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Preparation of Pd-Pt nano-particles on surfactant assisted sol-gel derived alumina and its application in glucose oxidation with molecular oxygen

Ali Nemati Kharat,* Bahareh Tamaddoni Jahromi and Taraneh Hajiashrafi

School of Chemistry, University College of Science, University of Tehran, Tehran, Iran

ABSTRACT

Activity and selectivity of nano-palladium particles supported on sol-gel derived alumina (with pore sizes in the range of 3-4 nm), in the oxidation of glucose to gluconic acid by molecular oxygen were studied. Modification of prepared catalysts with different amounts of platinum and also effect of bismuth addition as catalyst promoter was investigated. For comparison with related commercial catalysts, we prepared Pd particles on activated carbon. Different methods of metal ion reduction have been tested, and optimum conditions were evaluated. Morphological aspects of prepared catalysts have been investigated by Scanning Electron Microscopy (SEM). Specific surface area of prepared catalysts were measured by isothermal nitrogen adsorption on a volumetric apparatus. Presence of metal particles on the surface of catalysts confirmed by XRD, and their amounts were measured by Inductively Coupled Plasma (ICP).

Keywords: catalysis, nanoparticles, sol-gel process, glucose oxidation.

**Corresponding author*

INTRODUCTION

The interest in the application of carbohydrates as feedstock for chemical industries has increased considerably during the last few years.¹ In spite of their wide availability and low price, few catalytic processes are used for their transformations in the chemical industry. This is due to the lack of efficient and reliable catalytic methods. One of the main problem is rapid deactivation of the catalysts in aqueous systems.² Therefore, research in this area is completely wise. Various researchers have investigated the catalytic oxidation of alcohols and carbohydrates in aqueous medium using molecular oxygen.²⁻⁴ For practical reasons, heterogeneous catalysts operating in water are clearly preferred. Previous studies have demonstrated that the active catalysts consist of a noble metal (Pd, Pt) supported on carbon, sometimes in association with a heavy element acting as promoter. In the recent years, researches in this area have been focused on the oxidation of glucose into gluconic acid, using carbon-supported Pd-Bi catalysts.⁵ The interest for the reaction lies in the fact that gluconic acid is a biodegradable chelating agent and a key intermediate for foodstuffs and pharmaceuticals.⁶⁻⁹ In this catalytic system, bismuth acts as a promoter for the catalytic activity of palladium and platinum and retards the catalyst deactivation.

EXPERIMENT

Preparation of surfactant assisted sol-gel alumina

In a typical experiment 10 g of aluminum isopropoxide was dissolved in 200 ml isopropyl alcohol and while vigorously stirring, a solution containing 20 ml isopropyl alcohol, 4 ml water and 2.45 mmol of cetyl trimethyl ammonium bromide, CTAB, were added. The resulting mixture was refluxed for 5 hours and aged at 50 °C in a dessicator, after that a firm transparent gel resulted. Aging was continued for 90 more hours under the same conditions, which caused the gel converted to a fine powder. The resulting raw alumina was dried at 140 °C for 5 hours followed by calcination at 800 °C for 6 hours.

Preparation of Pd-Pt-Bi nano-particles on Alumina

0.1 g PdCl₂ was dissolved in minimum amount of distilled water containing several drops of hydrochloric acid. After addition of prepared Alumina (1 g), the slurry was mixed for several hours at 50°C. Solution of 0.2 g chloroplatinic acid in minimum amount of water was added to above mentioned slurry while mixing vigorously. Then 0.4 g bismuth nitrate pentahydrate dissolved in minimum amount of distilled water containing several drops of hydrochloric acid was added. The slurry was mixed for 4 hours at 50°C, then 30 ml ethylene glycol was added, and refluxed for 2 hours and stirred at 50°C overnight. After filtration, resulted powder was dried at 80°C and calcined at 600°C for 4 hours in an oxygen free atmosphere.

Preparation of Pd-Bi nano-particles on Activated Carbon

0.1 g PdCl₂ dissolved in 1 ml of distilled water containing several drops of hydrochloric acid was refluxed for 2 hours. After that 1 g of activated carbon was added. Resulting

suspension, after addition of 0.05 g bismuth nitrate, was reduced by 37% formalin solution at 80°C. After filtration resulted catalyst was calcined at 400°C for 4 hours.

Catalysts performance examination

The oxidation of glucose solution (1.00 mol/liter) was performed in a 150 ml thermostated glass reactor equipped with condenser, magnetic stirrer, an oxygen supply system, a burette containing sodium hydroxide solution (3.00 mol/liter) and a pH electrode. The acids formed during the oxidation of glucose were neutralized by addition of aqueous solution of sodium hydroxide to maintain pH constant at 9.5 in the reaction medium. The reaction was conducted at 55°C. The mixture was stirred at 1200 rpm, and oxygen was bubbled through at 2.0 liter/min. Extent of reaction was checked by consumption of sodium hydroxide solution and changing the PH of the solution. Selectivity for sodium gluconate or any unwanted side-products was checked by liquid chromatography coupled with a variable wavelength UV detector LaChrom L-7400 (Merck Hitachi) at 200 nm. Analyses were performed by Shimadzu HPLC equipped with a SPD-10AV UV-Vis (200 nm) and aRID-6A refractive index detectors. A Luna 5 Im NH2 100A column (Phenomenex, 250 3.0 mm) with 0.02 M H₃PO₄ (pH=2) as eluent (flow rate of 1 ml.min⁻¹) was used.

Catalysts characterization

A Zeiss-902A Transmission Electron Microscope (TEM) was used for analysis of prepared catalysts. Nitrogen gas adsorption, using ultra high purity nitrogen gas (99.999%), adsorbed volumetrically on samples at -196°C, led to their specific surface area evaluations. A stainless-steel automatic volumetric adsorption apparatus was used to make these measurements. Pore size distributions for diameters in the range of 10-500 Å were calculated using Barrett-Joyner-Halenda (BJH) method. X-ray diffraction (XRD) patterns were recorded by a Siemens D5000 diffractometer with Cu-K α radiation.

RESULTS AND DISCUSSION

Table 1 is shown results of oxidation of glucose by Pd-Pt catalysts on sol-gel derived

alumina. For comparison Palladium catalyst supported on activated carbon was prepared and tested. As it was shown in the table, some samples were promoted by bismuth salt. Metal promoters such as bismuth, was added to Pd-Pt metals by co-impregnation of the supported noble metal catalyst with an aqueous promoter salt solution. For Pd/C catalyst bismuth was loaded simply by addition of slightly acidic bismuth nitrate solution to reaction media and adjusting the pH by sodium hydroxide.

Table 1. Oxidation of glucose by different catalysts. ^a

| Catalyst | Pd/Pt ratio | Pd/Bi ratio | Total metal Loading (%) | Yield (%) | Reducing agent |
|---|-------------|-------------|-------------------------|-----------|-----------------|
| Pd-Pt/Al ₂ O ₃ | 4 | - | 5 | 97 | EG ^b |
| Pd-Pt/Al ₂ O ₃ | 4 | - | 5 | 95 | F ^c |
| Pd-Pt/Al ₂ O ₃ | 2 | - | 6 | 98 | EG |
| Pd-Pt/Al ₂ O ₃ | 2 | - | 6 | 98 | F |
| Pd-Pt-Bi/Al ₂ O ₃ | 4 | 0.5 | 7 | 99 | EG |
| Pd-Pt-Bi/Al ₂ O ₃ | 4 | 0.5 | 7 | 98.5 | F |
| Pd-Pt-Bi/Al ₂ O ₃ | 2 | 1 | 10 | 99 | EG |
| Pd-Pt-Bi/Al ₂ O ₃ | 2 | 1 | 10 | 98 | F |
| Pd/Al ₂ O ₃ | - | - | 5 | 68 | EG |
| Pt/Al ₂ O ₃ | - | - | 5 | 63 | EG |
| Pd/C | - | - | 5 | 71 | F |

Reduction of catalyst precursors were performed in the liquid phase by ethylene glycol or formalin solution.

The results of application of several %10 (w/w) Pt-Bi alumina supported catalysts with different Pt/Bi ratios for converting glucose to gluconic acid is shown in table 2. The role of bismuth is very important. The Pt supported catalyst without bismuth has no activity. As the amount of bismuth increases in the supported catalyst, the yield of product raises (Figure 1).

Table 2. Results of application of several Pt-Bi supported catalysts with different Pt/Bi ratios.

| Time (h) | Yield (%) | Oxygen rate (lit/min) | Pt/Bi |
|----------|-----------|-----------------------|-------|
| 1 | 4.8 | 6 | 5 |
| 1 | 10 | 6 | 4 |
| 1 | 12 | 6 | 3 |
| 1 | 80 | 6 | 2 |

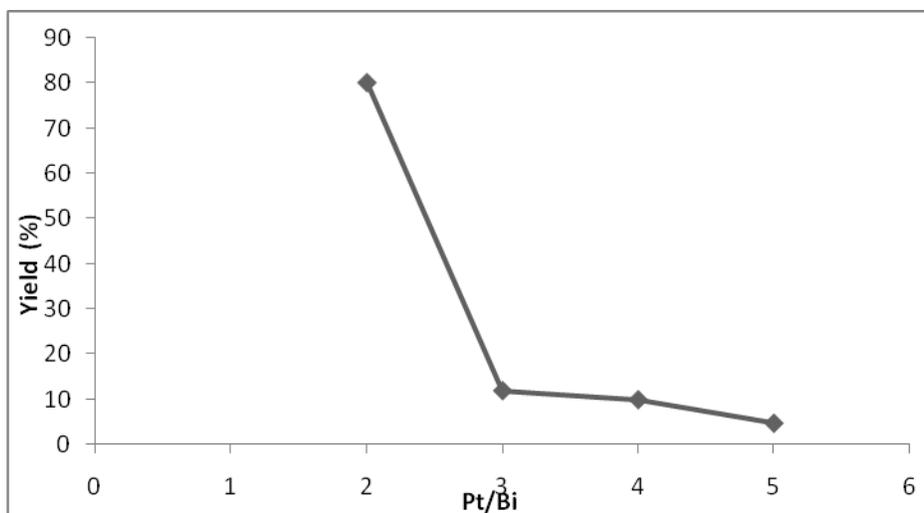


Figure 1. Effect of Pt/Bi ratio on the yield of product.

Some alumina supported catalysts with different amount of palladium, platinum and bismuth were prepared by sol-gel method. The greater the ratio of Pd/Pt, the higher yield for reaction (Figure 2). Among these catalysts, as shown in table 3, 5Pd-1Pt-4Bi/Al₂O₃ gives the highest yield. The initial rate and reaction extent for this catalyst is higher than other catalysts and gives more than %99 yield less than one hour. 5Pd-1Pt/Al₂O₃ has also shown %99 yield with greater oxygen concentration. Pd/Al₂O₃ has a very low activity in glucose oxidation reaction and adding bismuth nitrate has no significant effect in catalyst function.

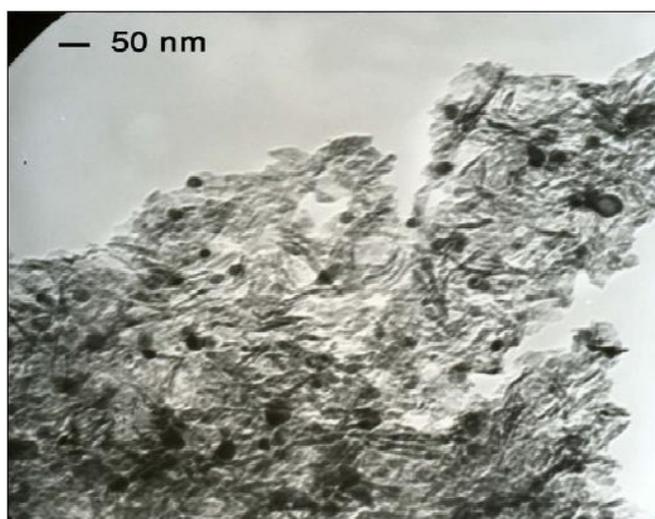


Figure 3. Scanning electron micrograph of Pd-Pt/Al₂O₃ (magnification 140000:1).

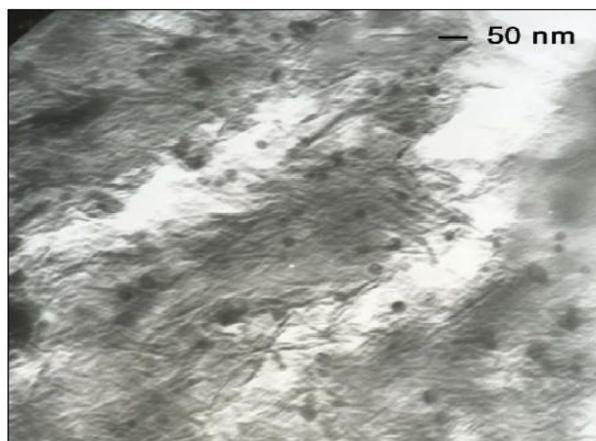


Figure 4. Scanning electron micrograph of Pd-Pt/Al₂O₃ (magnification 140000:1).

The figures 3 and 4 show scanning electron micrograph of Pd-Pt/Al₂O₃. Average size of metal particles is less than 10 nm. Distribution of metal particles on Al₂O₃ support is relatively uniform. The figure 5 shows scanning electron micrograph of Pd-Bi/Al₂O₃.

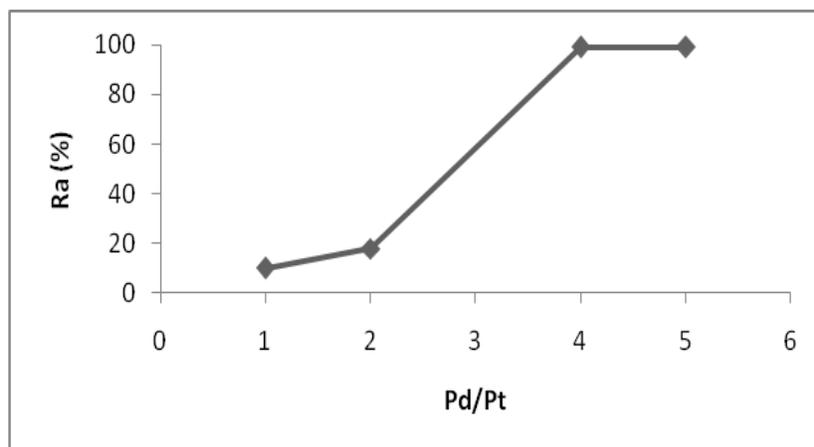
XRD spectra show most of particles on Al₂O₃ support are reduced in the form of metal. So, the yield of reduction reaction is high. The surface areas of 5Pd-4Pt/Al₂O₃ and Pd/C were measured by BET analysis. BET surface area for 5Pd-4Pt/Al₂O₃ is 187 m²/g and for Pd/C is 234 m²/g.



Figure 5. Scanning electron micrograph of Pd-Bi/Al₂O₃ (magnification 10000:1).

Table 3. Alumina supported catalysts with different amount of palladium, platinum and bismuth.

| Catalyst | Oxygen rate (lit/min) | Time (h) | Yield (%) |
|--|-----------------------|----------|-----------|
| 5Pd-1Pt-4Bi/Al ₂ O ₃ | 1 | 1 | 99 |
| 4Pd-1Pt/Al ₂ O ₃ | 1 | 1 | 99 |
| 5Pd-1Pt/Al ₂ O ₃ | 1 | 1 | 99 |
| 5Pd-1Pt/Al ₂ O ₃ | 1 | 4 | 99 |
| 2Pd-1Pt-1Bi/Al ₂ O ₃ | 1 | 1 | 24 |
| 2Pd-1Pt/Al ₂ O ₃ | 1 | 1 | 18 |
| 1Pd-1Pt-0.3Bi/Al ₂ O ₃ | 1 | 1 | 10 |
| Pd/Al ₂ O ₃ | 1 | 1 | 1.8 |


Figure 2. Effect of Pd/Pt ratio on the yield of product.

ACKNOWLEDGEMENTS

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