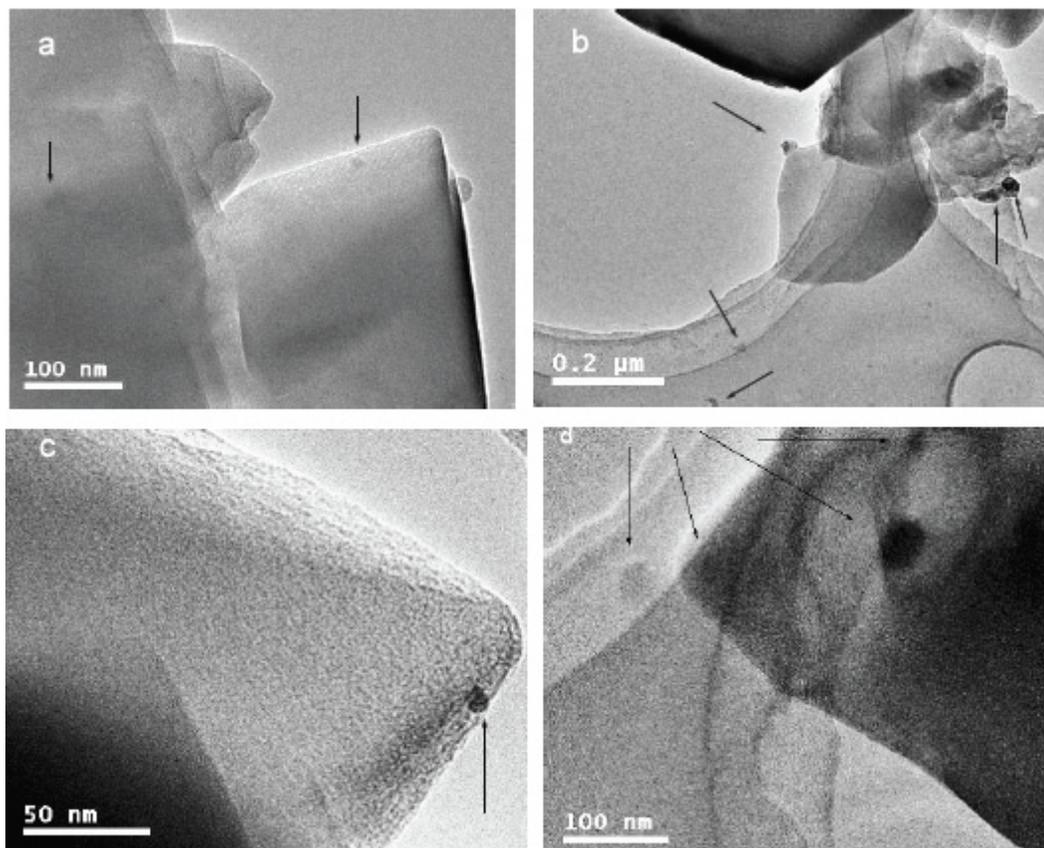
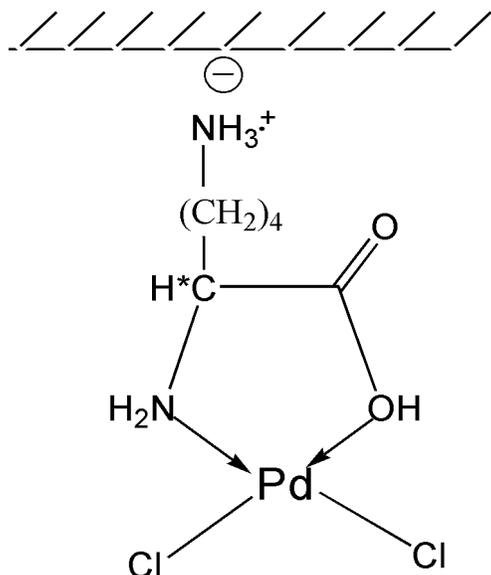


Fig. (1). The TEM images of Nano-1 catalyst.

and was immobilized in NaY. Its scheme was as follows (Scheme 1).



Scheme 1.

3.2. Characteristic of Palladium Nanoparticles Catalyst

Figs. (1-3) are the TEM images of Nano-1~3 samples prepared at different calcination conditions. It is found that when Nano-1 was calcinated at 120 °C for 24 h, the palladium particle sizes of Nano-1 (Fig. 1) distribute broadly, where a few Pd particles appeared in every image. But some small Pd particles can be clearly observed. The smaller particle size is within 10 nm, and the larger one is about 40-50 nm. The Nano-2 (Fig. 2) sample shows the occurrence of high dispersed uniform-sized Pd nanoparticles, which are mainly distributed between 5 nm and 10 nm. There are many Pd particles appearance in each image. However, the palladium particle sizes of Nano-3 (Fig. 3) distribute broadly. The smallest particle size is about 20 nm, and the largest one is about 60-70 nm. These results show that the [Pd(lysine·HCl)(Cl)₂] complex may be not completely decomposed at 120 °C for 24 h. It seems too long decomposing time, in which the Pd particles produced get together and

become larger. It seems too high for the decomposition temperature at 500 °C, because the Pd particles can assemble to become more larger particles at 500 °C. This further verifies that calcination temperature is very important, and delaying calcination time at a definite calcination temperature is disadvantage. Therefore, the better calcination condition should be at 300 °C for 2 h for supported [Pd(lysine·HCl)(Cl)₂] complex.

A representative local elemental analysis of Nano-2 sample was presented in Fig. (4). Nano-2 catalyst included the atoms of palladium, silicon, aluminum, sodium, oxygen and carbon atoms, and did not include any other kinds of atoms, including nitrogen and chlorine atoms. This verifies that the nitrogen or chlorine atoms are not presented in the catalyst. The silicon, aluminum, sodium and oxygen atoms may come from inorganic support (NaY), and a few carbon atoms may come from remainder of decomposed lysine. Therefore, Pd nanoparticles catalyst with uniform-sized Pd particles distribution and without ammonium or chlorine atoms in catalyst can be prepared by calcination of the supported [Pd(lysine·HCl)(Cl)₂] complex as precursor.

Otherwise, according to Figs. (1-3), when the Pd particle size is within 10 nm, the morphology of Pd nanoparticles is more or less hemispherical, and the Pd nanoparticles contact with the support closely. When the Pd particle size is above 20 nm, the morphology of Pd nanoparticles is not uniform, and the Pd nanoparticles locate on the outside surface of the support.

3.3. Catalytic Test Reaction

The hydrogenation activities and Pd contents of palladium nanoparticles catalysts were summarized in Table 1. The Pd contents were from 4.0 to 4.7 wt% in these catalysts. Benzoic acid could be hydrogenated to cyclohexane carboxylic acid at 130 °C by palladium nanoparticles catalysts prepared above, and the hydrogenation selectivity was better. There were different hydrogenation activities on different catalysts. The hydrogenation activity of Nano-2 sample calcined at 300 °C was the best. Comparing with Nano-2, the Nano-3 sample which is much larger Pd particle size, as well as the Nano-1 with a broad particle size and a few metal particles, showed poorer performance. In this case, the decrease

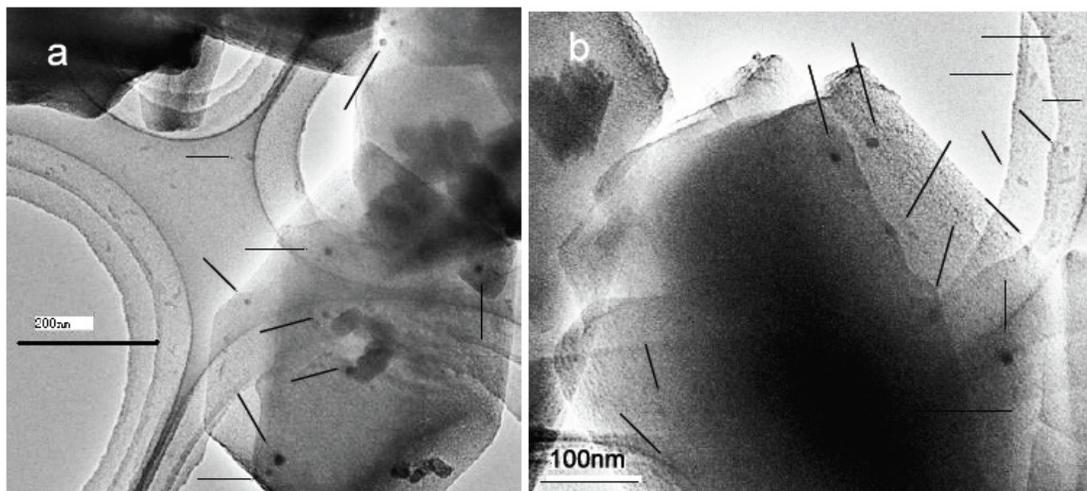


Fig. (2). The TEM images of Nano-2 catalyst.

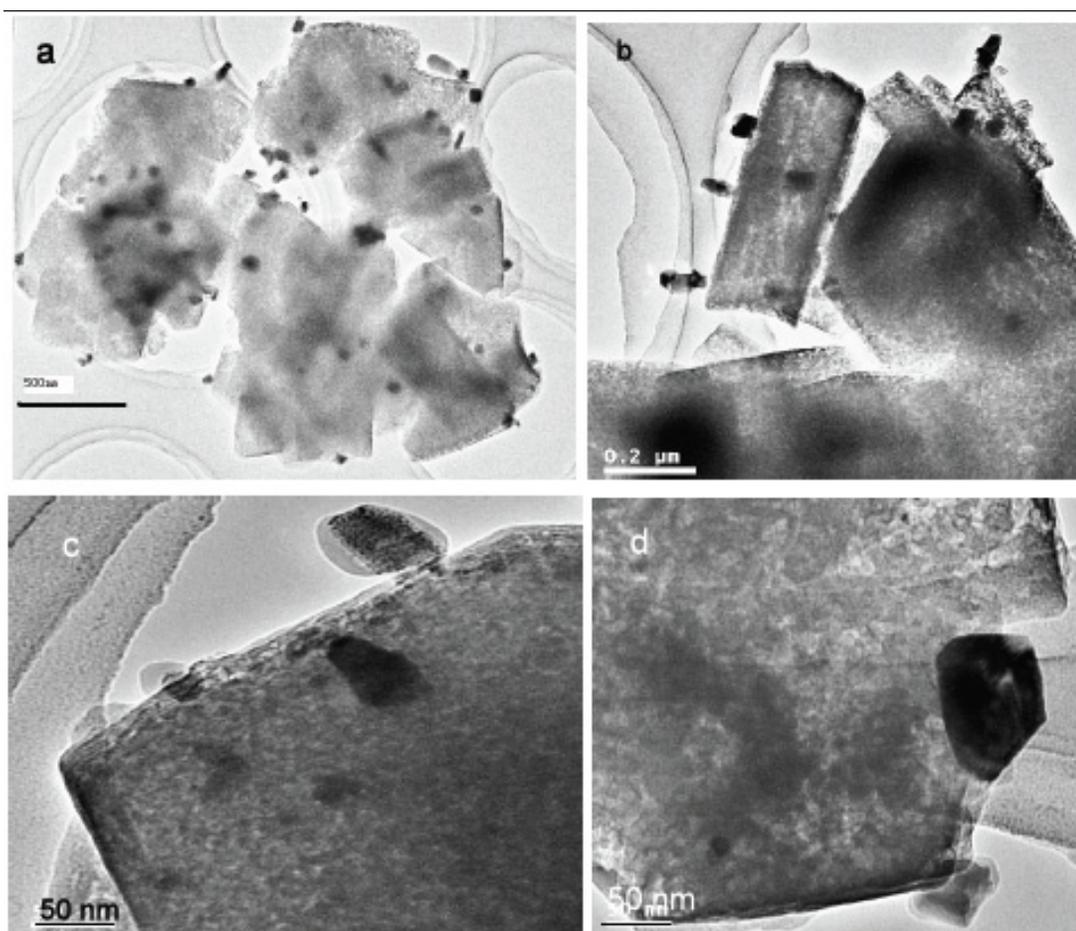


Fig. (3). The TEM images of Nano-3 catalyst.

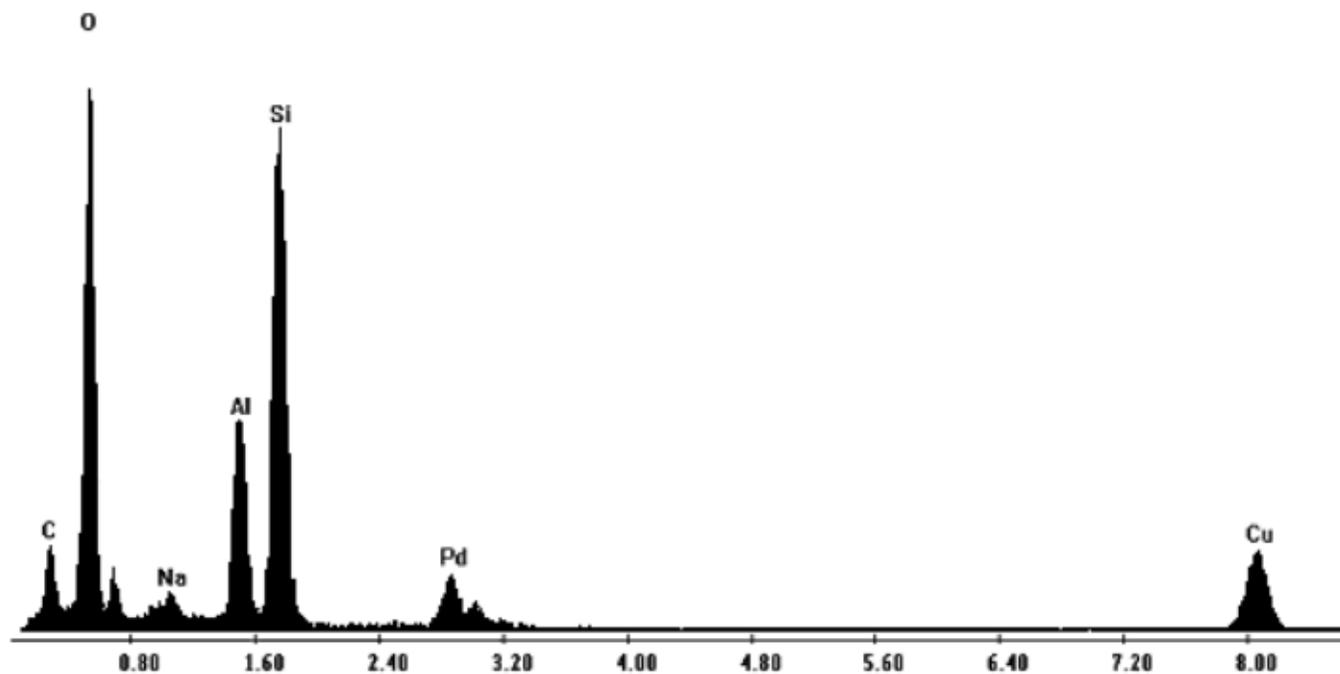


Fig. (4). The TEM local elemental analysis of Nano-2 catalyst.

in the catalytic performance is expected because of the increase in the Pd particle size or the decrease of the amount of the Pd metal particles. The hydrogenation conversion of

Nano-2 catalyst was above 89%, and the selectivity of cyclohexane carboxylic acid was above 96% at 130 °C and 1.2 Mpa.

Table 1. The Pd Contents and Catalytic Activities of Nano-1, Nano-2 and Nano-3 Catalysts for the Hydrogenation of Benzoic Acid

Catalyst	Pd Contents (wt.%)	T (°C)	H ₂ Press. (Mpa)	Reaction Conv. (%)	Reaction Select. (%)
Nano-1	4.0	130	1.2	68.8	86.9
Nano-2	4.5	130	1.2	89.1	96.5
Nano-3	4.7	130	1.2	55.3	84.2

4. CONCLUSION

The catalysts consisting of nanometer-sized Pd particles are synthesized by way of a simple technique. No nitrogen or chlorine atoms are present in the catalysts. These catalysts were tested for the hydrogenation of benzoic acid in ethanol under hydrogen pressure. Catalyst calcined at 300 °C for 2 h gave the best activity. The Pd particle size seems to play an important role in increasing the activity in the hydrogenation reaction.

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