Catalysis Letters
https://doi.org/10.1007/s10562-018-2409-1

Efficient Oxidation of Glucose into Gluconic Acid Catalyzed by Oxygen-Rich Carbon Supported Pd Under Room Temperature and Atmospheric Pressure

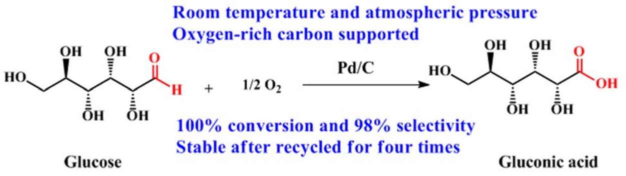
Anqiu Liu[1] · **Zhong Huang**[2] · **Xiaochen Wang**[1]

Received: 22 January 2018 / Accepted: 6 May 2018

Abstract

A new method has been developed for the oxidation of glucose into gluconic acid over Pd/C catalysts under the room temperature and atmospheric pressure. The carbon support was prepared by the hydrothermal treatment of renewable glucose, thus contained abundant active oxygen species. The Pd/C catalyst showed high catalytic activity towards the oxidation of glucose into gluconic acid. A 100% glucose conversion and a 98% gluconic acid yield were attained within 2 h at 0.1 MPa and room temperature. Structural analysis showed that the Pd paricle sizes of the catalysts were in the range of 10.1–16.2 nm influenced by the loading of Pd. The structure/size study showed that the catalyst with optimal particle size of 10.9 nm exhibited the highest TOF (0.2388 $mol_{glucose}$ mol_{Pd}/s). The catalyst showed no significant loss of activity after recycled for four times.

Graphical Abstract



Keywords Glucose · Gluconic acid · Aerobic oxidation · Carbon · Pd nanoparticles

1 Introduction

Due to the gradual decrease of the fossil-fuel resources, much effort has been devoted to search of renewable resources to supply chemicals and fuels for the society [1]. Biomass has been considered to be a promising alternative to fossil resource. Biomass is one of the most abundant renewable resources in the word. In addition, biomass can keep the carbon balance in the earth [2], as the released carbon dioxide from industry can be reconverted into biomass resources during the subsequent regrowth of biomass. To this context, a growing attention has been paid to develop various routes for the transformation of biomass resources into fuels and chemicals [3–5].

Glucose is the most abundant unit in the composition of biomass. Catalytic oxidation of glucose has been attracted a growing attention in recent years, as it yields important

---

Electronic supplementary material The online version of this article (https://doi.org/10.1007/s10562-018-2409-1) contains supplementary material, which is available to authorized users.

✉ Anqiu Liu
liuaq@hfuu.edu.cn

✉ Xiaochen Wang
wxc@hfuu.edu.cn

[1] Department of Chemistry and Materials Engineering, Hefei University, Hefei 230601, Anhui, People's Republic of China

[2] Hubei Xiangyun (Group) Chemical Industry Co., Ltd, Wuxue 435400, Hubei, People's Republic of China

biomass-derived chemicals such as gluconic acid and glucaric acids [6, 7]. Gluconic acid, as one of the most important oxidation products from glucose, has been widely used in the food and detergent industries as well as in cosmetics and medicine [8]. However, the selective oxidation of glucose into gluconic acid is challenging, due to the multifunctionality of the molecules. For example, the primary alcohol at C6 and the secondary alcohols at C2–C4 in glucose can also be oxidized, resulting in several kinds of by-products [9]. Furthermore, other reactions such as the over-oxidation reactions as well as isomerization of glucose can also occur [10].

Catalytic oxidation of glucose with molecular oxygen or air over heterogeneous catalysts is of great significance for the sustainable chemistry. The aerobic oxidation of glucose into gluconic acid was mainly performed over noble-metal catalysts such as Pd, Pt, and Au catalysts by the use of excess of base [11–18]. The supported Pt and Pd catalysts showed high catalytic activity towards the oxidation of glucose into gluconic acid, but these catalysts was not stable during the reaction process [19–22]. For example, Dirkx and Vanderbaan reported that the Pt/C catalyst deactivated fast, due to the formation of platinum oxide (PtO_2) [23]. Since the discovery of the activity of Au nanocluster by Haruta [18], Au catalysts have been extensively studied for the oxidation of glucose into gluconic acid during the last two decades [24–29]. Biella et al. reported that catalytic oxidation of glucose by Au/C with NaOH as base at 3 bar oxygen pressure and 323 K gave full glucose conversion with 99% of gluconic acid selectivity [28]. Recently, the Base-Free catalyst system has been developed for this reaction. For example, Yuan et al. reported that the aerobic oxidation of glucose catalyzed by Au/CMK-3 without base at 3 bar oxygen pressure and 383 K gave 92% glucose conversion with 80.5% of gluconic acid selectivity [25]. Acknowledging these important achievements, however, all of the present reaction systems needed to be heated (from 40 to 110 °C) or pressurized (from 2.3 to 50 bar) to ensure desirable gluconic acid selectivities at high glucose conversions. Therefore, it is constantly important to develop efficient methods for the oxidation of glucose into gluconic acid under room temperature and atmospheric pressure.

In recent years, carbon materials has been reported as a promising supports for the immobilization of metal nanoparticles, and applied in many types of chemical reactions due to the excellent properties of the carbon materials such as high electron conductivity and chemical inertness [30]. One distinct advantage of carbon materials is that they can be prepared from the abundant biomass. Compared with traditional active carbons, the carbon materials generated from the hydrothermal treatment of biomass bear abundant active oxygen species such as hydroxyl groups and carboxylic acid groups, which can anchor metal nanoparticles [31, 32] as well as promote the catalytic activity for oxidation [16], so the Pd immobilized on biomass derived carbon will be a efficient and stable catalyst for this reaction.

Herein, carbon material was prepared by the hydrothermal treatment of glucose and used for the immobilization of Pd nanoparticles, giving Pd/C catalyst. The Pd/C catalyst was used for the oxidation of glucose into gluconic acid (Scheme 1). This catalyst showed high catalytic activity and selectivity towards the oxidation of glucose into gluconic acid under room temperature and atmospheric pressure.

2 Experimental Section

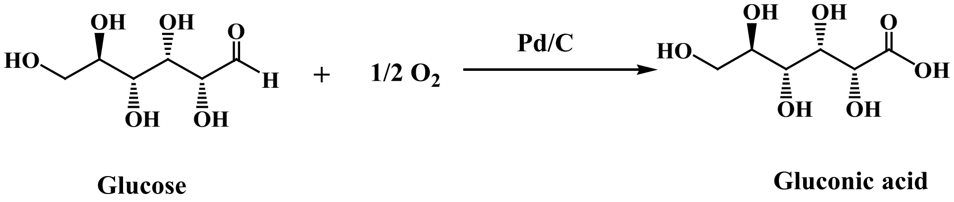
2.1 Materials

Glucose (99.5%) was purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Sodium tetrachloropalladate (Na_2PdCl_4, 98.0%), Palladium on activated carbon (Pd/AC, 5%) and gluconic acid were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). All the solvents were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). All the chemicals were analytical grade and used without further purification. Ultrapure water was used for the catalyst preparation and catalytic reactions.

2.2 Preparation of Carbon Supported Pd Catalysts

Firstly, the carbon microspheres were easily prepared by the hydrothermal treatment of glucose. Briefly, glucose (6.0 g) was dissolved in deionzed water (80 mL), and then the mixture was transferred into an autoclave, and then the mixture was heated at 200 °C for 12 h. After cooling to room temperature, the solid resides were recovered by filtration, and

Scheme 1 Schematic illustration of the oxidation of glucose into gluconic acid over Pd/C catalyst



washed with lots of water. Finally, it was dried in a vacuum oven to give carbon microspheres.

The decoration of Pd nanopartilces on the surface of carbon was performed by the solvent-thermal method. Typically, carbon microspheres (150 mg) were firstly homogeneously dispersed in ethylene glycol (40 mL) with the assist of ultrasonic for 1 h. Then Na_2PdCl_4 (30 mg) was added and the mixture was continually stirred for 10 min. Then the mixture was vigorously stirred at 105 °C for another 3 h. After cooling to room temperature, the mixture was filtrated and the solid catalyst was washed with large amounts of water to completely remove the physically absorbed Pd^{2+}. Finally, the catalyst was dried in a vacuum oven overnight, which was abbreviated as the Pd/C catalyst.

2.3 Catalyst Characterization

Transmission electron microscope (TEM) images were obtained using an FEI TecnaiG2-20 instrument. The sample powder were firstly dispersed in ethanol and dropped onto copper grids for observation. X-ray powder diffraction (XRD) patterns of samples were determined with a Bruker advanced D8 powder diffractometer (Cu Kα). All XRD patterns were collected in the 2θ range of 10–80° with a scanning rate of 0.016°/s. X-ray photoelectron spectroscopy (XPS) was conducted on a Thermo VG scientific ESCA MultiLab-2000 spectrometer with a monochromatized Al Kα source (1486.6 eV) at constant analyzer pass energy of 25 eV. The binding energy was estimated to be accurate within 0.2 eV. All BEs were corrected referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard. The Pd content in the Pd/C catalyst and in the reaction solution was quantitatively determined by inductively coupled atomic emission spectrometer (ICP-AES) on an IRIS Intrepid II XSP instrument (Thermo Electron Corporation).

2.4 Catalytic Oxidation of Glucose into Gluconic Acid

Glucose (1 mmol, 180 mg) and Na_2CO_3 (1 mmol, 106 mg) were added into 10 ml of water with a magnetic stirring to give a clean solution. Then, Pd/C (40 mg) was added to the mixture, and the reaction was started at room temperature by bubbling oxygen at a flow rate of 30 ml/min. After a certain time, the reaction was stopped. Then the catalyst was removed by centrifugation, and the liquid solution was analyzed by high performance liquid chromatography (HPLC).

2.5 Analytic Methods

Glucose and gluconic acid in the reaction solution were analyzed by HPLC. Glucose and gluconic acid were separated by a Whatman Partisil10 SAX column (250 × 4.6 mm, 5 μm), and detected by RI detector. The mobile phase was composed of an aqueous solution of 0.02 M H_3PO_4 and menthol with a volume ratio of (95:5) at the flow rate of 1.0 ml/min. The column oven temperature was maintained at 30 °C. The content of glucose and gluconic acid in samples was obtained directly by interpolation from calibration curves.

Glucose conversion and gluconic acid yield are defined as follows:

Glucose conversion = moles of glucose/moles of starting glucose × 100%

Gluconic acid yield = moles of gluconic acid/moles of starting glucose × 100%

2.6 Recycling of Catalyst

After reaction, the Pd/C catalyst was recovered via centrifugation and the spent catalyst was washed with excessive water to remove the physically absorbed chemicals. Then, it was dried in a vacuum over at 60 °C overnight. The spent catalyst was used for the next run under the same reaction conditions.

3 Results and Discussion

3.1 Catalyst Preparation and Characterization

The Pd/C catalyst was prepared in a facile and environmental-friendly way. As shown in TEM images of the Pd/C catalyst in Fig. S1, the carbon microspheres were clearly observed with a uniform size of 500 nm, and its surface was decorated with Pd nanoparticles. Under the hydrothermal conditions, the surface of the carbon spheres was enriched with oxygen functional groups such as hydroxyl groups and carboxylic acid groups [33].Then, the treatment of carbon microspheres with Na_2PdCl_4 in the ethylene glycol at 105 °C generated Pd nanoparticles on the carbon surface. The Pd weight percentage of the Pd/C-1 to Pd/C-3 catalyst were 1.8, 4.0 and 6.2% separately (Table 1). As shown in Fig. 1a–c, the average size of Pd nanoparticles measured by more than 100 particles of 10 photos increased from 10.1 to 16.2 nm

Table 1 The Pd(0) relative content of all the samples

Entry	Sample	% Pd (ICP)	% Relative content of Pd(0)
1	Pd/C-1	1.8	77.6
2	Pd/C-2	4.0	75.0
3	Pd/C-3	6.2	68.6
4	Pd/AC	5.0	86.7

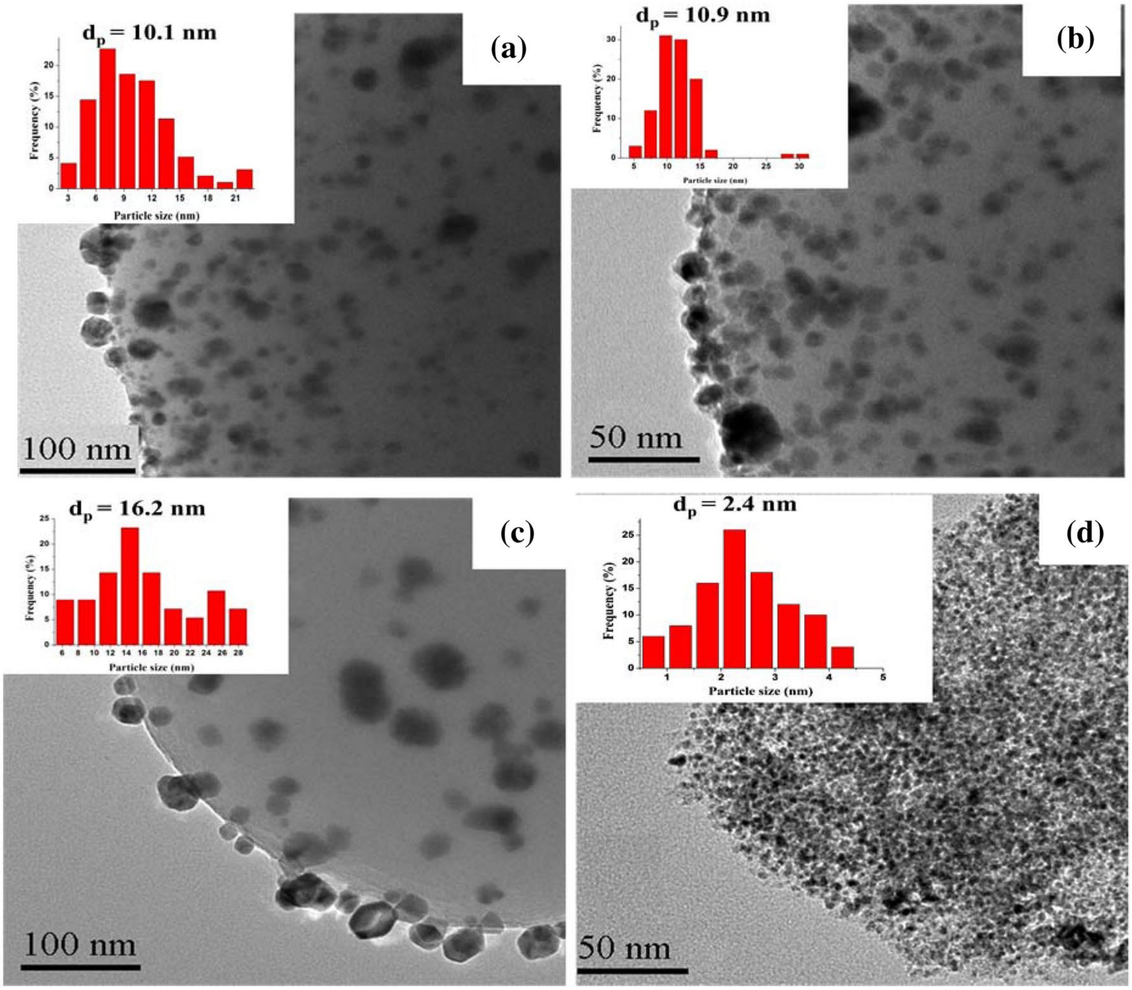


Fig. 1 TEM images of the **a** Pd/C-**1** catalyst, **b** Pd/C-**2** catalyst, **c** Pd/C-**3** catalyst, **d** commercial Pd/AC catalyst

when the loading of Pd increased from 1.8 to 6.2%. The Pd nanoparticles were homogeneously dispersed on the surface of carbon microspheres, which was caused by the strong interaction between the Pd nanoparticles with the oxygen-containing functional groups. However, some aggregation of Pd nanoparticles was also observed. The Pd nanoparticles of Pd/AC was also dispersed on the surface of carbon microspheres homogeneously with an obvious smaller particles size (Fig. 1d).

All catalysts were further characterized by XRD patterns, and the result was shown in Fig. 2. As we could see from the Fig. 2a, there were no characteristic peaks for carbon, indicating that carbon was amorphous with no crystalline structure. Sharp and well-defined peaks at 2θ values of 39.7°, 46.5°, and 68.9°were observed in the XRD spectrum of Pd/C (Fig. 2c–e), which were corresponded to the metallic Pd planes of (1 1 1), (2 0 0), (2 2 0), respectively, according to JCPDS No. 65-6174 [34]. The XRD peak intensity of Pd increased when loading of Pd increased (Fig. 2c–e).

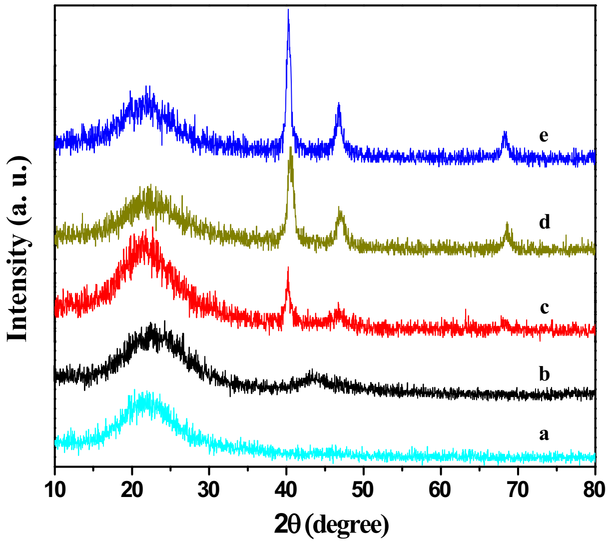


Fig. 2 XRD patterns of *a* C, *b* commercial Pd/AC, *c* Pd/C-1, *d* Pd/C-2, *e* Pd/C-3

The average Pd particle size of Pd/C-2 was estimated to be 10.8 nm by using the Scherrer equation [35] after background subtraction from Pd (1 1 1) peak at 2θ of 39.7°, which was consistent with TEM result. There were no characteristic peaks for Pd observed in the XRD spectrum of Pd/AC (Fig. 2b), indicating that the Pd particle size of Pd/AC was too small, which was corresponded to TEM result.

Figure 3A (a) shows the survey scan spectrum of the Pd/AC catalyst. It can be seen that there were only three peaks observed with the binding energy at 285.8, 532.8, and 339.4 eV, which were corresponded to C 1s, O 1s, and Pd 3d, respectively. Thus, it confirmed that the catalyst was consisted of Pd, C, and O with no other impurities. The survey scan spectrum of the Pd/C (Fig. 3A, b–d) showed the similar spectrum with that of Pd/AC, except with stronger O 1s intensity, which indicated that the surface of carbon microsphere synthesized from the hydrothermal reaction of glucose bears more oxygen-containing functional groups than active carbon (Fig. 3A, a). The oxygen containing groups have high affinity to anchor Pd nanoparticles for good electron donation ability. As the loading of Pd decreased, the XPS peak intensity of Pd also decreased (Fig. 3A, b–d), which was consisted with XRD. Figure 3B shows the Pd 3d high resolution XPS spectrum of Pd/C-1. As shown in the Fig. 3B, the Pd 3d core of Pd/C-1 level spectra contained two sets of doublets, one with binding energies (BEs) of 334.1 and 339.4 eV corresponding to $3d_{5/2}$ and $3d_{3/2}$ of Pd(0) [36], respectively, and the other with BEs of 335.5 and 340.4 eV corresponding to $3d_{5/2}$ and $3d_{3/2}$ of Pd(II), respectively. Therefore, the Pd species on the surface of Pd/C-1 sample is in a mixed-valence state of Pd(0) and Pd(II), and their relative content is 77.6% Pd(0) and 22.4% Pd(II) with dominant of Pd(0). The other samples shows similar high resolution XPS spectrum with Pd/C-1 (Fig. S2, a–c). As shown in Table 1, the Pd(0) species was found to be the majority Pd species of all the samples while there was also a few Pd(II) species exist. The relative content of Pd(0) decreases from when the loading of Pd increase (Table 1, entry 1–3).

3.2 Catalytic Oxidation of Glucose into Gluconic Acid Over Different Base

The activity of the Pd/C catalyst was evaluated by the oxidation of glucose with the use of molecular oxygen at room temperature. As base is usually necessary to promote the oxidation of glucose into gluconic acid. Therefore, the reaction was initially carried out by the use of different kinds of base, and the results are shown in Table 2. No glucose conversion was observed in the absence of base (Table 2, Entry 1), suggesting that base was crucial for the oxidation

Table 2 The results of glucose oxidation by the use of different base

Entry	Base	Base amount (mmol/ml)	Glucose conversion (%)	Gluconic acid yield (%)	Gluconic acid selectivity (%)
1	–	–	0	0	0
2	NaOH	0.15	100	65.4	65.4
3	Na_2CO_3	0.075	88.9	86.4	97.2
4	$KHCO_3$	0.15	88.2	87.0	98.6
5	K_2HPO_4	0.15	5.9	5.6	94.5
6	Pyridine	0.15	0	0	0
7[a]	Na_2CO_3	0.075	0	0	0

Reaction conditions: Glucose (270 mg, 1.5 mmol), Pd/C-2 catalyst (40 mg) and a setting amount of base were added into 10 ml of water, and the reaction was started at room temperature with oxygen flow rate of 30 ml/min for 30 min

[a] The reaction was carried out without catalyst (blank test)

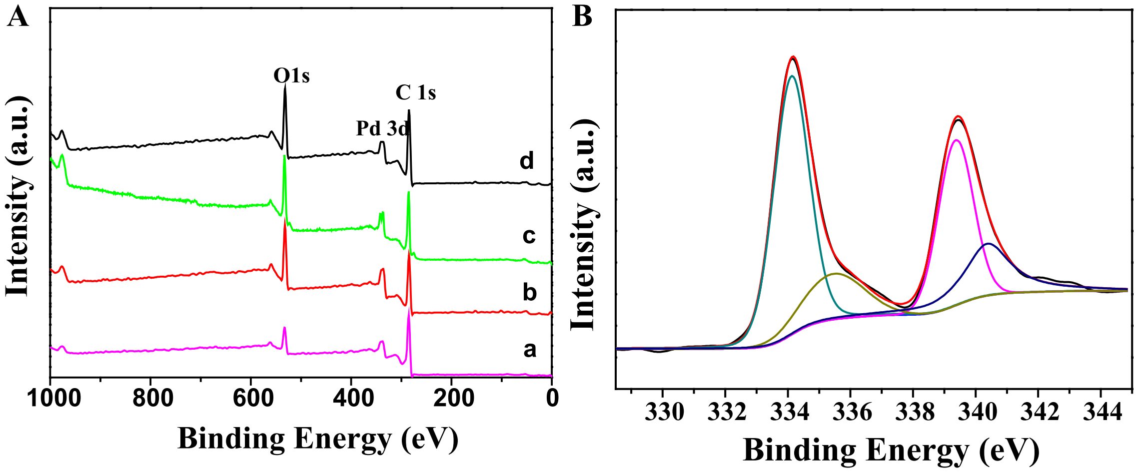


Fig. 3 **a** Full XPS spectrum of *a* Pd/AC, *b* Pd/C-3, *c* Pd/C-2, *d* Pd/C-1. **b** The high resolution of Pd3d XPS spectra for Pd/C-1

of glucose into gluconic acid. The base would play a role in the cleavage of C–H bond of the –CHO group in glucose molecule, which is an important process during the oxidation of aldehyde group to carboxylic group [23]. Therefore, various bases were used for the oxidation of glucose. Full glucose conversion was achieved after 1 h at room temperature when 1.5 mmol of NaOH was used. However, gluconic acid yield was only 65.4%, suggesting much more side reactions occurred. In fact, it is reported that glucose started to decompose in a strong alkaline solution at pH above 11 [23]. In fact, the initial pH reaction solution with NaOH was determined to be 13.2 by a pH detector, while the pH of other reaction solution was below 9. Therefore, much more side reactions occurred when the reaction was performed by the use of NaOH. That is the possible reason why the reaction solution was kept at a low constant pH value when catalytic oxidation of glucose was performed by the use of NaOH as base [37, 38]. High selectivity of gluconicacid was achieved when other base such as Na_2CO_3, $NaHCO_3$ and K_2HPO_4 were used (Table 2, Entries 2–4). However, the oxidation of glucose over K_2HPO_4 produced a very low conversion.

The organic base was also used for the oxidation of glucose over Pd/C catalyst. No glucose conversion was observed when pyridine was used. Two possible reasons should be accounted for this. On the one hand, the pH of the reaction solution was low. On the other hand, pyridine showed a strong coordination ability to metal due to its lone electron pairs, thus it might block the catalytic sites of the Pd/C catalyst. These results suggested that the catalytic activity and product selectivity was greatly affected by the kind of base. Na_2CO_3 and $NaHCO_3$ were proved to be the best bases for the oxidation of glucose into gluconic acid.

3.3 Effect of Glucose Concentration on the Oxidation of Glucose

To get more insight into the oxidation of glucose into gluconic acid, the oxidation of glucose was carried out with different concentration of glucose. Figure 4 depicted the effect of glucose concentration on the glucose conversion rate and the gluconic acid formation rate. The initial rates (R_0) were linearly proportional to the amount of glucose concentration in the range from 0.125 to 0.175 mol/l. These results suggested that the absorption of glucose on the surface of Pd/C catalyst should be rate-determining step for the oxidation of glucose into gluconic acid. However, as the concentration beyond 0.2 mol/l (Fig. 4), the gluconic acid formation rate seemed reaching a plateau, suggesting that the surface catalytic site of 20 mg of Pd/C catalysts was saturated by glucose molecules. It is notable that the gluconic acid formation rate was lower than the conversion rate from 0.2 to 0.28 mol/l, suggesting that absorption rate become higher than the reaction rate when the concentration exceed 0.2 mol/l, lead to the false calculated glucose conversion.

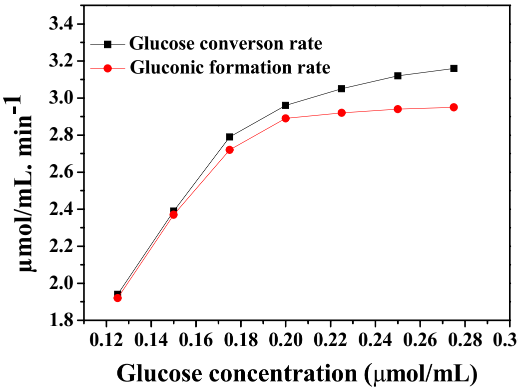


Fig. 4 The effect of glucose concentration on the oxidation of glucose over Pd/C catalyst. Reaction conditions: A setting amount of glucose, Na_2CO_3(79.5 mg) and Pd/C-2 catalyst (20 mg) were added into 10 ml of water, and the reaction was started at room temperature with oxygen flow rate of 30 ml/min for 30 min

Table 3 The reaction rate of glucose oxidation with different catalyst amount

Entry	Catalyst amount (mg)	Glucose consumption rate (μmol/ml/min)	Gluconic acid formation rate (μmol/ml/min)
1	5	0.60	0.59
2	10	1.21	1.18
3	20	2.39	2.37
4	30	3.62	3.55

Reaction conditions: glucose (270 mg, 1.5 mmol) and a setting amount of the Pd/C-2 catalyst were added into 10 mL of water, and the reaction was started at room temperature for 30 min with oxygen flow rate of 30 ml/min

In our reaction condition, the oxygen was purged from the bottom of the reactor at a flow rate of 20 ml/min, thus oxygen was excessive at a constant concentration. The reaction rate on glucose concentration can be expressed in the following equations:

$$r = k(\text{glucose})^a(O_2)^b = k_1(\text{glucose})^a(k_1 = k(O_2)^b)$$

As the reaction rate was linear to the concentration of glucose below 0.2 mol/l, the reaction order should be 1 with respect to glucose for glucose oxidation over Pd/C catalyst.

3.4 Effect of the Catalyst Amount on the Oxidation of Glucose into Gluconic Acid

The effect of the catalyst amount on the glucose oxidation into gluconic acid was studied, and the results are shown in Table 3. It can be seen that the reaction rate showed a linear relationship with the amount of the Pd/C catalyst in the initial reaction stage of 30 min. For example, glucose conversion rate was 0.60 μmol/ml/min by the use of 5 mg of Pd/C catalyst, and that proportionally increased to 3.62 μmol/ml/min by the use of 30 mg of Pd/C catalyst. The results were consistent with the results obtained with the results on the effect of glucose concentration on the glucose conversion rate (3.3). At a constant glucose concentration, the higher reaction rate with a higher catalyst loading should be due to the fact that much more catalytic sites were present with a higher catalyst loading, thus leading to a higher reaction rate.

3.5 Effect of Base Amount on the Oxidation of Glucose into Gluconic Acid

In order to get more insights into the effect of base on the oxidation of glucose into gluconic acid, the oxidation of glucose was carried out with different amount of Na_2CO_3, and the results are shown in Fig. 5. Interestingly, a linear relationship was observed between the concentration of Na_2CO_3 and gluconic acid formation rate when the base of Na_2CO_3 concentration increased from 0.025 to 0.075 mmol/ml. These results indicated that the reaction rate was depended on the concentration of base. According to the reported mechanism of the glucose oxidation, glucose firstly absorbed on the surface of the catalyst, and then the dehydrogenation of glucose yielded gluconolactone. The absorbed gluconolactone then desorbed from the catalytic surface by the hydrolysis with OH^-. Then the next cycle of the oxidation of glucose occurred on the surface of Pd/C catalyst. Therefore, the reaction rate of glucose oxidation depended on the amount of base. However, gluconic acid yield decreased gradually when Na_2CO_3 concentration increased from 0.1 to 0.2 mmol/ml, while the conversion of glucose increased gradually with the increase of Na_2CO_3 concentration. The reason should be that the higher concentration of Na_2CO_3 resulted in much more serious degradation of glucose. Thus, one equiv. amount of Na_2CO_3 can promote the oxidation of glucose into gluconic acid with a high selectivity and an acceptable conversion rate.

3.6 Time Course of the Oxidation of Glucose into Gluconic Acid

Figure 6 shows the time course of oxidation of glucose into gluconic acid over Pd/C catalyst. It can be seen that glucose conversion increased gradually with the increase of the reaction time, and the yield of gluconic acid increased gradually with the increase of the reaction time. It is noted that glucose consumption rate or gluconic acid formation rate was sharper in the early reaction stage than that obtained in the latter reaction stage. The reason is glucose concentration was higher in the initial reaction stage than that of the latter reaction stage. The highest gluconic acid yield of 98% and the glucose conversion of 100% were obtained after 2 h at room temperature.

Further increasing the reaction time from 2 to 6 h, gluconic acid yield was constant at 98% without degradation or further oxidation to other product such as glucaric acid. Therefore, the high selectivity of gluconic acid may due to the following two reasons. On the one hand, the use of stoichiometric amount of base did not cause the degradation of glucose. On the other hand, the oxidation product of gluconic acid was stable in our reaction system.

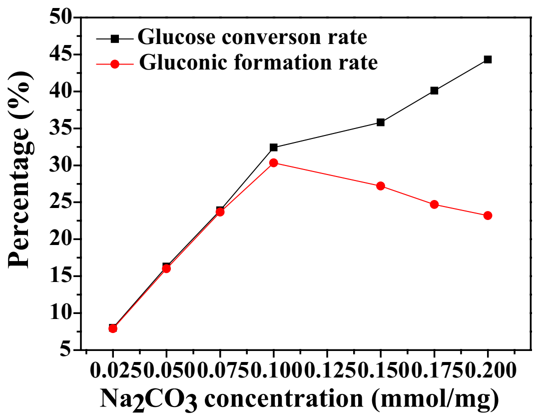


Fig. 5 The results of glucose oxidation with different amount of Na_2CO_3. Reaction conditions: glucose (270 mg, 1.5 mmol), Pd/C-2 catalyst (20 mg) and a setting amount of Na_2CO_3 were added into 10 ml of water, and the reaction was started at room temperature for 30 min with oxygen flow rate of 30 ml/min

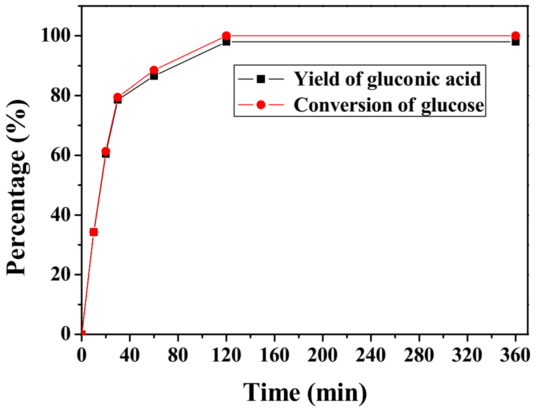


Fig. 6 Time cause of the glucose oxidation into gluconic acid over Pd/C-2 catalyst. Reaction conditions: glucose (270 mg, 1.5 mmol), Na_2CO_3 (80 mg, 0.75 mmol) and Pd/C-2 catalyst (40 mg) were added into 10 mL of water, and the reaction was started at room temperature with oxygen flow rate of 30 ml/min

3.7 Recycling Study of the Oxidation of Glucose into Gluconic Acid

The stability of the Pd/C catalyst was finally investigated. The oxidation of glucose into gluconic acid was used as the model reaction, and the reaction was performed at room temperature by the use of 40 mg of the Pd/C-2 catalyst. As shown in Fig. 7, it can be seen that glucose conversion and gluconic acid yield decreased only 9% for the 2th run which reduced to less than a half in the 3th run and stabilized in the 4th one, suggesting that the catalyst was stable [39]. Furthermore, the selectivity of gluconic acid was almost the same around 98%. It is reported that the lose of activity of Pd/C catalyst may due to over oxidation or leach of Pd/C catalys and so on [11, 16], however, ICP-AES detected that about 12% of Pd was lost in the spent catalyst after the fourth run, which indicated that the leach of Pd/C catalyst rather than the over oxidation of Pd was the main cause of the loss of activity. Actually, we did find that the color of the reaction solution turned pale yellow after reaction, indicating that some Pd nanoparticles leached into the reaction solution. It is reported that the product of gluconic acid had strong affinity ability to the metallic Pd nanoparticles [20]. Therefore, the leach of Pd/C catalyst should be caused by the coordination of gluconic acid with Pd nanoparticles.

3.8 Catalytic Screen

The catalysts were tested for selective oxidation of glucose to gluconic acid at room temperature. Figure 8 gives the conversions as a function of time for all the samples. It can be seen that the all the Pd/C catalysts can provide more than 60% conversion within 2.5 h while Pd/AC can only provide a conversion less than 40%. Furthermore, The activity of all the catalyst were evaluated by using turn-over-frequency (TOF) values(TOF = moles glucose/moles Pd × s × dispersion converted) calculated taking into account the palladium dispersion estimated from the average palladium particle size deduced from TEM [29, 39] and mathematically modeled for sphere particles and the real Pd contents measured from ICP (Table 4). As shown in Table 4, The TOF values of Pd/C catalyst (entry 1–3) were about 26–32 times higher than that of Pd/AC (entry 4), suggesting that the Pd/C catalysts have higher activity than Pd/AC. This may due to both the particle size of Pd and the character of supports. It is reported that the stability and reactivity of the catalysts for this oxidation reaction is strongly influenced by particle size of the noble metal [29, 39]. For example, Besson reported that Pd particles smaller than 2 nm had a high affinity to oxygen and deactivated fast [11], Haynes reported that the metal size of Pd/CB Catalysts with 7 nm Pd particles size exhibit highest activity in glucose oxidation [19]. As we can see from the TEM of all the samples (Fig. 1), the Pd particles size of Pd/AC was only 2.4 nm, which could loss of activity for over oxidation, while the Pd particles size of Pd/C are relatively larger (10.1–16.2 nm), which could avoid over oxidation and became more stable and active to this reaction. It is notable that the Pd/C-2 showed the best activity which was comparable with Pd/C-1 but obvious higher than Pd/C-3. This may also due to the Pd particles size for Pd/C-2 has almost the same Pd particles size with Pd/C-1 while relatively smaller than Pd/C-3 (Table 4, entry 1–3). The result suggest that larger Pd particles size may increase the stability of this catalyst, but may decrease the activity, so the Pd/C with Pd particles size of 10.9 nm may be a optimized one. The catalytic activity may also influenced by the

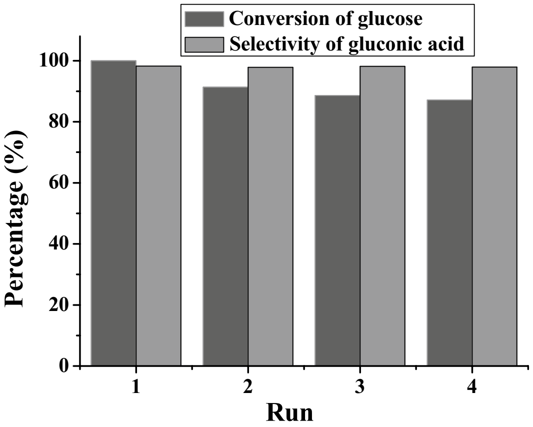


Fig. 7 The results of the recycling of the Pd/C-2 catalysts. Reaction conditions: glucose (270 mg, 1.5 mmol), Na_2CO_3(80 mg, 0.75 mmol), Pd/C-2 catalyst (40 mg)were added into 10 ml of water, and the reaction was started at room temperature for 2 h with oxygen flow rate of 30 ml/min

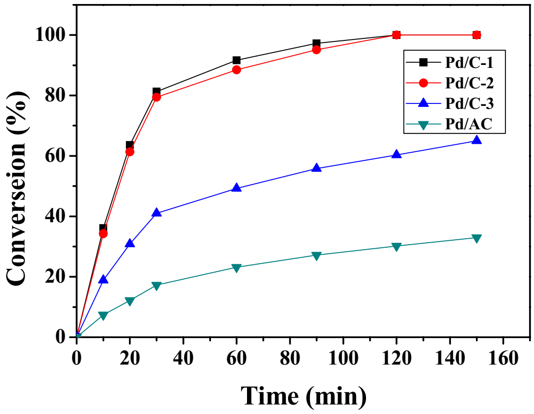


Fig. 8 Time cause of the glucose oxidation into gluconic acid of all catalyst. Reaction conditions: glucose (270 mg, 1.5 mmol), Na_2CO_3 (80 mg, 0.75 mmol) and and a setting amount of catalyst in glucose/Pd molar ratio of 100 were added into 10 ml of water, and the reaction was started at room temperature with oxygen flow rate of 30 ml/min for 2.5 h

Table 4 The results of glucose oxidation by the use of different catalysts

Entry	Sample	% Pd (ICP)	Average particle size (from TEM), nm	Glucose conversion (%)	Selectivity of gluconic acid (%)	Dispersion (%)	TOF, $s - 1 \times 10^3$
1	Pd/C-1	1.8	10.1	91.64	98.1	11.1	229.3
2	Pd/C-2	4.0	10.9	88.53	98.0	10.3	238.8
3	Pd/C-3	6.2	16.2	49.23	99.1	6.9	198.1
4	Pd/AC	5.0	2.4	23.14	96.8	46.7	7.49

Reaction conditions: glucose (270 mg, 1.5 mmol), Na_2CO_3 (80 mg, 0.75 mmol) and a setting amount of catalyst in glucose/Pd molar ratio of 100 were added into 10 ml of water, and the reaction was started at room temperature with oxygen flow rate of 30 ml/min for 1 h

character of supports. It is reported that the carbon materials bear abundant active oxygen species such as hydroxyl groups and carboxylic acid groups, which can anchor metal nanoparticles [31, 32] as well as promote the catalytic activity for oxidation [16]. As we can see from the XPS (Fig. 3), the carbon materials of Pd/C generated from the hydrothermal treatment of glucose bear obvious more oxygen than AC, which may increase both the activity and the stability of the catalysts. Additionally, the oxygen-rich carbon synthesized from glucose by hydrothermal method may benefits the absorption of glucose which contained lots of oxygen species such as hydroxyl groups and aldehyde groups, too. The improved absorption of glucose could promote the catalytic activity, as we had suggested that the absorption of glucose on the surface of Pd/C catalyst should be rate-determining step for the oxidation of glucose into gluconic acid when glucose concentration below 0.2 mol/l (Fig. 4). So the high activity of and stability our catalyst can be attributed to: (1) the relatively lager Pd particles size (10.1 ~ 16.2 nm) of our catalyst could be active and stable to this oxidation, (2) the support bears abundant oxygen species can anchor metal nanoparticles as well as promote the catalytic activity for oxidation, (3) the oxygen-rich carbon synthesized from glucose by hydrothermal method could benefits the absorption of glucose for chemical absorption.

Unprecedentedly, noble metals can efficiently convert glucose into gluconic acid at atmospheric pressure (Table 5, entries 2–7, 9), and even at the milder conditions of low temperature (40–70 C, 0.1 MPa; entries 13–17). Achieving high yield of gluconic acid at room temperature and

Table 5 Catalytic oxidation of glucose into gluconic acid/salt with O_2 as the oxidant[a]

Entry	Catalyst	T (K)	Oxidant	pH[c]	Catalyst ratio[b]	Time (h)	Con. (%)	Yield (%)	References.
1	Pd/C	298	30 ml/min (1 bar O_2)	<9	100	2	100	99	This work
2	Pd/CB	323	0.5 ml/min (1 bar O_2)	9	75	4	0–50	0–50	[19]
3	Pd/C	323	60 ml/min (1 bar air)	9.3	–	24	83	83	[12]
4	Pd/g-Al_2O_3-(P)	323	400 ml/min (1 bar $O_{2)}$	9	139	6	100	95	[20]
5	Pd/g-Al_2O_3-(C)	323	400 ml/min (1 bar O_2)	9	139	8	95	90.3	[20]
6	Pd–Bi/C	313	1.5 l/min (1 bar air)	9	787	2.6	99.6	99.4	[11]
7	Pd/HPS	353	100 ml/min (1 bar O_2)	<7.5	–	20	93.6	93.2	[21]
8[d]	Pt/C	413	50 bar air	–	–	1	63	46	[22]
9	Pt/HT	323	1 bar O_2	–	68	12	99	83	[14]
10	Au/TiO_2-SIM	433	3 bar O_2	–	438	1	71.1	67.3	[24]
11	Au/TiO_2-CIM	433	3 bar O_2	–	438	1	30.3	20.0	[24]
12	Au/CMK-3	383	3 bar O_2	–	1000	2	92	80.5	[25]
13	Au/TiO_2-DP	338	2.3 bar O_2	–	140	2	91	90	[18]
14	Au/ZrO_2-DP	338	2.3 bar O_2	–	140	2	89	88	[18]
15	Au/CeO_2-DP	338	2.3 bar O_2	–	140	2	89	87	[18]
16	Au/C	323	3 bar O_2	9.5	1000	0.5	100	99	[28]
17	Au/C	313	20 mL/min (1 bar O_2)	–	100	18	90	90	[29]

[a] All of the reactions were carried out in water in a batch reactor, except for entries 8

[b] The catalyst ratio = the molar ratio of glucose to the noble metal

[c] Some reactions were performed without pH control if there was no data in this column.

[d] The reaction was performed in a continuous flow reactor

atmospheric pressure is still extremely difficult so far for this reaction, though some Au/C catalysts exhibited excellent activity in the oxidation at low temperature (40–150 C) and oxygen pressure (0.1–0.3 MPa O_2). Actually, no report has appeared for a heterogeneous catalyst to promote the oxidation of glucose to gluconic acid under room temperature and atmospheric pressure at high activity and selectivity with O_2 as the oxidant [40]. Compare to Au/C catalysts (entries 16, 17), our catalyst has a comparable activity and selectivity but with a more mild condition (entry 1).

4 Conclusion

In summary, this paper has successfully prepared a series of glucose derived carbon supported Pd catalysts, which showed a high catalytic activity towards the oxidation of glucose with molecular oxygen at room temperature atmospheric pressure, while other catalyst systems needed to be heated or pressurized. The structure/size study showed that the Pd/C-2 had the highest TOF (0.2388 $\mathrm{mol_{glucose}\ mol_{Pd}/s}$) with optimal particle size of 10.9 nm. Full glucose conversion and high gluconic acid yield of 98.0% were obtained as Pd/C-2 was used for catalyst in a short reaction time of 2 h at room temperature and 0.1 Mpa O_2. The catalysts showed a good recyclability with only 13% loss of activity after the 4th cycle. The high activity and stability of this catalyst can be attributed to three reasons: first, the relatively lager Pd particles size (average 10.9 nm) makes the catalyst more active and stable to this oxidation. Second, the carbon materials bear abundant oxygen-containing groups which could anchor metal nanoparticles as well as promote the catalytic activity for oxidation. Third, the oxygen-rich carbon synthesized from glucose by hydrothermal method could benefits the absorption of glucose.

Acknowledgements This work is financially supported by the National Natural Science Funds of China (Grant No. 21606066), Natural Science Research Project of Anhui Colleges (Grant No. KJ2015B1105907), Talent Research Fund Project of Hefei University (Grant No. 14RC05).

References

1. Han J (2017) Integrated process for simultaneous production of jet fuel range alkenes and N-methylformanilide using biomass-derived gamma-valerolactone. J Ind Eng Chem 48:173–179
2. Goswami SR, Dumont MJ, Raghavan V (2016) Microwave assisted synthesis of 5-hydroxymethylfurfural from starch in $AlCl_3•6H_2O$/DMSO/[BMIM]Cl system. Ind Eng Chem Res 55:4473–4481
3. Winoto HP, Ahn BS, Jae J (2016) Production of γ-valerolactone from furfural by a single-step process using Sn-Al-Beta zeolites: optimizing the catalyst acid properties and process conditions. J Ind Eng Chem 40:62–71
4. Burguete P, Corma A, Hitzl M, Modrego R, Ponce E, Renz M (2016) Fuel and chemicals from wet lignocellulosic biomass waste streams by hydrothermal carbonization. Green Chem 18:1051–1060
5. Eblagon KM, Pereira MFR, Figueiredo JL (2016) One-pot oxidation of cellobiose to gluconic acid. Unprecedented high selectivity on bifunctional gold catalysts over mesoporous carbon by integrated texture and surface chemistry optimization. Appl Catal B-Environ 184:381–396
6. Ye JS, Liu ZT, Lai CC, Lo CT, Lee CL (2016) Diameter effect of electrospun carbon fiber support for the catalysis of Pt nanoparticles in glucose oxidation. Chem Eng J 283:304–312
7. Bin DS, Wang H, Li JX, Wang H, Yin Z, Kang JL, He BQ, Li ZH (2014) Controllable oxidation of glucose to gluconic acid and glucaric acid using an electrocatalytic reactor. Electrochim Acta 130:170–178
8. Deng WP, Zhang QH, Wang Y (2014) Catalytic transformations of cellulose and cellulose-derived carbohydrates into organic acids. Catal Today 234:31–41
9. Röper H, Lichtenthaler FW (1991) Carbohydrates as organic raw materials. Wiley, Weinheim, p 267
10. Harris JW, Cordon MJ, Di Iorio JR, Vega-Vila JC, Ribeiro FH, Gounder R (2016) Titration and quantification of open and closed Lewis acid sites in Sn-Beta zeolites that catalyze glucose isomerization. J Catal 335:141–154
11. Besson M, Lahmer F, Gallezot P, Fuertes P, Fleche G (1995) Catalytic oxidation of glucose on bismuth-promoted palladium catalysts. J Catal 152:116–121
12. Santhanaraj D, Rover MR, Resasco DE, Brown RC, Crossley S (2014) Gluconic acid from biomass fast pyrolysis oils: specialty chemicals from the thermochemical conversion of biomass. ChemSusChem 7:3132–3137
13. Doluda VY, Tsvetkova IB, Bykov AV, Matveeva VG, Sidorov AI, Sulman MG (2013) D-glucose catalytic oxidation over palladium nanoparticles introduced in the hypercrosslinked polystyrene matrix. Green Process Synth 2:25–34
14. Tathod A, Kane T, Sanil ES, Dhepe PL (2014) Solid base supported metal catalysts for the oxidation and hydrogenation of sugars. J Mol Catal A-Chem 388:90–99
15. Kusema BT, Murzin DY (2013) Catalytic oxidation of rare sugars over gold catalysts. Catal Sci Technol 3:297–307
16. Ma C, Xue W, Li J, Xing W, Hao Z (2013) Mesoporous carbon-confined au catalysts with superior activity for selective oxidation of glucose to gluconic acid. Green Chem 15:1035–1041
17. Jin X, Zhao M, Vora M, Shen J, Zeng C, Yan WJ, Thapa PS, Subramaniam B, Chaudhari RV (2016) Synergistic effects of bimetallic $PtPd/TiO_2$ nanocatalysts in oxidation of glucose to glucaric acid: structure dependent activity and selectivity. Ind Eng Chem Res 55:2932–2945
18. Wang Y (2014) Insights into the stability of gold nanoparticles supported on metal oxides for the base-free oxidation of glucose to gluconic acid. Green Chem 16:719–726
19. Haynes T, Dubois V, Hermans S (2017) Particle size effect in glucose oxidation with Pd/CB catalysts. Appl Catal A Gen 542:47–54
20. Liang X, Liu CJ, Kuai P (2008) Selective oxidation of glucose to gluconic acid over argon plasma reduced Pd/Al2O3. Green Chem 12:1318–1322
21. Doluda VY, Tsvetkova IB, Bykov AV, Matveeva VG, Sidorov AI, Sulman MG, Valetsky PM, Stein BD, Sulman EM, Bronstein LM (2013) Polymer-protected Au-containing Bi- and trimetallic nanoparticles as novel catalysts for glucose oxidation. Green Process Synth 2:25–34
22. Koklin AE, Klimenko TA, Kondratyuk AV, Lunin VV, Bogdan VI (2015) Transformation of aqueous solutions of glucose over the Pt/C catalyst. Kinet Catal 56:84–88

23. Dirkx JMH, Baan HSVD (1981) The oxidation of gluconic acid with platinum on carbon as catalyst. J Catal 67:14–20
24. Cao YL, Liu X, Iqbal S, Miedziak PJ, Edwards JK, Armstrong RD, Morgan DJ, Wang JW, Hutchings GJ (2016) Base-free oxidation of glucose to gluconic acid using supported gold catalysts. Catal Sci Technol 6:107–117
25. Qi P, Chen S, Chen J, Zheng J, Zheng X, Yuan Y (2015) Catalysis and reactivation of ordered mesoporous carbon-supported gold nanoparticles for the base-free oxidation of glucose to gluconic acid. ACS Catal 5:2659–2670
26. Della Pina C, Falletta E (2011) Gold-catalyzed oxidation in organic synthesis: a promise kept. Catal Sci Technol 1:1564–1571
27. Delidovich IV, Moroz BL, Taran OP, Gromov NV, Pyrjaev PA, Prosvirin IP (2013) Aerobic selective oxidation of glucose to gluconate catalyzed by Au/Al2O3 and Au/C: Impact of the mass-transfer processes on the overall kinetics. Chem Eng J 223:921–931
28. Biella S, Prati L, Rossi M (2002) Selective oxidation of D-Glucose on gold catalyst. J Catal 206:242–247
29. Megías-Sayago C, Bobadilla LF, Ivanova S, Penkova A, Centeno MA, Odriozola JA (2018) Gold catalyst recycling study in base-free glucose oxidation reaction. Catal Today 301:72–77
30. Liu WJ, JiangH (2015) Development of biochar-based functional materials: toward a sustainable platform carbon material. Chem Rev 115:12251–12285 YuHQ) .
31. Hara M, Yoshida T, Takagaki A, Takata T, Kondo JN, Hayashi S, Domen K (2004) A carbon material as a strong protonic acid. Angew Chem Int Ed 43:2955–2958
32. Toda M, Takagaki A, Okamura M, Kond JN, Hayashi S, Domen K, Hara M (2005) Biodiesel made with sugar catalyst. Nature 438:178–178
33. Liu B, Ren YS, Zhang ZH (2015) Aerobic oxidation of 5-hydroxymethylfurfural into 2,5-furandicarboxylic acid in water under mild conditions. Green Chem 17:1610–1617
34. Wang Y, He Q, Ding K, Wei H, Guo J, Wang Q, O'Connor R, Huang X, Luo Z, Shen TD (2015) Multi walled carbon nanotubes composited with palladium nanocatalysts for highly efficient ethanol oxidation. J ElectroChem Soc 162:F755–F763
35. Monshi A, Foroughi MR, Monshi MR (2012) Modified scherrerequation to estimate more accurately nano-crystallite size using XRD. World J Nano Sci Eng 2:154–160
36. Mceleney K, Crudden CM, Horton JH (2009) X-ray Photoelectron spectroscopy and the auger parameter as tools for characterization of silica-supported Pd catalysts for the Suzuki-Miyaura reaction. J Phys Chem C 113:1901–1907
37. Baatz C, Decker N, Prüße U (2008) New innovative gold catalysts prepared by an improved incipient wetness method. J Catal 258:165–169
38. MirescuA BerndtH, MartinA PrüßeU (2007) Long-term stability of a 0.45% Au/TiO_2 catalyst in the selective oxidation of glucose at optimised reaction conditions. Appl Catal A-Gen 317:204–209
39. Megías-Sayago C, Santos JL, Ammari F, Chenouf M, Ivanova S, Centeno MA, Odriozola JA (2018) Influence of gold particle size in Au/C catalysts for base-free oxidation of glucose. Catal Today 306:183–190
40. Zhang ZH, Hube GW (2018) Catalytic oxidation of carbohydrates into organic acids and furan chemicals. Chem Soc Rev 47:1351–1390