

Mono- and bimetallic catalysts for glucose oxidation

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Abstract

Mono- and bimetallic catalysts (Au, Pt, Pd and Rh) in form of supported particles or colloidal dispersions were tested in the aerobic oxidation of D-glucose to D-gluconic acid in water solution under mild conditions. Whereas the activity of single metals under acidic conditions was weak in the case of Au and Pt (TOF = 51–60 h⁻¹) and very low in the case of Rh and Pd (TOF < 2), the activity of the bimetallic particles resulted enhanced by combining Au with Pd and Pt. In the latter case high TOFs (max 924 h⁻¹) allow a new route to the synthesis of gluconic acid.

In the presence of alkali at pH 9.5, the oxidation of glucose to gluconate resulted remarkably improved either in the case of monometallic gold or bimetallic catalysts, but no evident synergetic effects among metals have been detected.

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1. Introduction

Industrial production of gluconic acid and derivatives is manufactured by glucose or glucose containing raw materials biochemical transformation [1]. The great commercial interest for aldonic acids, in particular gluconic acid and relative salts, is due to their wide use as water-soluble cleansing agents or additives for food and beverages. The difficulties in moulds and free enzymes separation, waste-water removal and low space–time yield of biochemical plants are spurring the research of alternative catalytic routes for producing gluconates since the 1970s [2–5]. These methods, however, can be industrially applied only if the catalyst shows good activity, selectivity, productivity and durability.

Beside platinum metal catalysts, sophisticated bi- and trimetallic Bi–Pd and Bi–Pd–Pt on carbon catalysts were proposed [6–10]. However, side reactions (i.e. carbohydrates isomerization) and catalyst deactivation reduce gluconate productivity avoiding their practical use.

Recently, gold has received a growing interest as a catalyst for the selective oxidation of organic molecules using oxygen under mild conditions and our research group has emphasized its unusual selectivity in oxidizing the primary alcoholic function to the corresponding carboxylate during the oxidation of

1,2-diols [11–13]. Moreover, the extension of gold catalysis to the selective oxidation of glucose led to promising results, thus suggesting a new route to gluconates in competition with enzymatic catalysis [14–18]. An important feature of gold is to be active either in form of supported metal or in form of nanometric colloidal particles (sol) and an advantage of gold with respect to biological systems is the possibility to work in a wide range of pH, from alkaline to acidic conditions. Since glucose oxidation in the absence of alkali resulted a slow process, in this research we investigated the possibility of improving the performance using bimetallic catalysts. In the present paper we report the preparation of bimetallic Au–M (M = Pt, Pd, Rh) catalysts and their use in the oxidation of glucose using dioxygen as the oxidant under mild conditions.

2. Experimental

2.1. Reagents and apparatus

Gold sponge of 99.9999% purity from Fluka, D-glucose monohydrate (Fluka) was used without further purification, PdCl₂ solution (21% w/w Pd and density 1.53 g/ml), RhCl₃ (40% w/w Rh), K₂PtCl₄ (46% w/w Pt, Alfa Aesar-Johnson Matthey GmbH), NaBH₄ purity > 96% from Fluka, carbon powder Vulcan XC72R from Cabot (average superficial area 254 m²/g, pH 8.0, pore volume 0.192 ml/g, density 96 g/l, sulphur content 0.5%), NaOH (Fluka, of 98% purity), HCl 37% (Fluka), H₂O milliQ, gaseous oxygen (SIAD, 99.9% pure).

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2.2. Preparation of the catalysts

2.2.1. Monometallic catalysts on carbon

Monometallic gold, platinum, rhodium and palladium catalysts on carbon were prepared by immobilizing the corresponding metal sol on carbon. Aqueous solutions of HAuCl_4 , K_2PtCl_4 , RhCl_3 or PdCl_2 (100 mg/l) were prepared and glucose was added as a protecting agent (metal:glucose = 1:50 w/w). Under stirring, a freshly prepared solution of NaBH_4 (0.1 M, $\text{NaBH}_4/\text{M} = 1$ w/w) was added to obtain a dark yellow (Au) and dark brown (Pt, Rh and Pd) colloidal dispersion (sol). The metal particles were immobilized by adding carbon to the metal dispersion, under stirring, until the solution became clear. The amount of support was calculated in order to produce a metal loading of 1%. After 1 h the slurry was filtered, the solid washed many times with distilled water and dried in the air for 12 h. XRD analysis was performed, using a Rigaku D III-MAX horizontal-scan powder diffractometer with $\text{Cu K}\alpha$ radiation, to determine the size of the metal crystallites using the Scherrer equation.

2.2.2. Bimetallic catalysts on carbon

Bimetallic catalysts were prepared as above by immobilizing the preformed metal sols. Mixtures of $\text{HAuCl}_4 + \text{K}_2\text{PtCl}_4$, $\text{HAuCl}_4 + \text{PdCl}_2$, $\text{HAuCl}_4 + \text{RhCl}_3$ were used as metal precursors of gold–platinum, gold–palladium and gold–rhodium catalysts, respectively.

2.2.3. Mono- and bimetallic catalysts as sols

According to the procedure described in Sections 2.2.1 and 2.2.2 monometallic and bimetallic sols were prepared and used without carbon support. The desired amount of sol was diluted in the reacting solution for catalytic tests.

2.3. Oxidation procedure

2.3.1. Oxidation at uncontrolled pH

Catalyst evaluation at uncontrolled pH (from initial pH 6.0 to ca. pH 2.6) was carried out varying the type of metal and, in the case of Au + Pt catalysts, the Au/Pt ratio. Reactions were performed in a thermostatted glass reactor (30 ml), provided with an electronically controlled magnetic stirrer connected to a large reservoir (5000 ml) containing dioxygen at 300 kPa. Glucose and the catalyst (reactant:metal = 3000 mol/mol) were mixed in distilled water (10 ml total volume). The reactor was pressurised at 300 kPa of O_2 and thermostatted at the appropriate temperature (343–363 K). After an equilibration time of 15 min, the mixture was stirred and analysis was carried out.

2.3.2. Oxidation at controlled pH

Glucose and catalyst (glucose:total metal = 20,000) in distilled water (total volume 15 ml) were stirred in a thermostatted glass reactor and dioxygen was bubbled (1000 ml min^{-1}) at atmospheric pressure. Glucose conversion versus time plot was registered by an automatic titrator (Titrino[®], Metrohm) at the controlled pH value of 9.5 and temperature 323 K.

2.4. Analysis of products

The products were identified and quantified by a comparison with original samples. Quantitative and qualitative analyses were performed by HPLC; C NMR was also used for qualitative analysis. In the case of free pH experiments, the conversion to gluconic acid was determined by NaOH-HCl inverse titration.

2.4.1. HPLC analysis

Analyses were performed on an ionic exchange Hamilton HC-75H form (305 mm \times 7.75 mm) column, using a succinic acid 0.55 mM solution as the eluent and a Shimadzu LC 10 AD instrument provided with a RID-10 A detector.

2.4.2. C NMR analysis

^{13}C NMR spectra were recorded in water on a Bruker 300 MHz without adjusting the pH. The assignment of peaks in the oxidation of glucose was made by comparison with standard spectra.

2.4.3. Titration procedure

Samples of the reacting mixtures, carried out at free pH, were treated with 1 M NaOH until pH 11–12 and then back-titrated with HCl 0.25 M. The titration curve (pH versus ml HCl added) highlighted two equivalent points, one corresponding to the excess of NaOH , the second to the organic acid at about pH 3.

3. Results and discussion

The reduction of the noble metal compounds HAuCl_4 , K_2PtCl_4 , PdCl_2 and RhCl_3 with NaBH_4 in the presence of glucose produces colloidal dispersions stable for some hours. The dimension of the particles was determined by XRD technique after immobilization on carbon: it ranged from 2.0 to 5.0 nm. In the case of the Au + Pt colloids, the peak position lied between the extreme values of the corresponding monometallic particles, suggesting that these bimetallic systems were in form of alloys (Table 1).

With the above catalysts, two series of experiments have been planned. In the first one the oxidation of glucose to free gluconic acid was investigated under moderate conditions (pressure 300 kPa, temperature 343–363 K), while in a second series of experiments the oxidation of glucose to gluconate in the presence

Table 1
XRD parameters of mono- and bimetallic catalysts

Metals	$2\theta^\circ$	D (nm)
Au	38.1	3.4
Pt	39.7	5.0
Pd	40.2	2.9
Rh	43.2	2.0
Au:Pt=4	38.4	4.8
Au:Pt=2	38.6	3.8
Au:Pt=1	38.9	3.3
Au:Pt=0.5	39.0	3.2
Au:Pt=0.25	39.1	3.0

Table 2

Catalytic activity of mono- and bimetallic catalysts. 1%M on carbon; $T = 343\text{ K}$; $P(\text{O}_2) = 300\text{ kPa}$; glucose/Au = 3000; reaction time = 6.5 h

Metals	Conversion %	TOF (h^{-1})
Au	11	51
Pt	13	60
Pd	<2	<2
Rh	<2	<2
Au–Pt, 1:1	64	295
Au–Pd, 1:1	20	92
Au–Rh, 1:1	<2	<2

of alkali was evaluated working at the fixed pH value of 9.5, atmospheric pressure and 323 K.

Kinetic tests have been carried out mainly with carbon supported metal particles owing to the high stability of these catalytic systems. In some cases catalysts were used in form of colloidal particles.

3.1. Uncontrolled pH experiments

Table 2 compares the catalytic performance of monometallic Au, Pd, Pt and Rh on carbon catalysts and bimetallic Au–M on carbon catalysts, having a common Au:M = 1 ratio(w/w) in the synthesis of free gluconic acid. Whereas monometallic systems are scarcely active, the conversion of glucose is enhanced by using Au–Pd and, in particular, Au–Pt catalysts. Mean TOF values up to 295 h^{-1} , referred to the total metal, have been calculated by titrating the produced gluconic acid after a reaction time of 6.5 h.

No other products, beside gluconic acid, have been detected by HPLC and NMR techniques.

Owing to the highest efficiency of the Au–Pt system, we made an optimization by changing the relative amount of the two metals from 4:1 to 1:4 (w/w). According to the results, reported in Table 3, the best performance was reached with supported catalysts having the Au:Pt = 2 ratio. The strong synergetic effect between gold and platinum metals is represented in Fig. 1 where unsupported bimetallic particles are also compared with the monometallic Au and Pt on carbon catalysts. We can outline that supported and unsupported bimetallic particles show a similar catalytic activity, which is ca. five times higher than the monometallic systems. The reported data were always achieved under catalyst-controlled kinetics, using appropriate stirring rate and catalyst:substrate ratio.

Table 3

Influence of Au:Pt ratio on supported catalysts. 1% (Au + Pt)/C; $T = 343\text{ K}$; $P(\text{O}_2) = 300\text{ kPa}$; glucose/Au = 3000; reaction time 2.5 h

Au:Pt	Conversion %	TOF (h^{-1})
4	29	348
2.5	68	816
2	77	924
1.5	62	744
1	20	240
0.5	23	276
0.25	26	312

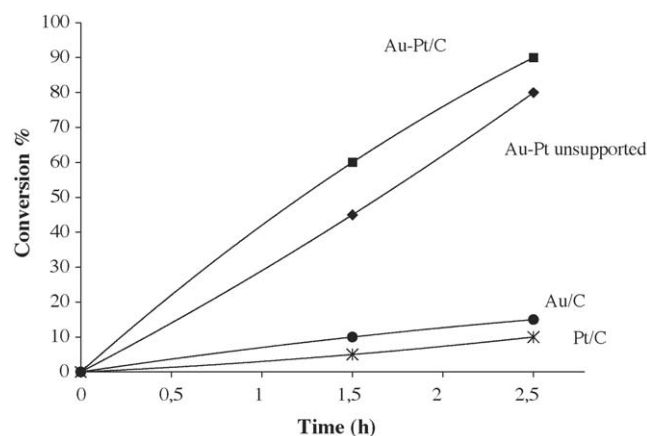


Fig. 1. Comparison between supported and unsupported catalysts. Au:Pt = 2:1 w/w; $P(\text{O}_2) = 300\text{ kPa}$; $T = 363\text{ K}$; glucose/Au = 3000.

3.2. Controlled pH experiments

Since a promoting effect of alkali in gold catalysed oxidation of glucose was established during previous studies [12,18], it seemed of interest to investigate the performance of Au–Pt bimetallic systems under basic conditions. For this purpose, the most effective catalytic combinations used under acidic conditions, Au:Pt = 2 and Au:Pt = 1, have been compared with monometallic gold, platinum and palladium catalysts, working with a Titrino apparatus at pH 9.5, atmospheric pressure and 323 K.

Under these conditions, the kinetic results reported in Table 4 showed faster reactions leading to gluconate: a stronger promoting effect of alkali resulted mainly in the case of supported catalysts, monometallic gold (TOF from 51 to 17200 h^{-1}) and bimetallic gold–platinum catalyst (TOF from 924 to 17600 h^{-1}). The similar activity obtained at pH 9.5 indicates the absence of synergetic effects between Au and Pt under these conditions. Correlations among unsupported catalysts are difficult to discuss owing to the instability of colloidal dispersions in the presence of alkali. However, after the 2.5 h test, gold–platinum and gold–palladium particles behave better than monometallic gold particles. In this latter case, a lower TOF value (4600 h^{-1}) has been found with respect to the value of 18043 h^{-1} previously calculated as initial rate [18]. A strong destabilizing effect of gluconate, leading in a short time to inactive large metal particles [18], could explain the lower TOF value mediated in the long time test. High TOF values found in the case of bimetallic

Table 4

Oxidation with mono- and bimetallic catalysts at pH 9.5. Glucose/Au = 20,000; $T = 323\text{ K}$; reaction time = 2.5 h

Metals	Type of catalyst	Conversion %	TOF (h^{-1})
Au	Supported	43	17200
Au–Pt (2:1)	Supported	44	17600
Au	Unsupported	12	4600
Pt	Unsupported	<2	<500
Pd	Unsupported	5	2000
Au–Pt (2:1)	Unsupported	26	10500
Au–Pd (1:1)	Unsupported	28	11600

unsupported catalysts could be due to a good stability of these colloids.

4. Conclusions

Comparing experiments in the absence and in the presence of alkali it is evident the great synergetic effect of platinum, along with a lower effect of palladium, working at low pH whereas almost no effect is present at pH 9.5. In the latter case bimetallic colloidal particles appeared more stable towards agglomeration than monometallic gold particles, allowing higher conversions. The different promoting effect of Pt and Pd under acidic and alkaline solution could be related to different reaction mechanisms. If we consider a reaction mechanism where alkali plays a strategic role, which favours the slow dehydrogenation step of glucose producing gluconate and H₂O₂ [18,19], no important effects of Pt and Pd metals on Au should be expected. However, no mechanistic studies are presently available in the case of glucose oxidation in acidic conditions for understanding the strong synergetic effect of platinum here detected.

From a synthetic point of view, the catalytic oxidation of glucose represents a target of practical interest in industrial chemistry [20] and in the present paper we have developed a catalytic system tailored for the synthesis of free gluconic acid having the preferred composition Au:Pt=2 (w/w).

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