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

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Abstract:

BACKGROUND: The selective conversion of cellulose to gluconic acid under mild conditions is challenging as it has abundant intra-and inter-molecular hydrogen bonds that protect the β-1,4-glycosidic bonds and make it intrinsically recalcitrant to deploymerize.

RESULTS: Au-Pd/TiO_2 and Au-Pt/TiO_2 catalysts prepared by sol immobilization method without pre-treatment are active and selective for the oxidation of glucose and cellobiose to gluconic acid under base-free conditions. Important preparation parameters are the pre-treatment of the catalyst and the metal ratio.

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

Keywords

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

Background

An efficient utilization of cellulosic biomass, an abundant and renewable resource in nature, has long been the focus of research and development efforts, with the aim to compete with and replace petroleum-based products.[1, 2] Recently, there have been several studies into the conversion of lignocellulosic materials into fuels and chemicals using various processes.[3-10] Unfortunately, the production of fuels from cellulose has a lower efficiency in terms of atom economy due to cellulose having a relatively high oxygen to carbon (O/C) ratio. Fuels usually possess a much lower O/C ratio, excess oxygen must be removed when cellulose is transformed into fuels.[11, 12] By contrast, transforming cellulose into oxygenates, such as gluconic acids, via glucose oxidation (through cellulose hydrolysis), which are widely used in the pharmaceutical and food industries, has been proven to be a highly atom-economic reaction as most of the oxygen-functional groups in the cellulose are preserved in the target products.[1, 13-16] Additionally, air can be used as an oxidant, which significantly reduces the processing cost compared with the hydrotreating processes. Unfortunately, the selective conversion of cellulose to gluconic acid under mild conditions still remains a large challenge as it has abundant intra-and inter-molecular hydrogen bonds that protect the β-1,4-glycosidic bonds and make it intrinsically recalcitrant to deploymerize.[17] To overcome this problem, either ionic liquids are used as the solvent (for example 1-butyl-3-methylimidazolium chloride (BMIMCl) and 1-butyl-3-methylimidazolium chloride etc.), due to their special abilities to dissolve cellulose, or alternatively reactions are run under extreme conditions (>100 °C, longer reaction times up to 18 hours).[18] However, the high cost and the toxicity of ionic liquids both increase the cost and are not environmental friendly. The extreme reaction conditions used during cellulose degradation are also not a good choice due to the low stability of gluconic acid at high temperatures. So far, there are no studies reported on the direct conversion of cellulose into gluconic acid.

Cellobiose, a D-glucose dimer connected by the same β-1,4-glycosidic linkage as that in cellulose, is the basic repeating structural unit as well as the simplest model molecule of cellulose although there are some structural differences between cellulose and cellubiose. Studies on the conversion of cellobiose may provide important clues for the rational design of efficient catalysts for cellulose transformations. Moreover, the insights obtained from cellobiose conversions could also be useful for transformations of the soluble oligosaccharides. However, only a few reports have attempted to examine the possibility of the conversion of cellobiose to gluconic acid by heterogeneous catalytic oxidation in an aqueous medium without pH adjustment.[19-23] Jason *et al*[24] reported hybrid mesoporous catalysts as an efficient catalytic system for the hydrolysis of cellubiose with activation energies comparable with the homogeneous catalysts. They found out that the hydrolysis reaction was catalyzed by hydrated protons. Tan *et al*. reported that cellobiose can be directly converted into gluconic acid over a Au/TiO_2 catalyst at 145 °C under 0.5 MPa O_2, 68% yield of gluconic acid was obtained after 3 h.[19] Later, Zhang *et al*. examined the conversion of cellobiose over gold nanoparticles with various supports.[20] It was found that insoluble substituted polyoxometalate ($Cs_2HPW_{12}O_{40}$) was the best support for the synthesis of gluconic acid in aqueous medium, with cellobiose conversion of 97.5% and gluconic acid selectivity of 98.9% at a reaction time of 3 h.[20] An *et al*. found that Au supported on $Cs_xH_{3-x}PW_{12}O_{40}$ (x=1.2, 1.7, and 2.2) exhibited full conversion of cellobiose with over 95% selectivity of gluconic acid after 3 h at 145 °C.[21] Amaniampong *et al*. revealed that cellobiose can be converted to gluconic acid over a Au/TiO_2 catalyst at 145 °C under 0.5 MPa O_2 with selectivity greater than 70 %.[22] This group further investigated the conversion of cellobiose over supported Au-M (M=Cu, Co, Ru and Pd) bimetallic catalysts and a complete conversion of cellobiose with a gluconic acid selectivity of 88.5% at 145 °C within 3 h was obtained for reactions performed over $Cu\text{-}Au/TiO_2$ catalyst.[23] Onda *et al*[25] showed Pt/sulphonated carbon as an active and selective catalyst for the conversion of cellubiose into glucnic acid when air was used as an oxidant. Recently, Au supported on carbon xerogel has been reported to be an active catalyst for the direct conversion of cellubiose into gluconic acid.[26] where mesoporous carbon decorated with the phenolic groups showed 80% selectivity to gluconic acid after 75 minutes of reaction.

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

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

Experimental methods

Catalyst preparation

All of the catalysts were prepared by using the Sol-immobilization method as reported previously.[33] In a typical synthesis aqueous solutions of $HAuCl_4·3H_2O$ (Sigma-Aldrich, 11.5 mg L^{-1}), $PdCl_2$ (Sigma-Aldrich, 10 mg L^{-1}), $H_2PtCl_6·6H_2O$ (Sigma-Aldrich, 10 mg L^{-1}), polyvinylalcohol (PVA) (1 wt%, Aldrich, M_w = 10000, 80% hydrolyzed) and $NaBH_4$ (0.1 M) were prepared. The requisite amount of a PVA solution was added to the metal precursor solution (diluted to 400 $cm^3 g^{-1}$catalyst). A freshly prepared solution of $NaBH_4$ was then added to form a dark-brown sol. After 30 min of sol generation, the colloid was immobilized by adding TiO_2 (Degussa P25). A small amount of H_2SO_4 was added under vigorous stirring to attain a pH of 1–2. After 2 h, the slurry was filtered, and the catalyst was washed thoroughly with distilled water (2 L) until the filtrate was neutral and then dried at (110 °C, 16 h, static air). The catalysts are labeled as x%Au–y%Pt (or Pd)/TiO_2, in which x and y stand for the nominal weight loading of Au and Pt (or Pd), respectively.

Catalyst post-synthesis treatment

a. Reflux method.

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

b. Heat treatment.

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

Characterization

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra DLD spectrometer, utilizing monochromatic Al radiation operating at 144 W (12 ma x 12 kV). Charge neutralization was performed using an magnetic immersion lens system and the subsequent spectra calibrated to the C(1s) line of carbon taken to be 284.8 eV. All data was analyzed using CasaXPS utilizing atomic sensitivity factors supplied by the manufacturer.

Powder X-ray diffraction (XRD) patterns were recorded using a Panalytical X'pert Pro diffractometer using Ni filtered CuKα radiation (operating at 40 kV, 40 mA). Scans were in the range of 10–80° 2θ.

Transmission electron microscopy (TEM) was carried out using a Jeol 2100 with a LaB_6 filament operating at 2000 kV. Samples were prepared by dispersing the powder catalyst in ethanol and dropping the suspension onto a lacey carbon film over a 300 mesh copper grid. Particle counts were based on 300 particles.

Oxidation reactions

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

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

Results and discussion

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

According to our previous work, the post-synthesis treatment for 1%Au/TiO_2 catalysts had a significant effect on the catalyst performance.[26] Therefore, the effect of post-treatment procedures on bimetallic Au-M (M = Pd, Pt) catalysts were investigated for the base free oxidation of glucose and the data is shown in Table 1. It can be seen from Table 1 that the calcined Au-Pd/TiO_2 catalyst exhibited 70.3% glucose conversion while the dried catalyst, without further calcination, showed lower glucose conversion (65.1%). Furthermore, the refluxed catalyst showed a very low conversion and subsequently lower yield of gluconic acid. Interestingly the Au-Pt/TiO_2 showed a slightly different trend with the highest activity and selectivity for the untreated catalyst, the lowest activity was again observed with the refluxed catalyst. It is important to mention that trace amounts of fructose, glycolic acid and 5-hydroxymethyl furfural (5-HMF) were also observed with all of these catalysts. No other byproducts were observed and carbon balance was always 95-100%. This leads us to think that interaction between the substrate and the PVA ligand may play an important role in the reaction, an effect which has been reported previously by Pratti and co-workers.[35]

For all samples (Au-Pd and Au-Pt), XPS analysis revealed all metals to be in their metallic state, exemplified by binding energies of 83.1 (Au($4f_{7/2}$), 334.7 (Pd($3d_{5/2}$)) and 70.3 eV (Pt($4f_{7/2}$)). For the Au-Pd systems, the Au/Pd ratio was 0.62 for the dried samples, decreasing slightly to 0.59 for the calcined sample, although the presence of a small amount of Pd(II) species is now also evident, whilst the refluxed sample is dominated by Au as evidenced by a Au/Pd ratio of 12 (Supplementary Information – Table S1). This suggests that the increase in Pd(II) may be beneficial to the catalytic system however the reflux treatment leads to an increase in the apparent gold loading which would suggest a redistribution of the metals, either increasing the dispersion of gold or reducing the distribution of palladium. In comparison, the Au-Pt system almost identical Au/Pt ratios of 1.31 and 1.28 for the fresh and calcined samples respectively were observed, whereas the refluxed sample exhibited a Au-Pt ratio of 1.65 indicating an increase in the Au content. For both these catalysts it seems clear that an increase in the surface gold content is detrimental to the catalyst activity suggesting the role of the secondary metal is important for this reaction.

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

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

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

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

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

XPS of the catalysts prepared with increasing PVA to metal ratio showed an initial decrease in the Au/Pt ratio from 2.34 (no PVA) to 1.35 (0.1 PVA) which would suggest a decrease in metal particle size. For higher PVA/metal ratios the Au/Pt metal ratio varies only slightly, (1.36 and 1.40 respectively) which is within confidence limits. The detailed analysis data are provided in Supplementary Information Table S2.

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

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

Effect of the metal loading

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

The catalytic data showed that the catalysts prepared with the lowest amounts of both metals showed a relatively low activity and a correspondingly lower yield of gluconic acid. An increase in amount of metals from 0.5% (total) to 1% (total) increased both the activity and selectivity and a further increase in the amount of metals to 2% fully converted glucose into ~90% gluconic acid yield. A further increase in the amount of metals to 5% (total) also showed a full conversion with a similar yield of gluconic acid. Glucaric acid, glycolic acid and fructose were produced in very small amounts.

Analysis of the different loadings by XPS (Supplementary Information Table S3) reveal metallic components as expected based on the results discussed earlier, however both low (0.25Au 0.5Pt) and high (2.5Au 2.5Pt) have a higher apparent Au content, exhibiting Au/Pt ratios of 2.49 and 3.35, whilst the 0.5 and 1 wt% loadings yield substantially lower ratios (1.42 and 1.12 respectively).

The XRD patterns of the Au-Pt catalysts prepared with the variation of metal ratios are shown in Figure 4. Irrespective of the amount of metals no reflections associated with Au or Pt was observed. A typical XRD pattern of P25 TiO_2 was apparent. However, one phase of rutile titania (110) at 27.1° angle[39] disappeared when the amount of metals was increased from 1.0 to 2%.

The differences of activity between the catalysts could be attributed to the loading of the metals, however if the ~~the total~~amount of metal ~~loading~~ in the reaction is standardized~~in the reaction would be higher~~ by calculating activity per unit metal, –the lower loaded catalysts prove to be more active. This suggests that as the metal loading increases the amount of the metal that acts as spectator species increases.~~when considered in terms of activity per unit metal, a~~ This cas~~ ca~~n be seen by the turn over frequencies (TOFs) reported in table 3.

TEM analysis was carried out on these catalysts to see if there was a relationship between the particle size and the total metal loading. The results are shown in Figure

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

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Further to this we used 1%Au-1%Pt/TiO_2 catalyst for the oxidation of cellobiose and cellulose. The catalyst was prepared by sol immobilization method and it went through no post-synthesis treatment. The ratio between PVA and metals was 1.2. The activity data is shown in Table 4.

From the oxidation data it is clear that cellulose showed a very low conversion and no gluconic acid was observed. The products detected were mainly in the region where we would expect to see polymers. 5.7% yield of cellupentose was also observed. Cellobiose showed higher conversion and 15% yield of gluconic acid with glucose observed as a side product. Cellobiose consists of two glucose units so the 15% yield of glucose could only be a breakdown of cellobiose followed by oxidation into gluconic acid. Side products from cellobiose oxidation were glucaric acid, and glycolic acid. From this data the Au-Pt/TiO_2 catalyst showed a promising activity for the conversion of cellobiose. Therefore, in next step we varied the temperature of reaction and the data is presented in Table 5.

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

Subsequently we performed a variation of reaction time for cellobiose oxidation with 1%Au-1%Pt/TiO_2 catalyst at 150 °C and the activity data is presented in Table 6. An increase in reaction time from 1 hour to 2 hours showed a significant increase in conversion from 51 to 65% and the gluconic acid yield increased from 28 to 42%. A further increase in reaction time to 3 hours increased both the conversion (74%) and gluconic acid yield (59%). Small amounts of glycolic acid and glucaric acid were also observed as side products.

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

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

Conclusions

We have reported that Au-Pd/TiO_2 and Au-Pt/TiO_2 catalysts prepared by sol immobilization method without pre-treatment are active and selective for the oxidation of glucose to gluconic acid under base-free conditions. Au-Pt/TiO_2 catalysts exhibited higher activity and yield of gluconic acid. The activity can be improved by tuning the pretreatment of catalysts and PVA to metal ratio, and these preparation parameters have a significant effect on the metal particle size. The optimized catalyst provided a reasonable yield of gluconic acid from cellobiose and has opened up a new catalyst system for cellobiose conversion in terms of a heterogeneous catalyst.

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Table *1*. Effect of post-synthesis treatments on bimetallic Au- M (M = Pd, Pt) 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_2	no	65.1	59.9	0.6	99.9
0.5%Au-0.5%Pd/TiO_2	air	70.3	63.3	0.9	10.8
0.5%Au-0.5%Pd/TiO_2	reflux	48.0	40.5	2.7	73.6
0.5%Au-0.5%Pt/TiO_2	no	80.0	70.2	1.8	174.1
0.5%Au-0.5%Pt/TiO_2	air	68.0	62.7	0.8	148.0
0.5%Au-0.5%Pt/TiO_2	reflux	71.2	65.6	1.2	155.0

Reaction conditions: glucose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction temperature 160 °C, reaction time 1h, O_2 3 bar.

Table *2*. Effect of the ratio of PVA to metal on 0.5%Au-0.5%Pt/TiO_2 catalysts for glucose oxidation

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

Reaction conditions: glucose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction temperature 160 ^{o}C, reaction time 1h, O_2 3 bar.

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

Au-Pt (%)/TiO_2	**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

Reaction conditions: glucose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction temperature 160 °C, reaction time 1h, O_2 3 bar.

Table *4*. Catalytic activity of 1%Au-1%Pt/TiO_2 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
α-Cellulose	17.4	no	no	trace

Reaction conditions: reactant 0.20 g, water 20.0 g, catalyst 0.05 g, reaction temperature 160 °C, reaction time 1h, O_2 3 bar.

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

Reaction conditions: Cellobiose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction time 1h, O_2 3 bar.

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

Reaction conditions: cellobiose 0.20 g, water 20.0 g, catalyst 0.05 g, reaction temperature 150 °C, O_2 3 bar.

Table *7*. Effect of cellobiose amount on 1%Au-1%Pt/TiO_2 (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

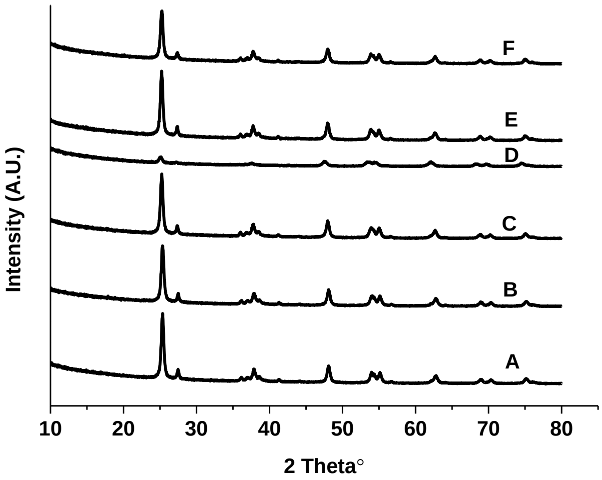

Figure *1*. XRD patterns of bimetallic catalysts with post-synthesis treatment. **A**. Au-Pd – no treatment, **B**. Au-Pd – calcined, **C**. Au-Pd – refluxed, **D**. Au-Pt – no treatment, **E**. Au-Pt – calcined, **F**. Au-Pt – refluxed.

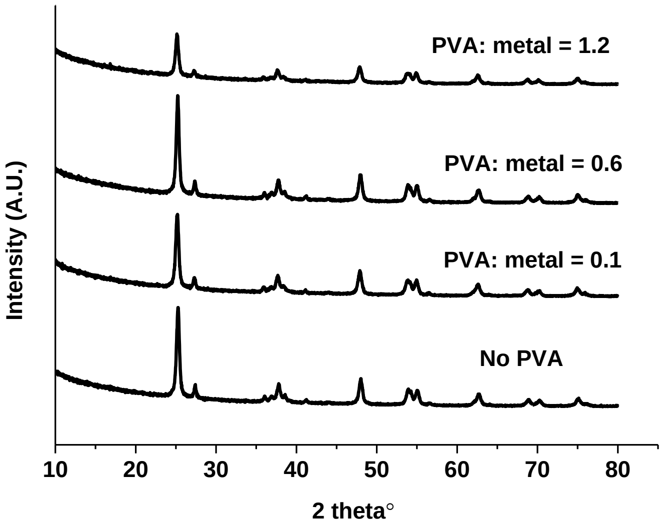

Figure *2*. XRD pattern of catalysts prepared with the variation of PVA to metal ratio

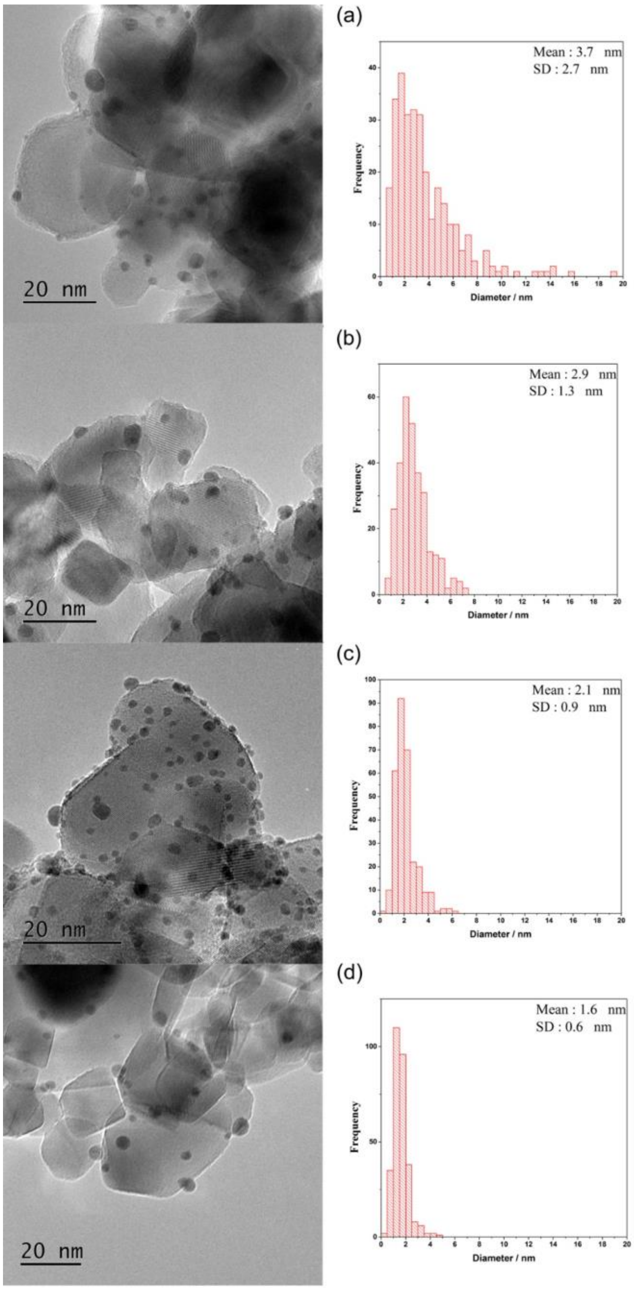

Figure *3.* TEM images and associated PSDs for 1%AuPt/TiO_2 catalysts prepared with different ~~metal:~~PVA:metal ratios. a) 0; b) 0.1; c) 0.6; d) 1.2.

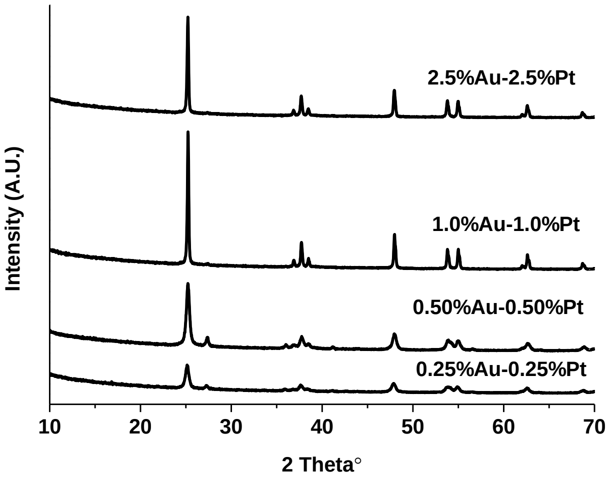

Figure 4. XRD patterns of Au-Pt/TiO_2 catalysts prepared with the carrying ratio.

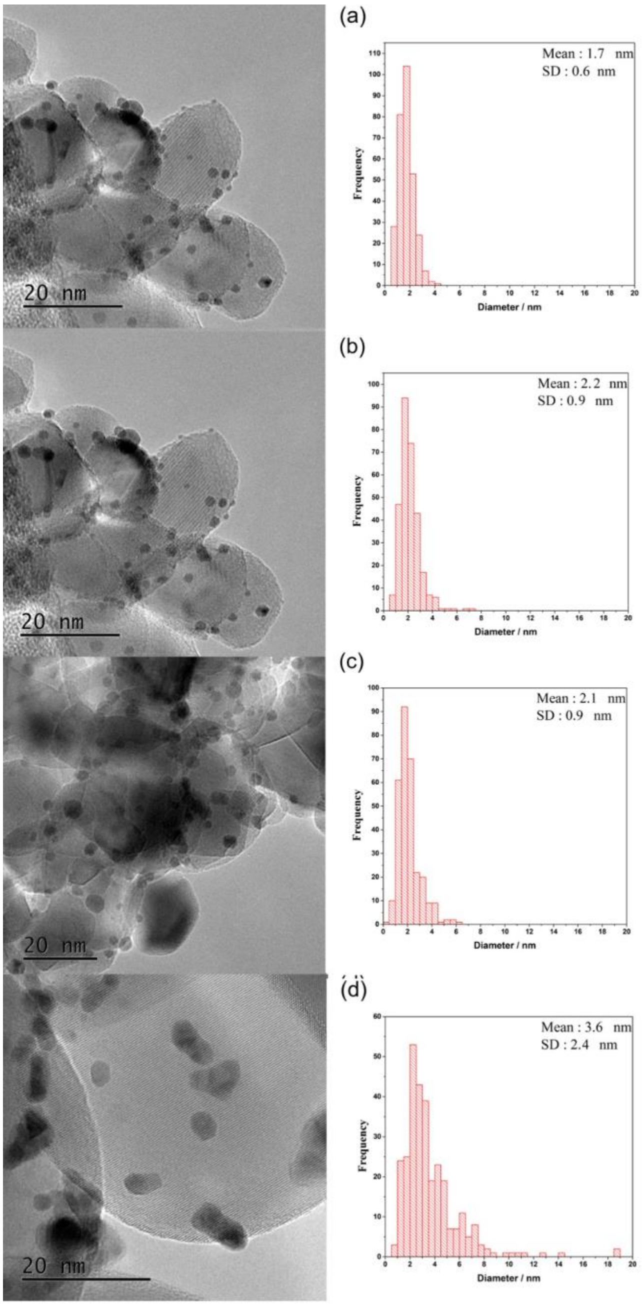

Figure *5.* TEM images and associated PSDs for AuPt catalysts prepared with different metal loadings. a) 0.25-0.25; b) 0.5-0.5; c) 1-1; d) 2.5-2.5.