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Effect of reduction method on the performance of Pd catalysts supported on activated carbon for the selective oxidation of glucose

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The effect of the reduction method on the catalytic properties of palladium catalysts supported on activated carbon for the oxidation of D-glucose was examined. The reduction methods investigated include argon glow discharge plasma reduction at room temperature, reduction by flowing hydrogen at elevated temperature, and reduction by formaldehyde at room temperature. The plasma-reduced catalyst shows the smallest metal particles with a narrow size distribution that leads to a much higher activity. The catalyst characteristics show that the plasma reduction increases the amount of oxygen-containing functional groups, which significantly enhances the hydrophilic property of the activated carbon and improves the dispersion of the metal.

reduction method, plasma, oxidation of glucose, Pd catalyst, activated carbon

1 Introduction

Activated carbon (AC) supported noble metal catalysts have been extensively applied for fine chemical syntheses, hydrogen storage, and electrocatalysis [1-6]. A major advantage of AC-based catalysts is that noble metals can be easily recovered from the used catalysts. With the rapid development of green chemistry, various carbon supported catalysts have attracted increasingly more attention. Oxidation of glucose to gluconic acid in the liquid phase is a typical example for green chemistry with the use of catalysts and renewable resources [5, 6]. Gluconic acid, used as an intermediate in the food and pharmaceutical industry and also as a biodegradable chelating agent, is produced by biochemical oxidation of glucose as the only industrial route. This biochemical process has some disadvantages, such as limited space-time yield and required population control regulations of the microorganisms [7]. Recent development, however, has shown great potential of the use of heterogeneous catalysts, such as carbon or metal oxide supported Pd, Pt and Au catalysts, for oxidation of glucose with oxygen or air [5, 6, 8-17].

The oxidation of glucose over the aforementioned noble metal catalysts is a structure-sensitive reaction. Both the initial rate and the deactivation are particle-size-dependent [14-17]. Because the oxidation requires a metal catalyst, the catalyst has to be reduced before the reaction. Different reduction methods could induce variation in particle size, morphology, and the metal-support interaction, and then impact the catalytic performances. The catalysts for oxidation of glucose are normally reduced by flowing hydrogen at elevated temperatures or by reducing chemicals, such as formaldehyde and hydrazine. Recently, we reported a green, simple and energy efficient glow discharge plasma reduction route to reduce supported metal catalysts using inert gas or even oxygen as the plasma forming gas [13, 18]. Electrons were considered as the reducing agent for the room temperature plasma reduction. The reducibility of metal ions by the non-hydrogen plasma can be determined

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by the value of standard electrode potential of the metal ions [18]. Those metal ions with positive standard electrode potential can be easily reduced by non-hydrogen plasma at ambient temperature.

The AC supported noble metal catalyst is normally reduced by chemicals. The development of the room temperature plasma reduction will reduce the use of chemicals, which is a really green reduction technology. According to the energy balance, the plasma reduction approach significantly reduces the energy consumption and the cost.

In this paper, we attempt to study the effect of the reduction method on the catalytic activity of AC supported Pd catalysts in the selective oxidation of glucose. A particle size effect with the oxidation of glucose will be confirmed in this work.

2 Experimental

2.1 Sample preparation

AC was commercially obtained from Norit Americas, Inc. (SX ULTRA grade). In order to prepare 3.5 wt% Pd/AC catalysts, the metallic precursor was introduced on the carbon via incipient wetness impregnation, using an aqueous solution of Pd(NO₃)₂. The sample was kept overnight and then dried in air at 110 °C for 12 h to remove residual moisture. The obtained sample was made into three pieces. One was reduced using a solution of formaldehyde (37 wt%) at room temperature for 3 h. The second part was reduced by the flowing hydrogen at 300 °C. The third part was reduced using argon glow discharge plasma, initiated at ambient temperature. Details of the plasma setup and procedure have been reported elsewhere [13, 18]. Briefly, the catalyst sample (about 0.5 g), loaded in a quartz boat, was placed in a quartz tube (i.d. 35 mm) with two stainless steel electrodes (o.d. 30 mm). The system was evacuated by a vacuum pump. When the pressure was adjusted to 50-100 Pa, the glow discharge plasma was initiated by applying approximately 900 V to the electrode using a high voltage amplifier (Trek, 20/20B). Argon (>99.999%) was used as the plasma-forming gas. The signal input for the high voltage amplifier was supplied by a function/arbitrary waveform generator (Hewlett-Packard 33120A) with a 100 Hz square wave. The current was about 4.5 mA. Each plasma reduction operation took 10 min, and each sample was reduced 6 times, with manual mixing of the sample between reduction operations to ensure even exposure to the plasma. A drop of water was added to the sample before each plasma operation. The gas temperature of the plasma was measured by infrared (IR) imaging (Ircon, 100PHT). The IR image indicated that the reduction occurred at ambient temperature.

2.2 Catalyst characterization

Porosities of the catalysts were tested with ChemBET-3000

using N_2 at 77 K, from which the adsorption-desorption isotherm was obtained. Brumauer-Emmett-Teller (BET) surface area and pore volume were obtained using nitrogen-BET equation, and the pore size distribution was calculated with the Horvath-Kawazoe method.

X-ray diffraction (XRD) patterns were recorded on a Rigaku Miniflex diffractometer using Cu K α radiation ($\lambda = 0.1543$ nm) at 30 kV and 15 mA, with a scan speed of 2° 2θ /min and a step of 0.02° 2θ , in a 30°–70° 2θ range.

X-ray photoelectron spectroscopy (XPS) analyses were performed using a Perkin-Elmer PHI-1600 spectrometer with Mg K α (1253.6 eV) radiation. The analyzer bandpass energy was 187.8 eV for survey spectra and 29.3 eV for high-resolution spectra. The binding energy was calibrated using the C_{1s} peak (284.6 eV) of adventitious carbon.

The transmission IR spectra were recorded on a Fourier transform infrared (FTIR) spectrometer (MAGNA-560, Nicolet) in the range of wave numbers of 4000–400 cm⁻¹ using the KBr pellet technique. The spectral resolution was 4 cm^{-1} and 100 scans were averaged for each spectrum.

Transmission electron microscopy (TEM) observations were conducted using a Philips Tecnai G^2 F-20 electron microscope.

2.3 Catalytic tests

Liquid-phase oxidation of D-glucose in alkaline solution proceeds as

$$C_6H_{12}O_6 + 1/2O_2 + NaOH \rightarrow C_6H_{11}O_7Na + H_2O$$

The reaction was carried out in a 250 mL four-necked glass flask equipped with mechanical stirring for threephase mixing, where 0.5 g catalyst and 100 mL glucose solution (0.4 mol/L) were added separately. Oxygen was bubbled into the solution at a constant flow rate of 400 mL/min. The overall reaction was carried out in a 50 °C water bath, and the pH value of the solution was maintained at 9.0 ± 0.2 by adding NaOH solution (1.0 mol/L) drop by drop, and detected by a pH electrode from HANNA Instruments.

Prior to reaction, nitrogen was blown into the solution to remove oxygen. When the flowing gas was switched to oxygen, the reaction started. The reaction proceeded continuously for 1 h. Oxygen gas was then stopped by blowing nitrogen instead for 15 min. The conversion could be calculated according to consumption of NaOH at the time.

The products of the reaction were analysed by a Finnigan Surveyor Plus high performance liquid chromatography (HPLC) equipped with a photo-diode array (PDA) detector. 5 mmol/L H_2SO_4 mixed in CH₃CN solution was used as the mobile phase, and 2 μ L filtration solution from the reaction mixture was injected into the columns to be analysed for 20 min. The selectivity was calculated using peak-area method.

3 Results and discussion

3.1 BET analyses

Table 1 shows the results of the BET analyses. The plasma reduced catalyst, denoted as Pd/AC-P, has the largest surface area among the three catalysts. The formaldehyde reduced catalyst, assigned as Pd/AC-F, presents the smallest surface area. This means the reduction using formaldehyde solution or hydrogen at elevated temperature induces a dramatic decrease in the catalyst surface area. The ambient temperature operation of the glow discharge plasma reduction is favored to preserve the pore structure of the activated carbon. In addition, during the plasma reduction, we did not use any other chemicals except argon. This helps to avoid side reactions, which would be harmful to the pore structure of the activated carbon.

3.2 XRD characterization

XRD patterns for the three samples are shown in Figure 1. The XRD patterns for all the samples show reflections at about $2\theta = 40.2^{\circ}$, 46.6° and 68.2°, indicating the existence of Pd(111), Pd(200) and Pd(220), respectively. The XRD characterization confirms that the argon glow discharge plasma can reduce the Pd/AC catalyst effectively at ambient temperature.

Figure 1 shows intense and sharp peaks of palladium reduced by flowing hydrogen and formaldehyde. This means that the Pd/AC-F and the hydrogen reduced catalyst, Pd/AC-H, have larger particle sizes. According to Scherr's equation, the average particle size for Pd/AC-F, Pd/AC-H and Pd/AC-P samples is 22.1, 17.6, and 6.8 nm, respectively. Evidently, the plasma reduction generates the smallest particles. From the activity tests, the particle size has a significant effect.

3.3 XPS results

Table 2 illustrates surface compositions of the catalysts from XPS results. Apparently, the relative content of palladium of Pd/AC-P was much higher than that of Pd/AC-F and Pd/AC-H, which indicates a migration of metal particles to the surface of carbon during the plasma reduction, or smaller particles with better dispersion were obtained from

Table 1 Structural properties of the catalysts



Figure 1 XRD patterns of AC, Pd/AC-F, Pd/AC-H and Pd/AC-P.

the plasma reduction. Failure to detect nitrogen species confirms a total conversion of the metal precursor. In addition, compared to the AC sample, the oxygen content significantly increases for Pd/AC-F, Pd/AC-H and Pd/AC-P samples. This indicates the impregnation and reduction processes induce an enrichment of oxygen content of all the carbon samples.

The C_{1s} peak can be deconvolved into a number of Gaussian peaks, including C–C (284.6 eV), C–O (286.2 eV), C=O (288.2 eV), O–C=O (289.9 eV), and π - π * shakeup (291.5 eV). Area ratios of the five deconvolved peaks are shown in Table 3 for the three samples, which suggests C–C bond is oxidized to generate new C–Ox groups on the surface after plasma reduction. The change becomes gradually weak in the sequence of C–O, C=O and O–C=O bonds [19].

3.4 IR analyses

Figure 2 shows the results of FTIR analyses and further confirms the change of oxygen-containing functional groups after the catalyst reduction. According to Figure 2, the catalyst reduction using formaldehyde or flowing hydrogen does not change the surface functionality notably. However, a remarkable change was observed after the plasma reduction. Figure 2 exhibits a large and wide peak centered at 3430 cm^{-1} that can be assigned to surface hydroxyl groups

	BET surface area (m^2/g)	Micropore area (m^2/g)	External surface area (m^2/g)	Micropore volume (cm^3/g)	External pore volume (cm^3/g)	Average pore size with HK method (nm)
AC	902.31	504.75	397.56	0.702	0.549	0.507
Pd/AC-H	749.87	480.90	268.97	0.614	0.471	0.412
Pd/AC-F	702.44	466.31	236.13	0.582	0.436	0.386
Pd/AC-P	890.33	501.87	388.46	0.696	0.545	0.498

 Table 2
 Surface composition of the catalysts

Catalwata	Surface components			Relative content	
Catarysis	С	0	Pd	Pd/C	O/C
AC	95.6	4.4	_	—	0.0460
Pd/AC-F	90.9	8.7	0.4	0.0044	0.0957
Pd/AC-H	91.3	7.4	1.3	0.0142	0.0811
Pd/AC-P	82.6	15.2	2.2	0.0266	0.1840

Table 3 Deconvolution of the C1s peaks for the catalysts

Catalysts	C–C	С–О	C=O	O-C=O peroxide	π - π^* shakeup
	284.6 eV	286.2 eV	288.2 eV	289.9 eV	291.5 eV
AC	69.06	17.45	5.68	4.11	3.69
Pd/AC-F	69.84	19.37	5.18	2.76	2.85
Pd/AC-H	66.29	19.49	5.23	4.61	4.38
Pd/AC-P	63.24	21.71	7.41	4.41	3.24



Figure 2 FTIR spectra of the catalysts.

or chemisorbed water [20]. This suggests that after the plasma reduction, the hydrophilic property of AC was significantly enhanced. The peak at 1390 cm⁻¹ represents thermally stable carboxyl carbonated structure [21], which apparently increased after the plasma reduction. Another peak enhancement is observed in the range of 1250-1000 cm⁻¹, which corresponds to cyclic ether groups [20]. In addition, there are more intense peaks of carbonyl groups at 1620 cm⁻¹ and 1570 cm⁻¹, suggesting that oxygen-containing groups are well combined with AC by plasma reduction, which is in accordance with XPS results.

3.5 TEM images

TEM images of Pd/AC-P, Pd/AC-H and Pd/AC-F are shown in Figure 3. The plasma reduced sample possesses uniform small metal particles with high dispersion, while the samples reduced by hydrogen and formaldehyde vary greatly in size and shape. Such difference is further illus-



Figure 3 TEM images of Pd/AC-P (a, b), Pd/AC-F (c, d) and Pd/AC-H (e, f).

trated in Figure 4 with the particle size distributions. Pd/AC-P apparently has smaller particles with an average size of 4.0–4.5 nm, while the average size of Pd/AC-F is 15.5–16.0 nm and it is 11.5–12.0 nm for Pd/AC-H. In addition, the distribution range of Pd/AC-P is much narrower than that of Pd/AC-F and Pd/AC-H, which may have significant impact on the reaction results.

3.6 Activity tests

Figure 5 and Table 4 present the results of glucose conversion as a function of time for Pd/AC-P, Pd/AC-H and Pd/AC-F catalysts. The activity of the plasma-reduced catalyst is much higher than that of Pd/AC-H and Pd/AC-F catalysts. Although the average selectivity of Pd/AC-P is slightly lower, the yield is much higher. The present study confirms that the size of the metal has a significant effect on the activity of glucose oxidation. The plasma reduction is a useful technology for size control, as previously confirmed for the investigations on the fuel cell catalyst and hydrogen storage material [1, 2].



Figure 4 Size distribution histograms of the catalysts.



Figure 5 Activity tests of the catalysts.

 Table 4
 Conversion at the time and average selectivity for the catalysts

Catalysts	Conversion in 1 h	Conversion in 2 h	Conversion in 3 h	Average selectivity
Pd/AC-F	31.75%	55.75%	73.00%	88.05%
Pd/AC-H	39.50%	61.00%	76.00%	87.40%
Pd/AC-P	92.25%	99.50%	100%	76.40%

4 Conclusions

The present work confirms that the glow discharge plasma could reduce the AC supported Pd catalysts. Compared to the catalysts reduced by hydrogen at elevated temperature and by formaldehyde, the plasma reduced Pd catalyst shows the smallest size with a narrow size distribution. This plasma reduced catalyst possesses the highest catalytic activity for the selective oxidation of glucose. Because Pd catalysts supported on AC have been extensively applied for fine chemical syntheses in industry and are normally reduced by chemicals, such as formaldehyde or even NaBH₄, the development of the room temperature plasma reduction will reduce the use of chemicals, which is a really green reduction technology and has a great potential for many other applications.

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- Wang Z, Yang FH, Yang RT. Enhanced hydrogen spillover on carbon surfaces modified by oxygen plasma. J Phys Chem C, 2010, 114: 1601–1609
- 2 Wang Z, Liu CJ, Zhang GL. Size control of carbon black-supported platinum nanoparticles via novel plasma reduction. *Catal Commun*, 2009, 10: 959–962
- 3 Li Y, Yang RT, Liu CJ, Wang Z. Hydrogen storage on carbon doped with platinum nanoparticles using plasma reduction. *Ind Eng Chem Res*, 2007, 46: 8277–8281
- 4 Wang LF, Yang RT. Hydrogen storage properties of carbons doped with ruthenium, platinum, and nickel nanoparticles. J Phys Chem C, 2008, 112: 12486–12494
- 5 Dimitratos N, Lopez-Sanchez JA, Hutchings GJ. Green catalysis with alternative feedstocks. *Top Catal*, 2009, 52: 258–268
- 6 Arcadi A. Alternative synthetic through new develoments in catalysis by gold. *Chem Rev*, 2008, 108: 3266–3325
- 7 Onda A, Ochi T, Kajiyoshi K, Yanagisawa K. A new chemical process for catalytic conversion of D-glucose into lactic acid and gluconic acid. *Appl Catal A*, 2008, 343: 49–54
- 8 Zhu JJ, Figueiredo JL, Faria JL. Au/activated-carbon catalysts for selective oxidation of alcohols with molecular oxygen under atmospheric pressure: Role of basicity. *Cata Commun*, 2008, 9: 2395–2397
- 9 Zhou Y, Wang S, Ding B, Yang Z. Preparation of onion-like Pd-Bi-Au/C trimetallic catalyst and their application. J Sol-Gel Sci Technol, 2008, 47: 182–186
- 10 Sievers C, Musin I, Marzialetti T, Olarte MBV, Agrawal PK, Jones CW. Acid-Catalyzed conversion of sugars and furfurals in an ionic-liquid phase. *ChemSusChem*, 2009, 2: 665–671
- 11 Gogova Z, Hanika J. Reactivation of a palladium catalyst during glucose oxidation by molecular oxygen. *Chem Papers*, 2009, 63: 520–526
- 12 Yin HM, Zhou CQ, Xu CX, Liu PP, Xu XH, Ding Y. Aerobic oxidation of D-glucose on support-free nanoporous gold. J Phys Chem C, 2008, 112: 9673–9678
- 13 Liang X, Liu CJ, Kuai P. Selective oxidation of glucose to gluconic acid over argon plasma reduced Pd/Al₂O₃. *Green Chem*, 2008, 10: 1318–1322
- 14 Lu J, Do I, Drzal LT, Worden RM, Lee I. Nanometal-decorated exfoliated graphite nanoplatelet based glucose biosensors with high sensitivity and fast response. ACS Nano, 2008, 2: 1825–1832
- 15 Mirescu A, Berndt H, Martin A, Prusse U. Long-term stability of a 0.45% Au/TiO₂ catalyst in the selective oxidation of glucose at optimised reaction conditions. *Appl Catal A*, 2007, 317: 204–209
- 16 Ishida T, Kinoshita N, Okatsu H, Akita T, Takei T, Haruta M. Influence of the support and the size of gold clusters on catalytic activity for glucose oxidation. *Angew Chem Int Ed*, 2008, 47: 9265–9268
- 17 Onal Y, Schimpf S, Claus P. Structure sensitivity and kinetics of D-glucose oxidation to D-gluconic acid over carbon-supported gold catalysts. J Catal, 2004, 223: 122–133
- 18 Liang X, Wang ZJ, Liu CJ. size-controlled synthesis of colloidal gold nanoparticles at room temperature under the influence of glow discharge. *Nanoscale Res Lett*, 2010, 5: 124–129
- 19 Tang S, Lu N, Wang JK, Ryu SK, Choi HS. Novel effects of surface modification on activated carbon fibers using a low pressure plasma treatment. *J Phys Chem C*, 2007, 111: 1820–1829
- 20 Lee D, Hong SH, Paek KH, Ju WT. Adsorbability enhancement of activated carbon by dielectric barrier discharge plasma treatment. *Surf Coat Technol*, 2005, 200: 2277–2282