

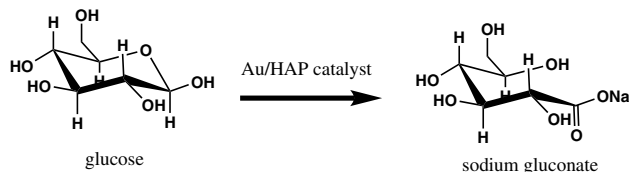
# Efficient Oxidation of Glucose into Sodium Gluconate Catalyzed by Hydroxyapatite Supported Au Catalyst

Xianxiang Liu<sup>1</sup>  · Yongjun Yang<sup>2</sup> · Shengpei Su<sup>1</sup> · Dulin Yin<sup>1</sup>

Received: 30 August 2016 / Accepted: 8 December 2016  
© Springer Science+Business Media New York 2016

**Abstract** Gold nanoparticles (NPs) with mean diameters of around 2 nm were successfully deposited onto the inorganic support hydroxyapatite to give the Au/HAP catalyst. The Au/HAP catalyst showed appreciably high catalytic activity for the aerobic oxidation of glucose to produce sodium gluconate at room temperature. Glucose conversions of 100% and sodium gluconate yield of 90.9% were achieved after 1 h at room temperature by the use of 0.5 equiv.  $\text{Na}_2\text{CO}_3$ . The developed catalytic system was easily-handled for the production of sodium gluconate. In addition, the Au/HAP catalyst was stable and could be reused for several times without the loss of its catalytic activity.

**Graphical Abstract** Au/HAP catalyst showed high activity and stability on the aerobic oxidation of glucose.



**Keywords** Biomass · Glucose · Sodium gluconate · Gold nanoparticles · Selective oxidation

## 1 Introduction

The widely available and renewable carbohydrates represent a promising alternative to fossil resources for the production of fine chemicals with high added value [1–3]. Glucose is the unit of C6 carbohydrates, which are abundant in nature. Thus, a great effort has been devoted to the catalytic transformation of glucose based carbohydrate into value added chemicals and high energy density liquid fuels such as 5-hydroxymethylfurfural, formic acid and gluconic acid via various kinds of chemical reactions [4–6].

Catalytic oxidation is an important kind of chemical reaction. Selective oxidation of glucose can generate several kinds of organic acids such as gluconic acid, 2-ketogluconic acid, and glucaric acid [7]. Among them, gluconic acid and its salts has been widely used in the food, pharmaceutical, paper and concrete industries, as well as water-soluble cleansing agents [8]. Currently, the industrial production of glucose is manufactured by the enzymatic oxidation of glucose or glucose-containing raw materials [9]. The biochemical method for the oxidation of glucose is efficient under mild conditions; however, this method still may demonstrate some serious economic and environmental disadvantages. For example, the enzymes are high cost and easily lose their catalytic activity. Thus, the replacement of biochemical method for the oxidation of glucose seems to be an attractive solution to the problem. There are many methods for the oxidation of glucose into gluconic acid such as the electrochemical method [10], catalytic chemical oxidation method [11], and photocatalytic oxidation method [12]. Among them, the catalytic oxidation of

✉ Xianxiang Liu  
lxx@hunnu.edu.cn

✉ Shengpei Su  
sushengpei@gmail.com

<sup>1</sup> National & Local Joint Engineering Laboratory for New Petro-chemical Materials and Fine Utilization of Resources, Key Laboratory of Chemical Biology and Traditional Chinese Medicine Research (Ministry of Education of China), College of Chemistry and Chemical Engineering, Hunan Normal University, Changsha 410081, Hunan, People's Republic of China

<sup>2</sup> Chenzhou Gao Xin Material Co., Ltd, Chenzhou 423000, Hunan, People's Republic of China

glucose particularly with the use of molecular oxygen as the terminal oxidant has received a great interest for the large-scale production of gluconic acid, as this method is economic and environmental-friendly.

Ideally, the chemical oxidation of glucose into gluconic acid should be performed in water under mild conditions, and the heterogeneous catalysts should be used in order to permit recycling. The heterogeneous catalysts used for the oxidation of glucose were mainly performed over noble metal catalysts such as Pd, Au, and Pt catalysts [13–17]. In early work, supported Pt and Pd catalysts, especially promoted with bismuth, showed high catalytic activity towards the aerobic oxidation of glucose in the presence of base [18, 19]. However, they were easily deactivated during the reaction, which was caused by the adsorption of reaction products and the oxygen poisoning on the active metal surface. Under slightly alkaline conditions with the timely consumption of the products and the addition of a second metal can be used to prevent the deactivation of the catalysts. Since the discovery of the Au catalysts towards chemical reactions [20], supported Au catalysts have been found to be remarkably active in glucose oxidation. During the last decade, gold-catalyzed oxidation of glucose has been extensively studied [21]. Some supported Au catalysts demonstrated both high catalytic activity and stability. For example,  $\text{Al}_2\text{O}_3$  supported Au catalyst ( $\text{Au}/\text{Al}_2\text{O}_3$ ) can be used for the continuously production of gluconic acid from glucose, and it showed a long-term stability under the reaction conditions. Thus, it makes supported gold catalysts the most likely candidates for the replacement of an enzyme catalysts in the industrial glucose oxidation [22].

Hydroxyapatite ( $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$ , denoted as HAP), a phosphate mineral with flexible structure, superior ion-exchange capacity, has been considered as more suitable carrier for a number of catalytic applications [23, 24]. Compared with other supports, HAP has been widely used for the immobilization of different metal nanoparticles for several types of chemical reactions [25–27]. For example, Venugopal and co-workers used HAP supported Ru catalysts for vapour phase hydrogenation of aqueous levulinic acid [26]. HAP has been identified as suitable support for Ru in the conversion of LA at ambient pressure, as Bronsted and Lewis acid sites in the HAP support was helpful to the dehydration. Zhang and co-workers have studied HAP-supported Pd nanoparticles ( $\text{Pd}/\text{HAP}$ ) for the oxidation of biomass-derived 5-hydroxymethylfurfural to 2,5-furandicarboxylic acid under mild conditions [27]. The high catalytic activity of the  $\text{Pd}/\text{HAP}$  catalyst was attributed to the small-sized Pd nanoparticles. The high stability of the  $\text{Pd}/\text{HAP}$  catalyst was due to the strong interaction of Pd nanoparticles and the HAP support. According to the previous reports, HAP has been identified as a good support of metal catalyst due to the following reasons: (i) Hydroxyapatite

can be a good support for several catalytic processes owing to its porous nature and for possessing both acidic and basic sites. (ii) HAP is a stable support under hot carboxylic acid (i.e., LA) unlike other conventional supports such as alumina and  $\text{MgO}$  [28]. In recent years, some supported Au catalysts have been studied for the oxidation of glucose [29, 30]. Some methods still suffers some disadvantages such as the harsh reaction conditions, and low selectivity. For example, Rossi and co-workers performed the oxidation of  $\text{CeO}_2$  supported Au catalysts, which produced a mixture products of gluconic acid, glucaric acid, glucuronic acid, 2-keto-gluconic acid and 5-keto-gluconic acid at  $150^\circ\text{C}$  [30]. Hence, it is still highly required to develop new methods for the oxidation of glucose into gluconic acid. To the best of our knowledge, it has received limited attention as supports for gold nanoparticles for the oxidation of glucose into gluconic acid. Herein, HAP supported Au catalyst ( $\text{Au}/\text{HAP}$ ) was prepared and used for the oxidation of glucose into sodium gluconate.

## 2 Experimental Section

### 2.1 Materials

Glucose (99.5%),  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$  were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China).  $\text{HAuCl}_4$  and sodium gluconate were purchased from Aladdin Chemicals Co. Ltd. (Beijing, China). All other reagents were purchased by local supplies (Changsha, China). All the solvents were freshly distilled before use. All the chemicals were of analytical grade and used without further purification. Ultrapure water was used for the catalyst preparation and catalytic reactions.

### 2.2 Catalyst Preparation

#### 2.2.1 Preparation of the HAP Support

HAP was prepared according to the known procedure with a slight modification [23].  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  (15.576 g, 0.066 mol) and a certain amount of  $\text{NH}_4\text{OH}$  were used to prepare 120 mL of solution A, making pH 11–12. Solution B (160 mL) was prepared with  $(\text{NH}_4)_2\text{HPO}_4$  (5.28 g, 0.04 mol) and a certain amount of  $\text{NH}_4\text{OH}$  with pH 11–12. The calcium solution was vigorously stirred at room temperature, and the phosphate solution was added drop wise over a period of 30 min to produce a milky, which was then stirred at  $90^\circ\text{C}$  in a water bath for 2 h. The precipitate was filtered, washed, dried at  $120^\circ\text{C}$  overnight.

### 2.2.2 Preparation of the Au/HAP Catalyst

Gold nanoparticles were deposited onto the support employing the homogeneous deposition–precipitation (HDP) method using urea as the precipitation agent as described in published procedures [23]. Typically, 1 g of HAP was dispersed in 30 mL of deionized water with the assist of ultrasonation for 30 min at room temperature.  $\text{HAuCl}_4$  solution (2.09 mL, 9.56 mg Au/mL) and 600 mg of urea were added (urea/Au=100, molar ratio) with the initial pH value of 7.6. The mixture was then stirred at 90 °C for 4 h. Under the basic conditions, the mixture of urea and  $\text{HAuCl}_4$  showed no influence on the stability of HAP. After reaction, the solution of the reaction increased to 9.7, which was should be caused by the decomposition of urea into  $\text{NH}_3$ . Then the reaction mixture was filtrated and washed for several times with deionized water. The resulting solid product was dispersed in 30.0 mL of deionized water. And then 15.0 mL  $\text{NaBH}_4$  (10.0 equiv) in ethanol was added dropwise at room temperature. The color of the mixture immediately changed from yellow to red, indicating that metallic Au was formed after the addition of  $\text{NaBH}_4$ . After the addition of  $\text{NaBH}_4$ , the reaction mixture was further stirred for another 2 h. Then, the mixture was filtrated and washed with plentiful water and then dried at 60 °C overnight. The prepared catalyst was denoted as Au/HAP, a red powder. The Au loading on Au/HAP was determined to be 1.57 wt.% by ICP-AES analysis.

### 2.3 Catalyst Characterization

Transmission electron microscope (TEM) images were obtained using an FEI Tecnai G<sup>2</sup>-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 K $\alpha$ ). All XRD patterns were collected in the 2 $\theta$  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 K $\alpha$  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 binding energies (Bes) were corrected referencing to the C1s (284.6 eV) peak of the contamination carbon as an internal standard. Elemental analysis was performed by a doublefocusing inductively coupled plasma mass spectrometer (ICP–MS, ELEMENT2). All measurements were made using a Scott-type spray chamber operating at room temperature and a Meinhard concentric nebulizer. The catalyst samples were dissolved in  $\text{HNO}_3$ .

CO chemisorption measurements were carried out on home-made equipment. apparatus from Micromeritics. The

samples (about 150 mg) were degassed at 110 °C for 4 h under 133 mbar of pressure. They were then submitted to a pretreatment under He at 100 °C for 30 min. The catalysts were then reduced under hydrogen during 2 h at 100 °C. The hydrogen was evacuated during 2 h and once at room temperature again, CO was swept onto the samples. The Au dispersion was calculated by considering a surface Au:CO stoichiometry.

### 2.4 Catalytic Oxidation of Glucose into Sodium Gluconate

In a typical run, glucose (1.5 mmol, 270 mg) and Au/HAP (40 mg) was added to 10 mL of water with a magnetic stirring. Then,  $\text{Na}_2\text{CO}_3$  (0.75 mmol, 80 mg) was added to the mixture and the reaction was started at room temperature by bubbling molecular oxygen (30 mL/min). After a certain reaction time, the Au/HAP catalyst was removed by centrifugation. Then the liquid solution was acidified with 0.05 M/L HCl until its pH <6. Finally, the liquid solution was analyzed by HPLC.

### 2.5 Analytic Method

Glucose and sodium gluconate in the reaction solution was analyzed by high performance liquid chromatography (HPLC). Glucose and sodium gluconate were separated by a Whatman Partisil10 SAX column (250×4.6 mm, 5  $\mu\text{m}$ ), and detected by R.I. detector. The mobile phase was composed of an aqueous solution of 0.02 M  $\text{H}_3\text{PO}_4$  and menthol with a volume ratio of (95:5) at the flow rate of 1.0 mL min<sup>-1</sup>. The column oven temperature was maintained at 30 °C. The content of glucose and sodium gluconate in samples was obtained directly by interpolation from calibration curves.

Glucose conversion and sodium gluconate yield are defined as follows:

Glucose conversion=(1–moles of glucose/moles of starting glucose)×100%.

Sodium gluconate yield=moles of sodium gluconate/moles of starting glucose×100%.

### 2.6 Recycling of the Catalyst

After reaction, the Pd/HAP catalyst was recovered via centrifugation and the spent catalyst was washed with excessive water to remove ant 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 Characterization of Au/HAP Catalyst

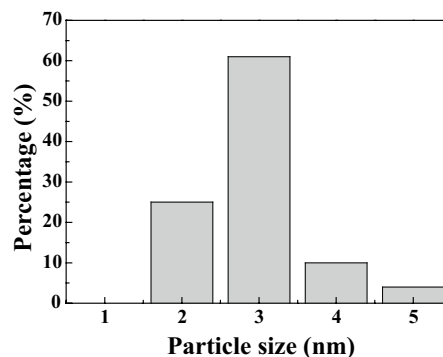
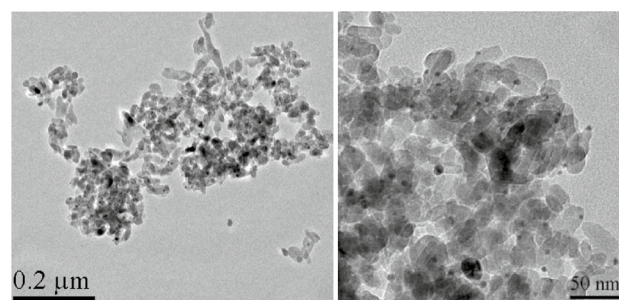
Firstly, the element composition of the as-prepared Au/HAP catalyst was studied by ICP. As shown in Table 1, the molar ratio of Ca to P was 5:3, which was the same as the initial molar ratio of  $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$  and  $(\text{NH}_4)_2\text{HPO}_4$ . The Au loading on Au/HAP was determined to be 1.57 wt.% by ICP-AES analysis. After reaction, this value remained the same, indicating that the catalyst was highly stable (as shown in Fig. 6). The as-prepared Au/HAP catalyst was then characterized by TEM images, and the typical image of Au/HAP is shown in (Fig. 1). It can be seen that HAP was presented in the form of Rod-like structure. Au nanoparticles were clearly deposited on the surface of the support. The average particle size of Au nanoparticles was calculated to be 3 nm by the measure of more than 200 particles of 20 photos. There was no apparent aggregation of Au nanoparticles on the surface of HAP.

The XRD pattern of the as-synthesized Au/HAP catalyst is further characterized by XRD technology, and the XRD patterns of the Au/HAP catalyst is shown in Fig. 2. These peaks with  $2\theta = 25.9^\circ, 31.9^\circ, 32.8^\circ, 34.0^\circ, 39.9^\circ, 46.7^\circ,$  and  $49.4^\circ$  were the characteristic peaks of HAP [31]. There results indicated that the decoration of Au nanoparticles did not change the structure of HAP, and the crystal structure of the HAP support was well maintained. In addition, a peak with  $2\theta = 38.2^\circ$  was also clearly observed, which is the characteristic peak of metallic Au, reflecting metallic Au nanoparticles were successfully formed and immobilized on the surface of the HAP. The particle size of Au nanoparticles was calculated to be 3.1 nm from the Scherrer equation, which was in good agreement with the TEM results.

XPS measurement is an important tool to further measure the composition of the catalyst and to verify the valance states of the elements. Figure 3 shows the XPS spectrum of the Au/HAP catalyst. As shown in (Fig. 3a), the peaks with the binding energy at 530.8, 439.5, 348.9, 236.2, 190.1, 133.2, 23.2 eV were assigned to O 1s, Ca 1s, Ca 2p, P 2s, P 2p, O 2s, respectively. These results indicated that the surface composition of the as-prepared catalyst was composed by elements O, Ca, and P. The XPS peak of Au 4f was too weak to be observed in (Fig. 3a), due to the low loading of Au in the Au/HAP

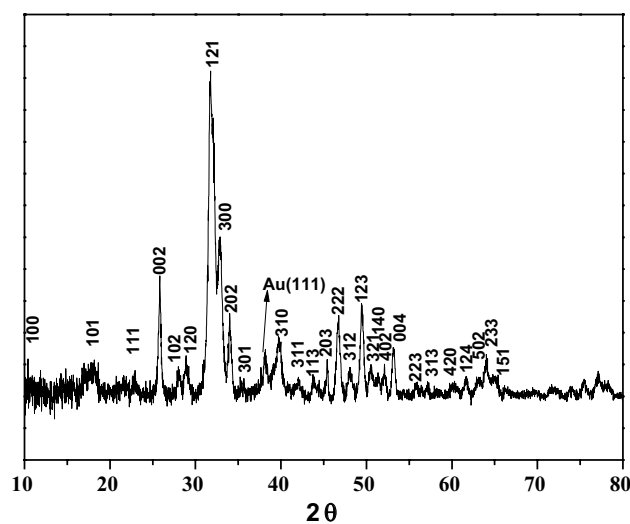
**Table 1** Elemental analysis of the Au/HAP catalyst

	Ca wt. %	P wt. %	Molar ratio of Ca/P	Au wt. %
Fresh catalyst	39.3	18.2	5:3	1.57
Spent catalyst	39.2	18.2	5:3	1.56

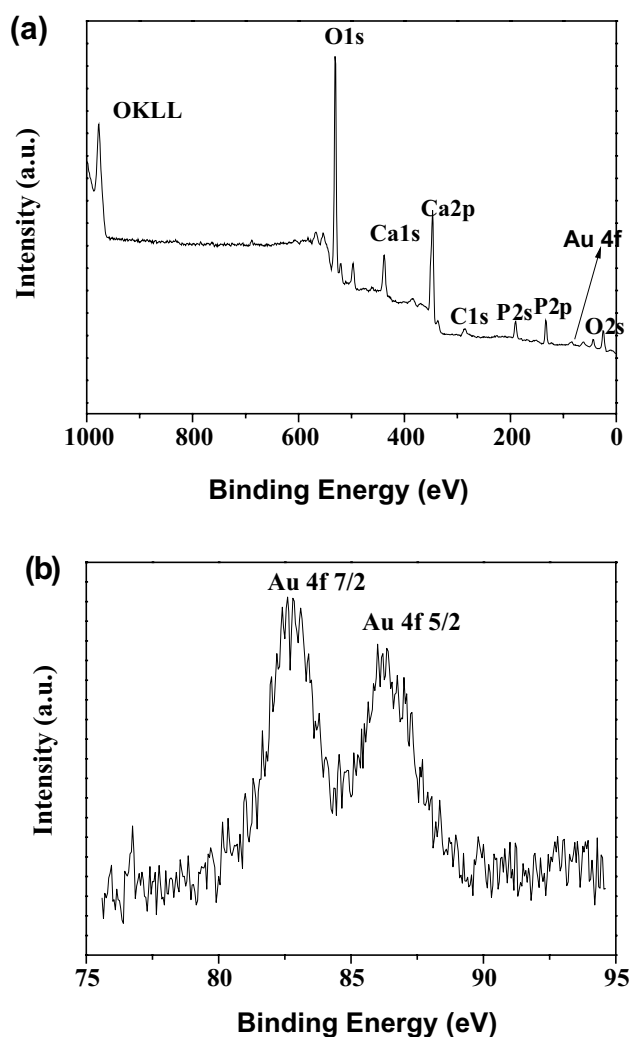


**Fig. 1** TEM images of the Au/HAP catalyst and particle size distribution

catalyst. The high resolution XPS spectrum of Au 4f region in the Au/HAP catalyst is shown in (Fig. 3b). Two well-separated peaks with the binding energy at about 83.0 and 86.6 eV were observed, which were assigned to the binding energy of Au  $4f_{7/2}$  and Au  $4f_{5/2}$  in metallic state.



**Fig. 2** XRD patterns of the Au/HAP catalyst



**Fig. 3** XPS spectra of the samples. **a** The survey scan of the Au/HAP catalyst, **b** Au 4f region

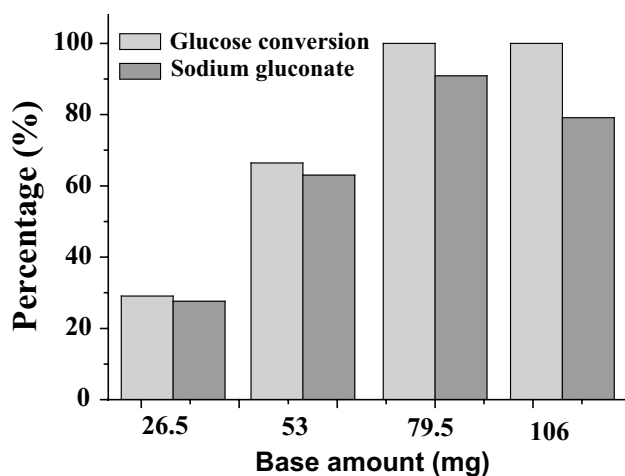
**Table 2** The results of glucose oxidation over Au/HAP catalyst by the use of various bases

Entry	Base	Glucose conversion (%)	Sodium gluconate yield (%)	Sodium gluconate selectivity (%)
1	–	–	–	–
2	Na <sub>2</sub> CO <sub>3</sub>	100	90.9	90.9
3	NaHCO <sub>3</sub>	100	91.1	91.1
4	NaOH	100	70.6	70.6
5	KH <sub>2</sub> PO <sub>4</sub>	41.5	38.1	91.8

*Reaction conditions* glucose (270 mg, 1.5 mmol) and base (1.5 mmol) were dissolved in 10 ml of water, and then the Au/HAP (40 mg) catalyst was added into the reaction mixture. The reaction was performed at room temperature for 1 h with the flush of oxygen at a rate of 30 ml/min

### 3.2 Catalytic Oxidation of Glucose Over Au/HAP Catalyst with Different Bases

Initially, the catalytic activity of Au/HAP catalyst was evaluated by the oxidation of glucose into sodium gluconate at room temperature. The use of base as additive is generally considered to be very crucial for the oxidation of glucose due to the following two reasons. On the one hand, the base is used to promote the oxidation of glucose into sodium gluconate over metal catalysts with the assist to capture the hydrogen in the aldehyde group. On the other hand, the base is used for the neutralization of the product gluconic acid to give gluconate salt, as gluconic acid has a strong affinity to absorb on the surface of the metal catalysts, which cause the metal catalysts deactivation during the reaction process. For example, we also carried out the oxidation of glucose over Au/HAP catalyst without the use of base, and no conversion of glucose was observed after 1 h at room temperature (Table 2, entry 1). For most cases, the oxidation of glucose into sodium gluconate was carried out at a constant pH by the continuous addition of NaOH solution. In order to simplify the reaction process, the oxidation of glucose over Au/HAP catalyst was carried out by the initial addition of base at a time. Table 1 shows the results of the glucose oxidation over Au/HAP catalyst by the use of different bases with the stoichiometric amount to neutralize the sodium gluconate. It is observed that the base showed a great effect on the catalytic activity towards the glucose oxidation. To our delight, goods results were achieved by the use of Na<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub>. Full glucose conversions and similar sodium gluconate yields were produced by the use of Na<sub>2</sub>CO<sub>3</sub> (0.5 equiv) and KHCO<sub>3</sub> (1.0 equiv) after 1 h at room temperature (Table 2, entries 2 and 3). Interestingly, it was noted that full glucose conversion was also observed by the use of NaOH, the sodium gluconate yield was only 70.6% (Table 2, entry 4), which was much lower than those obtained by the use of Na<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub>. It is reported that the glucose tended to undergo side reactions such as the degradation and the isomerization reactions when the pH of the reaction solution was beyond 11 [19]. However, the byproducts could not be detected under our reaction conditions. Furthermore, the degradation trend became more seriously at a higher pH. As a matter of fact, the pH of the reaction solution by the use of NaOH was calculated to be 13.2, while the pH of the reaction solution by the use of Na<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub> was low of 9. The oxidation of glucose by the use of KH<sub>2</sub>PO<sub>4</sub> produced a moderate sodium gluconate with a yield of 38.1% with glucose conversion of 41.5% (Table 2, entry 5). Therefore, taking the reaction rate and the selectivity into consideration, Na<sub>2</sub>CO<sub>3</sub> and KHCO<sub>3</sub> with moderate alkalinity were the best base for the oxidation of glucose into sodium gluconate over Au/HAP catalyst.



**Fig. 4** The results of glucose oxidation into sodium gluconate by the use of different amount of  $\text{Na}_2\text{CO}_3$ . *Reaction conditions* glucose (270 mg, 1.5 mmol) and a certain amount of base (1.5 mmol) were dissolved in 10 ml of water, and then the Au/HAP (40 mg) catalyst was added into the reaction mixture. The reaction was performed at room temperature for 1 h with the flush of oxygen at a rate of 30 ml/min

**Table 3** The results of catalyst amount on the oxidation of glucose

Entry	Catalyst amount (mg)	Glucose conversion (%)	Sodium gluconate yield (%)	Sodium gluconate selectivity (%)
1	10	14.1	13.3	94.3
2	20	27.7	25.3	91.3
3	30	38.6	35.1	90.9
4	40	45.1	41.6	92.2
5	50	50.8	45.2	88.8

*Reaction conditions* glucose (270 mg, 1.5 mmol) and  $\text{Na}_2\text{CO}_3$  (79.5 mg, 0.75 mmol) were dissolved in 10 ml of water, and then a certain amount of Au/HAP catalyst was added into the reaction mixture. The reaction was performed at room temperature for 10 min with the flush of oxygen at a rate of 30 ml/min

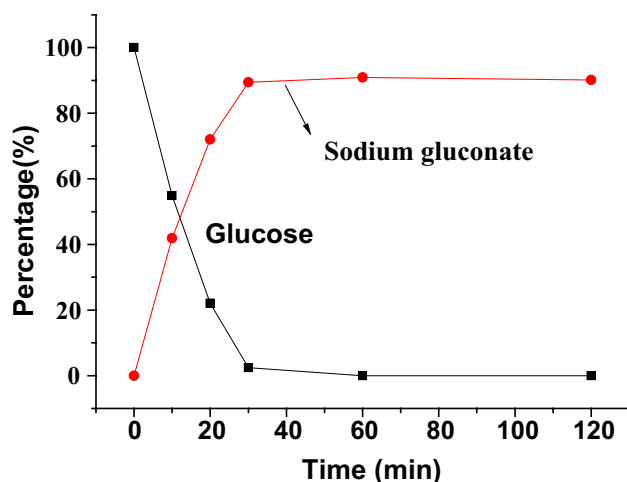
### 3.3 The Effect of Base Amount on the Oxidation of Glucose into Sodium Gluconate

As discussed above, the base showed a crucial effect on the oxidation of glucose into sodium gluconate. In order to give a clear insight into the effect of base on this reaction, the oxidation of glucose over Au/HAP catalyst was carried out with different amount of  $\text{Na}_2\text{CO}_3$ . As shown in Fig. 4, glucose conversion and sodium gluconate yield increased with the increase of the amount of  $\text{Na}_2\text{CO}_3$ . It is interesting to note that glucose conversion or sodium gluconate yield showed a linear relationship with the initial amount of  $\text{Na}_2\text{CO}_3$ . That means the reaction rate seemed to be depended on the amount of base. As discussed above,

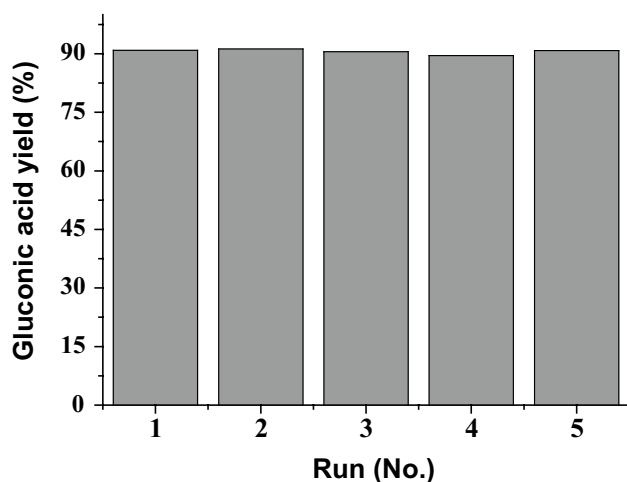
the base played two important roles in the oxidation of glucose into sodium gluconate. One role is the promotion of the catalytic oxidation reaction by the abstract of hydrogen atom in the aldehyde group. The other role is used to neutralize the sodium gluconate absorbed on the catalyst surface. Therefore, it is easily to understand that the glucose conversion and sodium gluconate yield increased with the increase of the catalyst amount in range from 26.5 to 79.5 mg (stoichiometric ratio). The best results were achieved using the stoichiometric amount of  $\text{Na}_2\text{CO}_3$  with 80 mg, which afforded glucose conversion of 100% and sodium gluconate yield of 90.9%. Further increasing to base amount to 106 mg, sodium gluconate yield decreased to 79.1%. The reason should be that a large amount of  $\text{Na}_2\text{CO}_3$  caused other side reactions, such as the isomerization of glucose into fructose and the degradation of glucose into other small organic molecules such as formic acid, acetic acid and so on [32]. In fact, a slight decrease of sodium gluconate selectivity was also observed with the increase of  $\text{Na}_2\text{CO}_3$  amount from 26.5 to 80 mg. Therefore,  $\text{Na}_2\text{CO}_3$  with the stoichiometric amount was the best conditions for the oxidation of glucose into sodium gluconate (Fig. 4).

### 3.4 The Effect of Catalyst Amount on the Oxidation of Glucose into Sodium Gluconate

The oxidation of glucose was carried out by the use of different amount of the Au/HAP catalyst in order to study the effect of the catalyst amount on the oxidation of glucose. The oxidation of glucose was carried out at room temperature for 10 min by the use of 0.5 equiv.  $\text{Na}_2\text{CO}_3$  (Table 3). It can be seen the reaction rate of glucose oxidation strongly depended on the catalyst amount, especially for the catalyst loading in a low range. For all cases, the higher the catalyst amount was, the higher the reaction rate was. The increase of the reaction rate with an increase of the catalyst loading should be due to that the much more catalytic sites of the higher loading Au/HAP. Increasing the amount of Au/HAP from 10 to 30 mg, the glucose conversion rate seems to be proportional to the catalyst loading, suggesting that the absorption of glucose onto the catalyst surface should be the rate determining step. Further increasing the Au/HAP amount beyond 30 mg, the glucose conversion rate also increased, but the increasing tendency gradually decreased. The reason should be that there is not sufficient amount of glucose to saturate the Au sites of the catalyst surface. Interestingly, it is noted that the selectivity of sodium gluconate was kept at a constant value around 90%. These results indicating that the catalyst amount showed no effect on the selectivity. The selectivity of glucose oxidation mainly influence by the concentration of base as described above.



**Fig. 5** Time course of glucose oxidation into sodium gluconate. *Reaction conditions* glucose (270 mg, 1.5 mmol) and  $\text{Na}_2\text{CO}_3$  (79.5 mg, 0.75 mmol) were dissolved in 10 ml of water, and then the Au/HAP (40 mg) catalyst was added into the reaction mixture. The reaction was performed at room temperature for 1 h with the flush of oxygen at a rate of 30 ml/min



**Fig. 6** The recycling experiments of the glucose oxidation into sodium gluconate over Au/HAP catalyst. *Reaction conditions* glucose (270 mg, 1.5 mmol) and  $\text{Na}_2\text{CO}_3$  (79.5 mg, 0.75 mmol) were dissolved in 10 ml of water, and then the Au/HAP (40 mg) catalyst was added into the reaction mixture. The reaction was performed at room temperature for 1 h with the flush of oxygen at a rate of 30 ml/min

### 3.5 Time Course of Glucose Oxidation into Sodium Gluconate

Time course of glucose oxidation into sodium gluconate over Au/HAP catalyst was recorded, and the results are depicted in Fig. 5. It can be seen that the Au/HAP catalyst was very active for the oxidation of glucose into sodium gluconate at room temperature. Glucose conversion of 45.1% and sodium gluconate yield of 39.7% were achieved

in a short reaction time of 10 min. It is observed that glucose was almost completely converted after 30 min. The glucose oxidation rate and the sodium gluconate formation rate in the initial stage were higher than those obtained in the latter reaction stage. The reason should be that glucose concentration was the highest in the initial reaction stage. With the reaction time course increasing, the concentration of glucose gradually decreased. Therefore, the reaction rate of glucose oxidation was slower at the later reaction stage. It is also noted that the sodium gluconate yield was almost kept stable around 90% from 30 to 120 min. Therefore, the side reactions during the oxidation of glucose into sodium gluconate were caused by the degradation of glucose not by the degradation of sodium gluconate. In addition, the stability of sodium gluconate is also one of the reasons for the high selectivity of glucose oxidation into sodium gluconate. Furthermore, we have also detected whether the  $\text{CO}_3^{2-}$  was introduced into the spent catalyst. The spent catalyst was treated with HCl, and  $\text{CO}_2$  was released. Then we collected the gas and quantified the amount of  $\text{CO}_2$  by Agilent MicroGC 7890B. The content of carbon in the spent catalyst was calculated to be 0.47 wt.%, suggesting a very little amount of  $\text{CO}_3^{2-}$  was introduced into the spent catalyst.

The dispersion of the as-prepared Au/HAP catalyst was determined to be 21% by CO chemisorption measurements. Thus the TOF values for the Au/HAP catalyst towards the glucose oxidation was calculated to be  $1.24 \text{ mol glucose molAu}^{-1} \text{ s}^{-1}$  at room temperature, which was a little lower than the mesoporous carbon-confined Au catalysts at  $40^\circ\text{C}$  [33].

### 3.6 Recycling of the Au/HAP Catalyst

Finally, the stability of the as-prepared Au/HAP was investigated. As discussed above, the highest sodium gluconate yield was achieved by the use of 0.5 equiv  $\text{Na}_2\text{CO}_3$  at room temperature with 40 mg of Au/HAP for 1 h. Thus, a repeated experiment was carried out to test the stability of the catalyst under these reaction conditions. After the first run, the Au/HAP catalyst was recovered via centrifugation at 10,000 rpm. Then the spent catalyst was washed thoroughly with deionized water and used in the successive run in wet form without drying. The second run was carried out under the same reaction conditions. As shown in Fig. 6, the catalyst showed a high stability without the loss of its catalytic activity.

## 4 Conclusion

In summary, an effective method was developed for the oxidation of glucose into sodium gluconate over Au/HAP catalyst. Several important parameters were studied for the

oxidation of glucose into sodium gluconate. It was found that the base played a crucial role in the conversion of glucose and the selectivity of sodium gluconate. High glucose conversion of 100% and sodium gluconate yield of 90.9% were produced after 1 h at room temperature by the use of 0.5 equiv.  $\text{Na}_2\text{CO}_3$ . More importantly, the Au/HAP catalyst could be recycled and reused for several times without the loss of its catalytic activity.

**Acknowledgements** This work was financially supported by the National Natural Science Foundation of China (No. 21606082).

## References

- Liu B, Zhang ZH (2016) *ChemSusChem* 9:2015–2036
- Gallezot P (2012) *Chem Soc Rev* 41:1538–1558
- Liu B, Zhang ZH (2015) *ACS Catal* 6:326–338
- Dutta S, Pal S (2014) *Biomass Bioenerg* 62:182–197
- Movil-Cabrera O, Rodriguez-Silva A, Arroyo-Torres C, Staser JA (2016) *Biomass Bioenerg* 88:89–96
- Agirrezabal-Telleria I, Gandarias I, Arias PL (2014) *Catal Today* 234:42–58
- Mallat T, Brönnimann C, Baiker A (1997) *Appl Catal A* 149:103–112
- Önal Y, Schimpf S, Claus P (2004) *J Catal* 223:122–133
- Hustedede H, Haberstroh HJ, Schinzig E (1989) *VCH Weinheim* 449–456
- Gros P, Bergel A (2005) *AICHE J* 51:989–997
- Deng WP, Zhang QH, Ye W (2014) *Catal Today* 234:31–41
- Bellardita M, Garcia-Lopez EI, Marci G, Megna B, Pomilla F R, Palmisano L (2015) *RSC Adv* 5:59037–59047
- Rautiainen S, Lehtinen P, Vehkamäki M, Niemelä K, Kemell M, Heikkilä M, Repo T (2015) *Catal Commun* 74:115–118
- An DL, Ye AH, Deng WP, Zhang QH, Wang Y (2012) *Chem Eur J* 18:2938–2947
- Santharaj D, Rover MR, Resasco DE, Brown RC, Crossley S (2014) *ChemSusChem* 7:3132–3137
- Koklin AE, Klimenko TA, Kondratyuk AV, Lunin VV, Bogdan VI (2015) *Kinet Catal* 56:84–88
- Delidovich IV, Moroz BL, Taran OP, Gromov NV, Pyrjaev PA, Prosvirin IP, Bukhtiyarov VI, Parmon VN (2013) *Chem Eng J* 223:921–931
- Nikov I, Paev K (1995) *Catal Today* 24:41–47
- Abadi A, van Bekkum H (1995) *J Mol Catal A* 97:111–118
- Haruta M (2003) *Chem Rec* 3:75–87
- Kusema BT, Tönnov T, Mäki-Arvela P, Salmi T, Willför S, Holmbom B (2013) *Catal Sci Technol* 3:116–122
- Mirescu A, Berndt H, Martin A, Prübe U (2007) *Appl Catal A* 317:204–209
- Sun H, Su FZ, Ni J, Cao Y, He HY, Fan KN (2009) *Angew Chem Int Ed* 48:4390–4393
- Choudary BM, Chidara S, Kantam ML, Venkanna GT, Bojja S (2005) *J Am Chem Soc* 127:9948–9949
- Zhang ZH, Yuan ZL, Tang DG, Ren YS, Lv KL, Liu B (2014) *ChemSusChem* 7:3496–3504
- Sudhakar M, Kumar VV, Naresh G, Kantam ML, Bhargava SK, Venugopal A (2016) *Appl Catal B* 180:113–120
- Zhang ZH, Zhen JD, Liu B, Lv KL, Deng KJ (2015) *Green Chem* 17:1308–1317
- Paul Lange J, Price R, Ayoub PM, Louis J, Petrus L, Clarke L, Gosselink H (2010) *Angew Chem Int Ed* 49:4479–4483
- Cao YL, Liu X, Iqbal S, Miedziak PJ, Edwards JK, Armstrong RD, Morgan DJ, Wang JW, Hutchings GJ (2016) *Catal Sci Technol* 6:107–117
- Wojcieszak R, Cuccovia IM, Silva MA, Rossi LM (2016) *J Mol Catal A* 422:35–42
- Opre Z, Ferri D, Krumeich F, Mallat T, Baiker A (2007) *J Catal* 251:48–58
- Biella S, Prati L, Rossi M (2002) *J Catal* 206:242–247
- Ma C, Xue W, Li J, Xing W, Hao Z (2013) *Green Chem* 15:1035–1041