

1 **An investigation into bimetallic catalysts for base free oxidation of**  
2 **cellobiose and glucose**

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1 **Abstract:**

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3 **BACKGROUND:** The selective conversion of cellulose to gluconic acid under mild  
4 conditions is challenging as it has abundant intra-and inter-molecular hydrogen bonds  
5 that protect the  $\beta$ -1,4-glycosidic bonds and make it intrinsically recalcitrant to  
6 depolymerize.

7 **RESULTS:** Au-Pd/TiO<sub>2</sub> and Au-Pt/TiO<sub>2</sub> catalysts prepared by sol immobilization  
8 method without pre-treatment are active and selective for the oxidation of glucose and  
9 cellobiose to gluconic acid under base-free conditions. Important preparation  
10 parameters are the pre-treatment of the catalyst and the metal ratio.

11 **CONCLUSION:** The optimized catalyst provided a good yield of gluconic acid from  
12 cellobiose and has opened up a new catalyst system for cellobiose conversion in terms  
13 of a heterogeneous catalyst.

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16 **Keywords**

17 Glucose; Cellobiose; Au-Pd; Au-Pt; Base-free condition; Oxidation; Gluconic acid.

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## 1 **Background**

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3 An efficient utilization of cellulosic biomass, an abundant and renewable resource in  
4 nature, has long been the focus of research and development efforts, with the aim to  
5 compete with and replace petroleum-based products.<sup>1, 2</sup> Recently, there have been  
6 several studies into the conversion of lignocellulosic materials into fuels and chemicals  
7 using various processes.<sup>3-10</sup> Unfortunately, the production of fuels from cellulose has  
8 a lower efficiency in terms of atom economy due to cellulose having a relatively high  
9 oxygen to carbon (O/C) ratio. Fuels usually possess a much lower O/C ratio, excess  
10 oxygen must be removed when cellulose is transformed into fuels.<sup>11, 12</sup> By contrast,  
11 transforming cellulose into oxygenates, such as gluconic acids, via glucose oxidation  
12 (through cellulose hydrolysis), which are widely used in the pharmaceutical and food  
13 industries, has been proven to be a highly atom-economic reaction as most of the  
14 oxygen-functional groups in the cellulose are preserved in the target products.<sup>1, 13-16</sup>  
15 Additionally, air can be used as an oxidant, which significantly reduces the processing  
16 cost compared with the hydrotreating processes. Unfortunately, the selective  
17 conversion of cellulose to gluconic acid under mild conditions still remains a large  
18 challenge as it has abundant intra-and inter-molecular hydrogen bonds that protect the  
19  $\beta$ -1,4-glycosidic bonds and make it intrinsically recalcitrant to depolymerize.<sup>17</sup> To  
20 overcome this problem, either ionic liquids are used as the solvent (for example 1-  
21 butyl-3-methylimidazolium chloride (BMIMCl) and 1-butyl-3-methylimidazolium  
22 chloride etc.), due to their special abilities to dissolve cellulose, or alternatively

1 reactions are run under extreme conditions (>100 °C, longer reaction times up to 18  
2 hours).<sup>18</sup> However, the high cost and the toxicity of ionic liquids both increase the cost  
3 and are not environmental friendly. The extreme reaction conditions used during  
4 cellulose degradation are also not a good choice due to the low stability of gluconic  
5 acid at high temperatures. So far, there are no studies reported on the direct conversion  
6 of cellulose into gluconic acid.

7 Cellobiose, a D-glucose dimer connected by the same  $\beta$ -1,4-glycosidic linkage as that  
8 in cellulose, is the basic repeating structural unit as well as the simplest model  
9 molecule of cellulose although there are some structural differences between cellulose  
10 and cellobiose. Studies on the conversion of cellobiose may provide important clues  
11 for the rational design of efficient catalysts for cellulose transformations. Moreover,  
12 the insights obtained from cellobiose conversions could also be useful for  
13 transformations of the soluble oligosaccharides. However, only a few reports have  
14 attempted to examine the possibility of the conversion of cellobiose to gluconic acid  
15 by heterogeneous catalytic oxidation in an aqueous medium without pH adjustment.<sup>19-</sup>  
16 <sup>23</sup> Jason *et al*<sup>24</sup> reported hybrid mesoporous catalysts as an efficient catalytic system  
17 for the hydrolysis of cellobiose with activation energies comparable with the  
18 homogeneous catalysts. They found out that the hydrolysis reaction was catalyzed by  
19 hydrated protons. Tan *et al.* reported that cellobiose can be directly converted into  
20 gluconic acid over a Au/TiO<sub>2</sub> catalyst at 145 °C under 0.5 MPa O<sub>2</sub>, 68% yield of  
21 gluconic acid was obtained after 3 h.<sup>19</sup> Later, Zhang *et al.* examined the conversion of  
22 cellobiose over gold nanoparticles with various supports.<sup>20</sup> It was found that insoluble

1 substituted polyoxometalate ( $\text{Cs}_2\text{HPW}_{12}\text{O}_{40}$ ) was the best support for the synthesis of  
2 gluconic acid in aqueous medium, with cellobiose conversion of 97.5% and gluconic  
3 acid selectivity of 98.9% at a reaction time of 3 h.<sup>20</sup> An *et al.* found that Au supported  
4 on  $\text{Cs}_x\text{H}_{3-x}\text{PW}_{12}\text{O}_{40}$  ( $x=1.2, 1.7, \text{ and } 2.2$ ) exhibited full conversion of cellobiose with  
5 over 95% selectivity of gluconic acid after 3 h at 145 °C.<sup>21</sup> Amaniampong *et al.*  
6 revealed that cellobiose can be converted to gluconic acid over a Au/TiO<sub>2</sub> catalyst at  
7 145 °C under 0.5 MPa O<sub>2</sub> with selectivity greater than 70 %.<sup>22</sup> This group further  
8 investigated the conversion of cellobiose over supported Au-M (M=Cu, Co, Ru and  
9 Pd) bimetallic catalysts and a complete conversion of cellobiose with a gluconic acid  
10 selectivity of 88.5% at 145 °C within 3 h was obtained for reactions performed over  
11 Cu-Au/TiO<sub>2</sub> catalyst.<sup>23</sup> Onda *et al.*<sup>25</sup> showed Pt/sulphonated carbon as an active and  
12 selective catalyst for the conversion of cellulose into glucic acid when air was used  
13 as an oxidant. Recently, Au supported on carbon xerogel has been reported to be an  
14 active catalyst for the direct conversion of cellulose into gluconic acid.<sup>26</sup> where  
15 mesoporous carbon decorated with the phenolic groups showed 80% selectivity to  
16 gluconic acid after 75 minutes of reaction.

54 Synthesis of gluconic acid from glucose is usually performed under a strict control of  
55 pH. There are a number of reports of heterogeneous catalysts, including supported Pd,  
56 Pt, Pt, and Au nanoparticles.<sup>27-29</sup> where pH control is reported to be crucial in order to  
57 obtain high rates of glucose conversion and this is achieved by the addition of a  
58 sacrificial base, usually sodium hydroxide.<sup>30, 31</sup> Therefore, from the viewpoint of green  
59 chemistry, there is a need to develop heterogeneous catalysts that can catalyse the

1 oxidation of glucose under base-free conditions.

2 In our previous work, we found that the catalyst preparation method had a crucial  
3 influence on the catalytic activity of supported Au catalysts for base-free glucose  
4 oxidation and the sol-immobilization was found to be the best method.<sup>32</sup> Additionally,  
5 both the pretreatment of catalysts and the ratio of polyvinyl alcohol (PVA) to metal  
6 (wt/wt) are also important parameters with respect to both the activity and selectivity  
7 in the oxidation of glucose to gluconic acid. It is believed that bimetallic catalysts  
8 normally exhibit better catalytic activity in comparison with pure metals because the  
9 interaction between the two metals can modify the surface and electronic properties of  
10 the catalysts. In addition, almost all of the literature reported above suggests that the  
11 direct conversion of cellulose into gluconic acid requires bi-functional catalysts which  
12 not only perform cascade type of reactions in one pot but also improve the product  
13 selectivity and overall activity of the catalytic system. Therefore, we anticipated that  
14 the use of bimetallic catalysts based on gold where the secondary metal could improve  
15 both the initial degradation of cellulose and the further oxidation would be beneficial.  
16 In this work, gold based bimetallic catalysts (Au-Pd, Au-Pt) were employed in glucose  
17 and cellobiose oxidation to gluconic acid in an aqueous medium without pH control.

## 18 **Experimental methods**

### 19 *Catalyst preparation*

20 All of the catalysts were prepared by using the Sol-immobilization method as reported  
21 previously.<sup>33</sup> In a typical synthesis aqueous solutions of  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  (Sigma-Aldrich,  
22  $11.5 \text{ mg L}^{-1}$ ),  $\text{PdCl}_2$  (Sigma-Aldrich,  $10 \text{ mg L}^{-1}$ ),  $\text{H}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$  (Sigma-Aldrich,  $10$

1 mg L<sup>-1</sup>), polyvinylalcohol (PVA) (1 wt%, Aldrich, M<sub>w</sub> = 10000, 80% hydrolyzed) and  
2 NaBH<sub>4</sub> (0.1 M) were prepared. The requisite amount of a PVA solution was added to  
3 the metal precursor solution (diluted to 400 cm<sup>3</sup>g<sup>-1</sup>catalyst). A freshly prepared  
4 solution of NaBH<sub>4</sub> was then added to form a dark-brown sol. After 30 min of sol  
5 generation, the colloid was immobilized by adding TiO<sub>2</sub> (Degussa P25). A small  
6 amount of H<sub>2</sub>SO<sub>4</sub> was added under vigorous stirring to attain a pH of 1–2. After 2 h,  
7 the slurry was filtered, and the catalyst was washed thoroughly with distilled water (2  
8 L) until the filtrate was neutral and then dried at (110 °C, 16 h, static air). The catalysts  
9 are labeled as x%Au–y%Pt (or Pd)/TiO<sub>2</sub>, in which x and y stand for the nominal weight  
10 loading of Au and Pt (or Pd), respectively.

11

#### 12 *Catalyst post-synthesis treatment*

##### 13 *a. Reflux method.*

14 The dried catalyst was refluxed with hot water following the method described  
15 previously.<sup>34</sup> Typically, catalyst (1 g) was refluxed at 90 °C in water (150 mL) with  
16 stirring (1000 rpm for 60 min). The catalyst was recovered by filtration and washed  
17 with distilled water (2 L) and dried (110 °C, 16 h).

##### 18 *b. Heat treatment.*

19 Calcination was performed on the dried catalyst in static air at 250 °C for 3 h.

#### 20 *Characterization*

21 X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD  
22 spectrometer, utilizing monochromatic Al radiation operating at 144 W (12 ma x 12

1 kV). Charge neutralization was performed using an magnetic immersion lens system  
2 and the subsequent spectra calibrated to the C(1s) line of carbon taken to be 284.8 eV.  
3 All data was analyzed using CasaXPS utilizing atomic sensitivity factors supplied by  
4 the manufacturer.

5 Powder X-ray diffraction (XRD) patterns were recorded using a Panalytical X'pert Pro  
6 diffractometer using Ni filtered CuK $\alpha$  radiation (operating at 40 kV, 40 mA). Scans  
7 were in the range of 10–80° 2 $\theta$ .

8 Transmission electron microscopy (TEM) was carried out using a Jeol 2100 with a  
9 LaB<sub>6</sub> filament operating at 2000 kV. Samples were prepared by dispersing the powder  
10 catalyst in ethanol and dropping the suspension onto a lacey carbon film over a 300  
11 mesh copper grid. Particle counts were based on 300 particles.

#### 12 *Oxidation reactions*

13 Reactions were carried out using a low pressure Colliver glass reactor (50 ml). Glucose  
14 or cellobiose (0.20 g), catalyst (0.05 g) and water (20 g) were added into the reactor,  
15 which was then purged with oxygen three times before the reactor was sealed and  
16 pressurized with oxygen (3 bar). The reaction mixture was heated to 160 °C for 1 h  
17 under constant stirring (1000 rpm), then cooled to room temperature. The products  
18 were analyzed by HPLC using an Agilent 1200 fitted with a metacarb 67H column,  
19 and UV and RI detectors.

20 All of the catalytic tests were repeated at least three times and the data were found to  
21 be within an experimental error of 1-3%.

22



## 1 **Results and discussion**

### 2 *Effect of the catalyst post-synthesis treatment on the base-free oxidation of glucose*

3

4 According to our previous work, the post-synthesis treatment for 1% Au/TiO<sub>2</sub> catalysts  
5 had a significant effect on the catalyst performance.<sup>26</sup> Therefore, the effect of post-  
6 treatment procedures on bimetallic Au-M (M = Pd, Pt) catalysts were investigated for  
7 the base free oxidation of glucose and the data is shown in Table 1. It can be seen from  
8 Table 1 that the calcined Au-Pd/TiO<sub>2</sub> catalyst exhibited 70.3% glucose conversion  
9 while the dried catalyst, without further calcination, showed lower glucose conversion  
10 (65.1%). Furthermore, the refluxed catalyst showed a very low conversion and  
11 subsequently lower yield of gluconic acid. Interestingly the Au-Pt/TiO<sub>2</sub> showed a  
12 slightly different trend with the highest activity and selectivity for the untreated  
13 catalyst, the lowest activity was again observed with the refluxed catalyst. It is  
14 important to mention that trace amounts of fructose, glycolic acid and 5-  
15 hydroxymethyl furfural (5-HMF) were also observed with all of these catalysts. No  
16 other byproducts were observed and carbon balance was always 95-100%. This leads  
17 us to think that interaction between the substrate and the PVA ligand may play an  
18 important role in the reaction, an effect which has been reported previously by Pratti  
19 and co-workers.<sup>35</sup>

20 For all samples (Au-Pd and Au-Pt), XPS analysis revealed all metals to be in their  
21 metallic state, exemplified by binding energies of 83.1 (Au(4f<sub>7/2</sub>), 334.7 (Pd(3d<sub>5/2</sub>))  
22 and 70.3 eV (Pt(4f<sub>7/2</sub>)). For the Au-Pd systems, the Au/Pd ratio was 0.62 for the dried

1 samples, decreasing slightly to 0.59 for the calcined sample, although the presence of  
2 a small amount of Pd(II) species is now also evident, whilst the refluxed sample is  
3 dominated by Au as evidenced by a Au/Pd ratio of 12 ([Supplementary Information –  
4 Table S1](#)). This suggests that the increase in Pd(II) may be beneficial to the catalytic  
5 system however the reflux treatment leads to an increase in the apparent gold loading  
6 which would suggest a redistribution of the metals, either increasing the dispersion of  
7 gold or reducing the distribution of palladium. In comparison, the Au-Pt system almost  
8 identical Au/Pt ratios of 1.31 and 1.28 for the fresh and calcined samples respectively  
9 were observed, whereas the refluxed sample exhibited a Au-Pt ratio of 1.65 indicating  
10 an increase in the Au content. For both these catalysts it seems clear that an increase  
11 in the surface gold content is detrimental to the catalyst activity suggesting the role of  
12 the secondary metal is important for this reaction.

13 The XRD pattern of the bimetallic catalysts are shown in Figure 1. Typically all of  
14 these catalysts showed reflections of pure titania (P25). No phases related with Au, Pd  
15 and Pt could be identified which was either due to a very small particle size (less than  
16 5 nm) or a homogeneous dispersion of the metals on the titania surface. This also  
17 supports the XPS data, specifically, that the increase in apparent gold content is not  
18 due to agglomeration of the palladium/platinum particles.

19

20 The above comparison of catalytic data in Table 1 showed that the untreated Au-Pt  
21 catalyst showed much higher activity and selectivity than the Au-Pd catalyst.  
22 Therefore, we chose the Au-Pt catalyst system to study further variation of preparation

1 parameters.

2 *Effect of the PVA to metal ratio on base-free oxidation of glucose*

3 The amount of stabilizing agent (PVA) can affect the catalytic activity by controlling  
4 the number of exposed active sites as well as the metal particle size. The balance  
5 between ligand interaction and number of exposed sites has been discussed previously  
6 by Prati and co-workers,<sup>35</sup> we have previously shown that increasing the amount of  
7 PVA on the catalyst leads to a decrease in activity,<sup>36</sup> therefore, we prepared various  
8 catalysts by varying the amount of PVA to metal ratio in the range of 0 to 1.2 in order  
9 to find a balance between ligand shielding effect and the size of metal particles. The  
10 prepared catalysts did not go through any post synthesis treatment other than a drying  
11 step at 110 °C overnight. All the catalysts were tested for glucose oxidation under  
12 standard reaction conditions and the data is presented in Table 2.

13 An analysis of data showed that there was an increase in both catalytic activity and  
14 selectivity of gluconic acid with an increase in PVA to metal ratio. The catalyst  
15 synthesized with the highest ratio of PVA to metal (1.2) showed the highest conversion  
16 of glucose (80%) and also the highest yield of gluconic acid was observed. We also  
17 observed some side products mainly glucaric acid and glycolic acid along with a traces  
18 amount of fructose and 5-HMF.

19

20 XPS of the catalysts prepared with increasing PVA to metal ratio showed an initial  
21 decrease in the Au/Pt ratio from 2.34 (no PVA) to 1.35 (0.1 PVA) which would suggest  
22 a decrease in metal particle size. For higher PVA/metal ratios the Au/Pt metal ratio

1 varies only slightly, (1.36 and 1.40 respectively) which is within confidence limits.

2 [The detailed analysis data are provided in Supplementary Information Table S2.](#)

3  
4 The XRD patterns of the Au-Pt catalysts prepared by variation of PVA to metal ratio  
5 are shown in Figure 2, again there were no reflections related to Au and Pt. All of the  
6 catalysts presented typical pattern of titania indicating a very small particle size or a  
7 homogeneous dispersion of metals on the surface. As there were no reflections related  
8 to the metals observable in the XRD we carried out TEM analysis on the catalyst with  
9 the varying metal to PVA ratio to get an indication of the particle size distribution.  
10 Representative images of the different catalysts along with their associated particle  
11 size distributions are shown in Figure 3. All the catalysts had an average particle size  
12 that was below what we would expect to be able to observe by XRD. It is clear that  
13 the use of PVA results in a smaller average particle size, when no PVA is used (Figure  
14 3a) the average particle size is 3.67 nm, compared with our standard ratio (1.2, figure  
15 3d) which has an average particle size of 1.6 nm. The use of PVA also leads to a much  
16 narrower spread of the particle size as indicated by the reduction in the standard  
17 deviation from 2.71, with no PVA, to 0.62 for the 1.2 ratio catalyst. The catalysts  
18 prepared with PVA:metal ratios in between these have average particles sizes and  
19 standard deviations that are between those of the 0 PVA and 1.2 PVA samples. The  
20 activity of the catalyst correlates inversely with the average particle size, the smaller  
21 the average particle the more active the catalyst is. This suggests that the particle size  
22 is a significant factor that affects the activity of the catalyst.

1 Generally, it is considered that the activity is a compromise between the particle size  
2 of the metal and the shielding effect of the PVA ligand.<sup>37</sup> However in the case of these  
3 catalysts the shielding effect did not seem to contribute, either because the maximum  
4 amount of PVA used in these catalyst preparations was below the amount required to  
5 cause this effect, there is good diffusion of the glucose through the PVA layer or the  
6 PVA is removed under reactions conditions, an effect that we have reported previously.  
7 <sup>38</sup> From this analysis we conclude that the metal particle size is the key factor for the  
8 conversion of glucose.

9

#### 10 *Effect of the metal loading*

11

12 After identification of the optimum conditions for sol immobilization preparation we  
13 varied the amount of Au and Pt metals. Various catalysts with different Au and Pt  
14 loadings in the range of 0.5 to 2.5% were prepared by the sol immobilization method.  
15 PVA to metals ratio was kept constant at the optimum 1.2 ratio and the catalysts did  
16 not go through any post-synthesis treatment. All of the catalysts were tested for glucose  
17 oxidation and the data is presented in Table 3.

18 The catalytic data showed that the catalysts prepared with the lowest amounts of both  
19 metals showed a relatively low activity and a correspondingly lower yield of gluconic  
20 acid. An increase in amount of metals from 0.5% (total) to 1% (total) increased both  
21 the activity and selectivity and a further increase in the amount of metals to 2% fully  
22 converted glucose into ~90% gluconic acid yield. A further increase in the amount of

1 metals to 5% (total) also showed a full conversion with a similar yield of gluconic acid.

2 Glucaric acid, glycolic acid and fructose were produced in very small amounts.

3 Analysis of the different loadings by XPS ([Supplementary Information Table S3](#))

4 reveal metallic components as expected based on the results discussed earlier, however

5 both low (0.25Au 0.5Pt) and high (2.5Au 2.5Pt) have a higher apparent Au content,

6 exhibiting Au/Pt ratios of 2.49 and 3.35, whilst the 0.5 and 1 wt% loadings yield

7 substantially lower ratios (1.42 and 1.12 respectively).

8 The XRD patterns of the Au-Pt catalysts prepared with the variation of metal ratios are

9 shown in Figure 4. Irrespective of the amount of metals no reflections associated with

10 Au or Pt was observed. A typical XRD pattern of P25 TiO<sub>2</sub> was apparent. However,

11 one phase of rutile titania (110) at 27.1° angle<sup>39</sup> disappeared when the amount of metals

12 was increased from 1.0 to 2%.

13 The differences of activity between the catalysts could be attributed to the loading of

14 the metals, however if the the total amount of metal loading in the reaction is

15 standardized in the reaction would be higher by calculating activity per unit metal, -the

16 lower loaded catalysts prove to be more active. This suggests that as the metal loading

17 increases the amount of the metal that acts as spectator species increases, when

18 considered in terms of activity per unit metal, a This can be seen by the turn over

19 frequencies (TOFs) reported in table 3.

20

21 TEM analysis was carried out on these catalysts to see if there was a relationship

22 between the particle size and the total metal loading. The results are shown in Figure

1 5, the difference between the particle size of the first 3 loadings is relatively small  
2 (Figure 5a-c), 1.74-2.10 nm, once the loading gets higher there is a significant increase  
3 in the average size to 3.64 nm. This suggests that the particle size is determined at the  
4 formation of the sol stage until a point where the relative concentration of the metals  
5 on the support surface is sufficient for particle agglomeration to occur. There is  
6 evidence of particle agglomeration visible in figure 5d. Overall, the TEM does not  
7 show a correlation between particle size and activity, which suggests that the  
8 differences in ~~observed~~ activity ~~observed~~ are related to the total metal loading of the  
9 catalyst.

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10 Further to this we used 1% Au-1% Pt/TiO<sub>2</sub> catalyst for the oxidation of cellobiose and  
11 cellulose. The catalyst was prepared by sol immobilization method and it went through  
12 no post-synthesis treatment. The ratio between PVA and metals was 1.2. The activity  
13 data is shown in Table 4.

14

15 From the oxidation data it is clear that cellulose showed a very low conversion and no  
16 gluconic acid was observed. The products detected were mainly in the region where  
17 we would expect to see polymers. 5.7% yield of cellupentose was also observed.  
18 Cellobiose showed higher conversion and 15% yield of gluconic acid with glucose  
19 observed as a side product. Cellobiose consists of two glucose units so the 15% yield  
20 of glucose could only be a breakdown of cellobiose followed by oxidation into  
21 gluconic acid. Side products from cellobiose oxidation were glucaric acid, and glycolic  
22 acid. From this data the Au-Pt/TiO<sub>2</sub> catalyst showed a promising activity for the

1 conversion of cellobiose. Therefore, in next step we varied the temperature of reaction  
2 and the data is presented in Table 5.

3 An increase in temperature from 130 to 140 °C showed an increase in conversion from  
4 31.6 to 51.5% and gluconic acid yield also increased from 6.5 to 20.5%. Further  
5 increase in the temperature to 150 °C showed no change in conversion but the yield of  
6 gluconic acid increased from 20.5% to 28%. Interestingly another increase up to  
7 160 °C decreased the conversion by 10% and also the gluconic acid yield was  
8 decreased to almost half. This decline in activity and selectivity with an increase in  
9 temperature can be linked with the deposition of carbon species or polymers on the  
10 catalyst surface at high temperature which could be responsible for a lower number of  
11 active sites. Similarly to the other reactions, the side products were glycolic acid and  
12 glucaric acid.

13 Subsequently we performed a variation of reaction time for cellobiose oxidation with  
14 1% Au-1% Pt/TiO<sub>2</sub> catalyst at 150 °C and the activity data is presented in Table 6. An  
15 increase in reaction time from 1 hour to 2 hours showed a significant increase in  
16 conversion from 51 to 65% and the gluconic acid yield increased from 28 to 42%. A  
17 further increase in reaction time to 3 hours increased both the conversion (74%) and  
18 gluconic acid yield (59%). Small amounts of glycolic acid and glucaric acid were also  
19 observed as side products.

20 Finally we varied the amount of cellobiose (substrate) within a range of 0.10-0.30 g  
21 using the 1% Au-1% Pt catalyst and the activity data are presented in Table 7. A  
22 decrease in conversion was observed with an increase in amount of the substrate from



1 0.10 to 0.20g but a volcano type trend was observed in gluconic acid yield. This  
2 suggests that product inhibition may be a problem in these reactions, with a minor,  
3 difficult to detect, impurity formed when there is sufficient substrate, which cause  
4 deactivation of the catalyst.

5

## 6 **Conclusions**

7 We have reported that Au-Pd/TiO<sub>2</sub> and Au-Pt/TiO<sub>2</sub> catalysts prepared by sol  
8 immobilization method without pre-treatment are active and selective for the oxidation  
9 of glucose to gluconic acid under base-free conditions. Au-Pt/TiO<sub>2</sub> catalysts exhibited  
10 higher activity and yield of gluconic acid. The activity can be improved by tuning the  
11 pretreatment of catalysts and PVA to metal ratio, and these preparation parameters have  
12 a significant effect on the metal particle size. The optimized catalyst provided a  
13 reasonable yield of gluconic acid from cellobiose and has opened up a new catalyst  
14 system for cellobiose conversion in terms of a heterogeneous catalyst.

15

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15

1 **Table 1.** Effect of post-synthesis treatments on bimetallic Au- M (M = Pd, Pt)

2 catalysts for glucose oxidation

Catalyst	Post-synthesis treatment	Conversion (%)	Yield (%)		TOF (mol(glucose)/ mol(metal)/h
			Gluconic acid	Fructose	
0.5% Au- 0.5% Pd/TiO <sub>2</sub>	no	65.1	59.9	0.6	99.9
0.5% Au- 0.5% Pd/TiO <sub>2</sub>	air	70.3	63.3	0.9	10.8
0.5% Au- 0.5% Pd/TiO <sub>2</sub>	reflux	48.0	40.5	2.7	73.6
0.5% Au- 0.5% Pt/TiO <sub>2</sub>	no	80.0	70.2	1.8	174.1
0.5% Au- 0.5% Pt/TiO <sub>2</sub>	air	68.0	62.7	0.8	148.0
0.5% Au- 0.5% Pt/TiO <sub>2</sub>	reflux	71.2	65.6	1.2	155.0

3 *Reaction conditions:* glucose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction

4 temperature 160 °C, reaction time 1h, O<sub>2</sub> 3 bar.

5

1 **Table 2.** Effect of the ratio of PVA to metal on 0.5% Au-0.5% Pt/TiO<sub>2</sub> catalysts

2 for glucose oxidation

PVA/ metals (w/w)	Conversion (%)	Yield (%)		
		Gluconic acid	Glucaric acid	Glycolic acid
<b>0</b>	63.2	50.9	2.0	0.5
<b>0.1</b>	74.5	67.5	2.0	0.5
<b>0.6</b>	72.5	68.1	1.0	0.2
<b>1.2</b>	80.0	70.2	1.8	0.3

3 *Reaction conditions:* glucose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction

4 temperature 160 °C, reaction time 1h, O<sub>2</sub> 3 bar.

5

1 **Table 3.**Effect of Au and Pt loading for glucose oxidation

Au-Pt (%)/TiO <sub>2</sub>	Conversion (%)	Yield (%)			TOF (mol(glucose)/ mol(metal)/h
		Gluconic acid	Glucaric acid	Glyolic acid	
0.25 - 0.25	45.0	39.2	trace	trace	195.8
0.50 - 0.50	80.0	70.2	1.8	trace	174.1
1.0 – 1.0	100	88.9	3.4	0.7	108.8
2.5 - 2.5	100	88.6	3.6	0.6	43.5

2 *Reaction conditions:* glucose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction

3 temperature 160 °C, reaction time 1h, O<sub>2</sub> 3 bar.

4

1 **Table 4.** Catalytic activity of 1%Au-1%Pt/TiO<sub>2</sub> with different substrates

Substrate	Conversion (%)	Yield (%)		
		Gluconic acid	Glucaric acid	Glucose
Glucose	100	88.9	3.4	-
Cellobiose	40.3	14.5	1.4	15.6
$\alpha$ -Cellulose	17.4	no	no	trace

2 *Reaction conditions:* reactant 0.20 g, water 20.0 g, catalyst 0.05 g, reaction

3 temperature 160 °C, reaction time 1h, O<sub>2</sub> 3 bar.

4



1 **Table 5.** Effect of the reaction temperature for cellobiose oxidation

Reaction T (°C)	Conversion (%)	Yield (%)		
		Gluconic acid	Glucose	Glucaric acid
130	31.6	6.5	1.7	3.4
140	51.7	20.5	Trace	7.0
150	51.6	27.9	Trace	4.6
160	40.3	14.5	15.6	1.4

2 *Reaction conditions:* Cellobiose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction time

3 1h, O<sub>2</sub> 3 bar.

4

1 **Table 6.** Effect of the reaction time for cellobiose oxidation

Reaction time (h)	Conversion (%)	Yield (%)		
		Gluconic acid	Glycolic acid	Glucaric acid
1	51.6	27.9	1.2	4.6
2	65.0	42.3	1.4	4.4
3	73.8	59.0	1.4	2.9

2 *Reaction conditions:* cellobiose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction

3 temperature 150 °C, O<sub>2</sub> 3 bar.

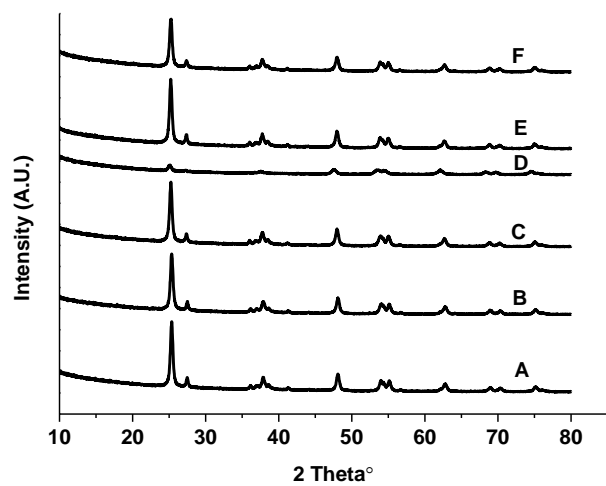
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1 **Table 7.** Effect of cellobiose amount on 1% Au-1% Pt/TiO<sub>2</sub> (1.2 PVA:metal) catalyst

Cellobiose amount	Conversion (%)	Yield (%)		
		Gluconic acid	Glycolic acid	Glucaric acid
0.10	90	47.0	4.3	12.8
0.20	73.8	59.0	1.4	2.9
0.30	74.9	44.4	1.6	2.8

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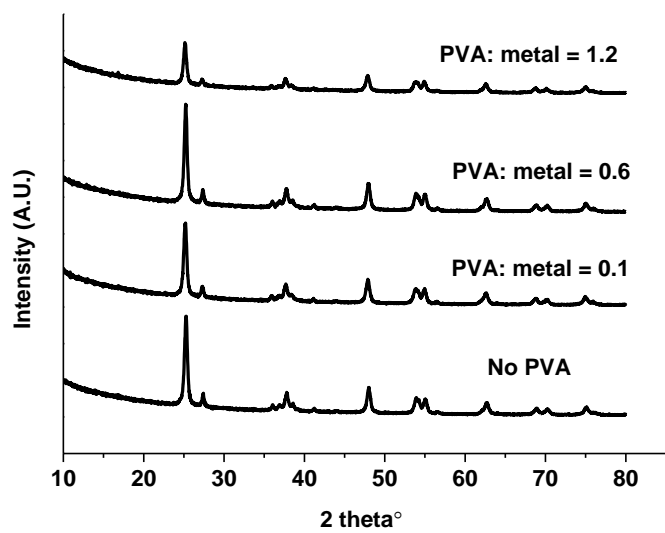
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2 **Figure 1.** XRD patterns of bimetallic catalysts with post-synthesis treatment.

3 **A.** Au-Pd – no treatment, **B.** Au-Pd – calcined, **C.** Au-Pd – refluxed, **D.** Au-Pt

4 – no treatment, **E.** Au-Pt – calcined, **F.** Au-Pt – refluxed.

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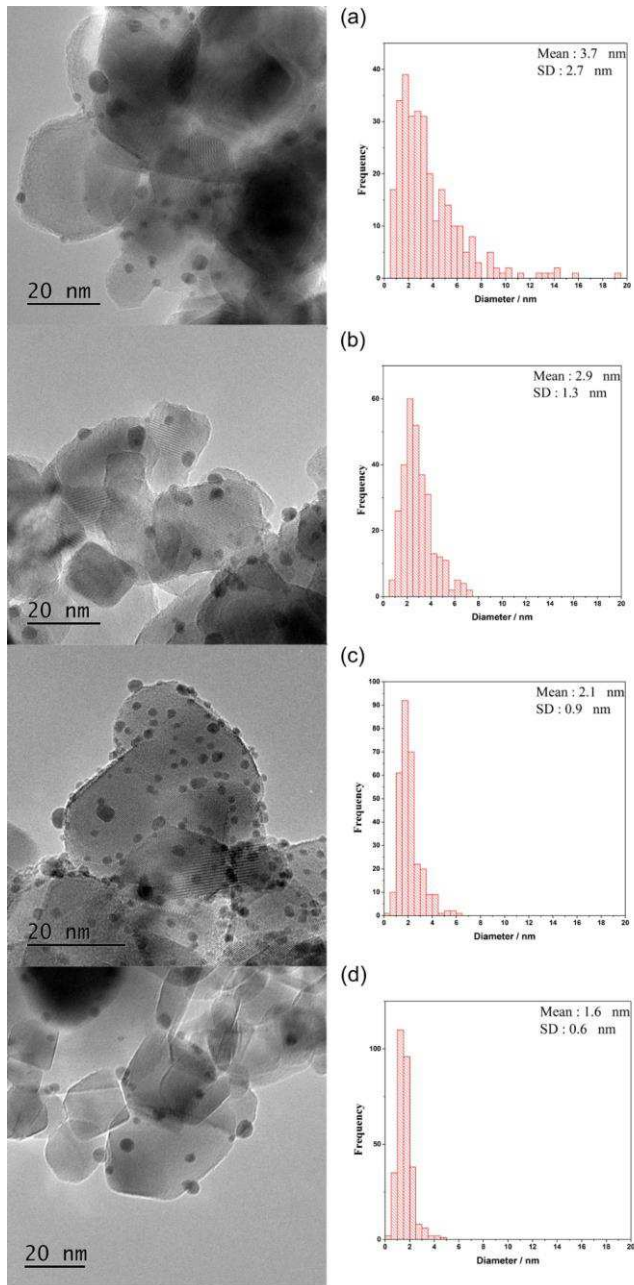


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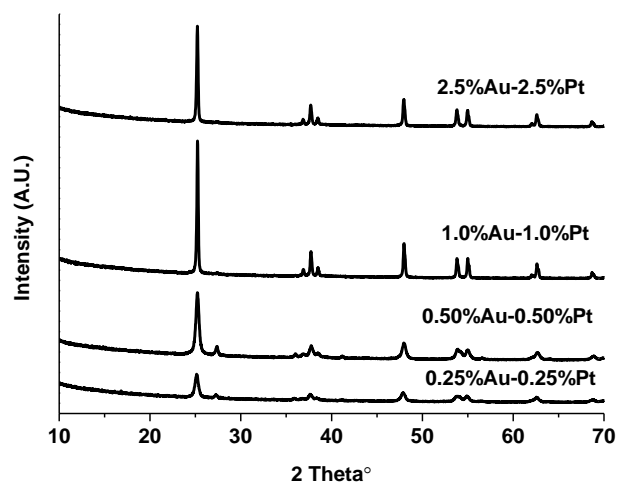
2 **Figure 2.** XRD pattern of catalysts prepared with the variation of PVA to metal

3 ratio

4

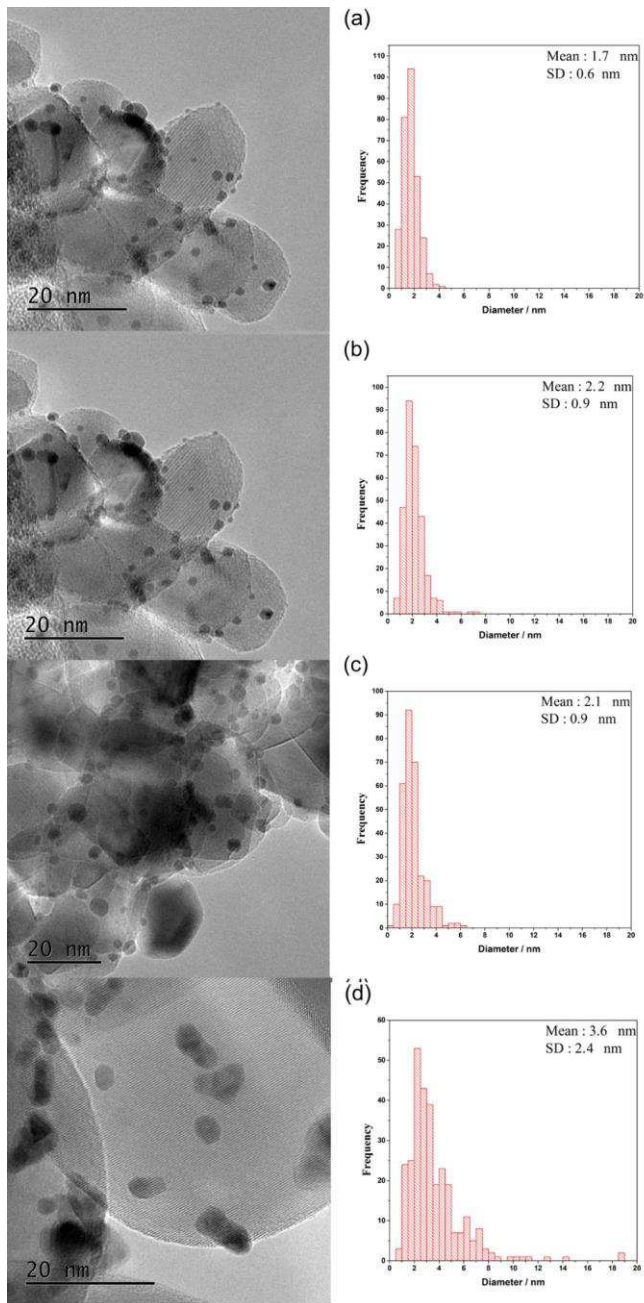


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 2 **Figure 3.** TEM images and associated PSDs for 1% AuPt/TiO<sub>2</sub> catalysts  
 3 prepared with different metal:PVA:metal ratios. a) 0; b) 0.1; c) 0.6; d) 1.2.



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**Figure 4.** XRD patterns of Au-Pt/TiO<sub>2</sub> catalysts prepared with the carrying ratio.



1  
 2 **Figure 5.** TEM images and associated PSDs for AuPt catalysts prepared with  
 3 different metal loadings. a) 0.25-0.25; b) 0.5-0.5; c) 1-1; d) 2.5-2.5.