

Selective Oxidation of D-Glucose on Gold Catalyst

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The selective oxidation of D-glucose to D-gluconic acid was performed at both controlled (7–9.5) and free pH values in an aqueous solution in the presence of a gold on carbon catalyst using dioxygen as the oxidant under mild conditions (323–373 K, $pO_2 = 100\text{--}300$ kPa). No isomerization of glucose to fructose was observed during the reaction, and total selectivity to D-gluconate was obtained. A comparative study of gold and commercial palladium and platinum-derived catalysts highlighted the unique property of supported gold, i.e., it is active at low pH (2.5), whereas at a buffered higher pH (9.5), gold and bismuth-doped platinum-palladium on carbon catalysts show comparable selectivity, though gold has a higher activity. Moreover, upon recycling, gold is more stable toward deactivation, although this also depends on the operative pH. © 2002 Elsevier Science (USA)

Key Words: selective oxidation; gold catalyst; liquid-phase oxidation; gluconic acid.

1. INTRODUCTION

Gluconic acid and its salts are important industrial products, they are used as water-soluble cleansing agents or as additives in food and beverages (1). For commercial purposes these products are exclusively prepared by the oxidation of glucose or glucose-containing raw materials.

Although the currently used oxidation method is based on biochemical transformation, recent developments have indicated that the catalytic route may be a valid alternative for producing gluconate on an industrial scale. In fact, early studies at the beginning of the 1970s (2–5) led to many papers and patents, the most important of which reported on the beneficial effect of doping platinum metal-group catalysts with heavy metals such as bismuth or lead (6–9). It has been reported that by using bismuth on palladium or platinum/palladium on carbon catalysts, some of the factors that limit the use of the catalytic route to produce gluconate appear to have been overcome; high selectivity and excellent conversion (>99%) were obtained. However, aspects such as the nature of the catalyst and the role of bismuth are still under discussion despite the many papers on this subject (10–14). Moreover, catalyst durability is also related to bismuth leaching, as was observed under the commonly used oxidative conditions (temperature range 303–333 K, pH 8–10, glucose 20–30 wt %, catalyst/glucose ratio 0.5–2%)

(15). Slightly alkaline conditions are apparently necessary to increase the reaction rate and to avoid drastic deactivation of the catalyst; conversely, such conditions are also responsible for side reactions that reduce gluconate productivity. Another important economic drawback of using bases is the production of gluconate instead of the free acid. Thus, from an industrial point of view, the fermentation process is still preferred to the catalytic process, despite problems related to microbe separation, control of by-products and the disposal of waste water.

Therefore, only the development of catalysts with excellent activity/selectivity (i.e., productivity) and durability will facilitate the oxidation of glucose with a catalyst, using dioxygen as the oxidant. In our previous studies on the oxidation of 1,2-diols, we emphasized the unusual selectivity of gold catalysts in oxidizing the primary alcoholic function to the corresponding carboxylate, in contrast to the lower selectivity shown by palladium or platinum on carbon catalysts (16–18). Moreover, we concluded that gold is less sensitive to overoxidation and/or self-poisoning than platinum or palladium.

As in the oxidation of alcohols the formation of an intermediate aldehyde was postulated (17). This prompted us to investigate gold as the catalyst for the selective oxidation of the aldehydic group. Therefore, given the reported valuable application of catalytic oxidation to the transformation of carbohydrates, we decided to investigate D-glucose as first substrate. The presence of both alcoholic and aldehydic (hemiacetal) groups in such a substrate also enabled us to study the competitive oxidation of these two different functional groups in the presence of the gold catalyst and, in comparison, in the presence of platinum- and palladium-based catalysts. Moreover, the oxidation of a free aldehydic group in competition with a primary alcoholic group (*n*-propanol and *n*-butanal) was also investigated to gain better insight into the reaction mechanism.

2. EXPERIMENTAL

2.1. Reagents and Apparatus

D-Glucose, *n*-propanol, and *n*-butanal (Fluka) were used without further purification. NaOH (Merck) was 99.9%

pure and stored under nitrogen. Gaseous oxygen (SIAD) was 99.99% pure. Gold powder (Fluka) was of the highest purity grade. Commercial 5% Pd/C (MPB5) was supplied by Süd Chemie-M.T., 5% Pt/C (ESCAT10) by Engelhard and 1%Pt–4%Pd–5%Bi/C (CEF 196XRA/W) by Degussa. BiONO₃ was used in a hydrochloric acid solution (16.2 g liter⁻¹ of bismuth). Polyvinyl alcohol (M 10,000) and NaBH₄ were purchased from Merck. The possible reaction products (gluconic acid, δ -glucono-lactone, 2-keto gluconic acid, fructose, glucose, saccharic acid, oxalic acid, gulonic acid, glucuronic acid, tartaric acid, tartronic acid, propanal, propionic and butyric acids), all from Fluka, were used as reference compounds. Activated carbon (X40S from CAMEL) (5–100 μ) with a specific area of 1100 m²/g was used after washing with distilled water until a neutral pH was reached.

2.2. Preparation of the Catalysts

2.2.1. Gold on carbon. Gold on carbon was prepared by immobilizing gold sol as reported previously (19, 20). An aqueous HAuCl₄ solution of the desired concentration was prepared (100 μ g/ml). To this was added the 2 wt% solution of the protective agent polyvinylalcohol (PVA), while stirring vigorously. Then, dropwise, a freshly prepared solution of NaBH₄ (0.1M) was added to reduce the gold. The sol was immobilized on carbon by adding the support to the metal dispersion while stirring vigorously until the solution was clear (about 1 h). The amount of support was calculated as having a final gold loading of 1 wt%. After 1 h, the slurry was filtered and the total absorption of gold was checked by ICP analysis of the filtrate.

The catalyst was filtered and then washed with hot water until the filtrate was chloride free (AgCl test); it was used wet. The metal contents of the fresh and used catalysts were determined by ICP analysis (Jobin Yvon JY24). XRPD (Rigaku D III-MAX horizontal-scan powder diffractometer with CuK α radiation) and XPS (M-Probe Instrument [SSI] equipped with a monochromatic AlK α source [1486.6 eV]) analyses were performed to determine the size of the metal crystallites and the atomic percentage of gold on the carbon surface (2–5 nm).

2.2.2. Bimetallic catalysts. The 5%Pd–5%Bi on carbon catalyst was prepared according to the impregnation method, as previously reported (21) on commercial 5% Pd on carbon.

2.3. Oxidation Procedure

All the experiments at a controlled pH were carried out at atmospheric pressure by bubbling dioxygen through the slurry (20 Ncm³ min⁻¹) and controlling the pH (7, 8, and 9.5). The experiments were performed by using a 718 STAT Titrino (Metrohom) equipped with a 0.3M NaOH reserve.

Glucose and the catalyst (S/M = 1000) were typically mixed in distilled water (4 wt% solution). The temperature of the stirred mixture was kept at 323 K and, as soon as the reaction started, a solution of NaOH 0.3M was added automatically to maintain the pH of the solution at a fixed value (7, 8, or 9.5 \pm 0.1). The samples were analyzed at various times by ¹³C-NMR and/or HPLC.

When the pH was not controlled, the reactions were carried out in a temperature-controlled glass reactor (30 ml) with an electronic magnetic stirrer connected to a large reservoir (5,000 ml) containing oxygen at 300 kPa. A flow-time diagram of the oxygen uptake was plotted by a mass flow controller connected to a PC through an A/D board.

Glucose and the catalyst (reactant/metal = 1000) were mixed in distilled water (4 wt% solution). The reactor was pressurized at 300 kPa of O₂ and the temperature was kept at 363 K. After a period of equilibration (15 min), the mixture was stirred and the products were analyzed by time (every 10 min). In recycling tests, following the first run, the catalyst was filtered off and, after washing with distilled water or another specified treatment, was reused in the next run with a freshly prepared solution of glucose.

2.4. Analysis of Products

The products were identified and quantified by comparing them with actual samples. Both the quantitative and qualitative analyses were performed by HPLC; ¹³C-NMR was also used for qualitative analysis. The quantitative analysis of the acidic products was deduced from the amount of NaOH that was added for neutralization and performed by titration (inverse).

2.4.1. HPLC analysis. Analyses were performed on a Varian 9010 instrument equipped with a Varian 9050 UV (210 nm) and a Waters 2410 R.I. detectors. An Alltech OA-1000 column (300 \times 6.5 mm) was used with aqueous H₂SO₄ 0.01M (pH 2.1) (0.4 ml/min) as the eluent. Glucose and gluconic acid peaks overlap but glucose does not adsorb at the used λ for UV detection (210 nm); thus, the amount of glucose was determined by subtracting the gluconic acid contribution quantified at 210 nm. Alternatively, the glucose quantitative analysis was carried out using a column (Supelcosil LC-NH₂ [250 \times 4.6 nm]) specially designed for sucrose with CH₃CN/H₂O 45/55 as the eluent. This latter analysis also confirmed the absence of isomerization of glucose to fructose.

2.4.2. NMR analysis. ¹³C-NMR spectra were recorded in water on a Bruker 300 MHz without adjust the pH. The assignment of peaks in the oxidation of glucose was made by comparing with standard spectra.

2.4.3. Titration procedure. If necessary, a sample of the reaction mixture was neutralized (until pH 10–11) with NaOH 1M and then back-titrated with HCl 0.1N. The titration curve (pH versus ml HCl added) highlighted two

equivalent points, one corresponding to the excess of NaOH, the second to an organic acid at pH about 3.

3. RESULTS AND DISCUSSION

3.1. Oxidation at Controlled pH

We recently reported on the use of a gold on carbon catalyst in the selective oxidation of 1,2-diols to α -hydroxyacids (16–18). Although we proved a difference in the activity of the gold catalysts, depending on the preparation procedure (20), an intrinsic higher selectivity of gold toward primary alcoholic function with respect to palladium or platinum catalysts was noted. Strong alkaline conditions were required for gold to speed up the reaction, whereas in the other cases this also enhanced selectivity. However, we also noted that unlike Pd and Pt, the presence of an alkali to oxidize the alcoholic group is necessary when using gold-supported catalysts. Aldehyde is the supposed intermediate of the reaction; thus, we tested gold on carbon as the catalyst in the oxidation of glucose, keeping in mind that, when glucose is used as the reagent, a strong alkaline solution cannot be used, because the reagent starts to decompose at a pH above 11. Therefore, our experiments were conducted at a pH of 7–9.5 in order to avoid alkali-promoted reactions such as retro-Claisen, Cannizzaro, condensation, or isomerization.

In addition, most patents and papers dealing with this subject report experiments conducted in a weakly alkaline medium at a controlled pH of 9 to 10, because it was recently shown that the catalytic activity of Pd or Pt on carbon, with or without Bi-doping strongly depends on the pH (22–24). In fact, carrying out the oxidation at 323 K, without controlling the pH, led to the rapid poisoning of the catalysts, which was ascribed to strong adsorption of the reaction product.

At a pH of 9.5 and by bubbling oxygen through the slurry at 20 Ncm³ min⁻¹ and a temperature of 323 K, we confirmed the beneficial effect of adding bismuth to monometallic Pd or Pt catalysts (6–9) (Fig. 1a). Surprisingly we also obtained a reversed activity in the series Au/C, Pd/C, and Pt/C with respect to that observed in alcoholic group oxidation in ethane-1,2-diol (16–18), gold being superior to Pt. Pd was found to be inactive. Moreover, gold was much more active than commercial Pt–Pd–Bi or Pd–Bi catalysts that were specifically designed for glucose oxidation.

The difference in the various catalysts increases when the pH of the reaction decreases. At pH 8, a drastic decrease in the TOF of the Pt–Pd–Bi and Pd–Bi on carbon catalysts occurred; this decrease corresponded to the catalyst activity as dependent on time or conversion: at about 50 to 70% conversion of glucose, the activity of these catalysts was near zero (Fig. 1b). This shows that the catalyst was clearly poisoned, probably due to the reaction products. TOFs do not differ very much from the value obtained at pH 9.5 at the beginning of the reaction, but, as the reaction proceeds,

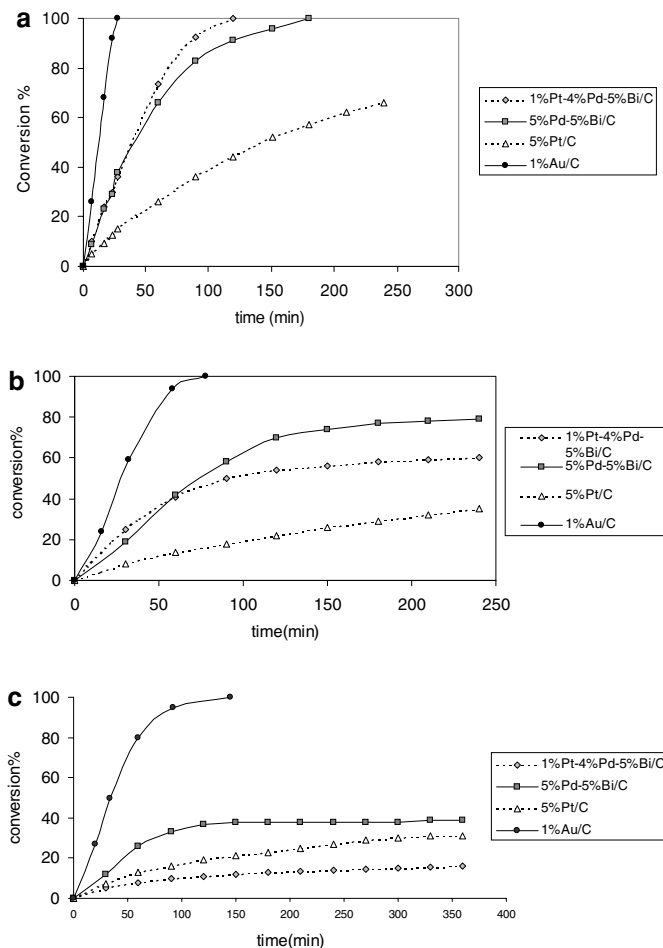


FIG. 1. Glucose oxidation under pH-controlled conditions. Reaction conditions: glucose 4 wt%; glucose/M = 1000; O₂ flow = 20 ml/min; T = 323 K: (a) the pH was maintained at 9.5 by adding dropwise NaOH 0.3M; (b) the pH was maintained at 8 by adding dropwise NaOH 0.3M; (c) the pH was maintained at 7 by adding dropwise NaOH 0.3M.

the reaction rate decreases to around zero after about 2 h (corresponding to 55–70% glucose conversion). Thus, the overall TOF value is considerably lower at pH 8 than at pH 9.5 and, most importantly, 100% conversion of glucose cannot be reached.

In contrast, in the case of gold on carbon at pH 8, the reaction was complete in little more than an hour, with almost the same initial rate observed at pH 9.5 or 8. However, in this case too, a slight decrease in the reaction rate was observed above 95% glucose conversion (Fig. 1b), resulting in a lower TOF value at pH 8 than that obtained at pH 9.5.

When the pH was decreased to 7, we found that deactivation of Pt–Pd–Bi and Pd–Bi on the carbon catalyst proceeded at considerably lower conversion than at pH 8 (Fig. 1c); at pH 7 this deactivation appeared to be more rapid for Pt–Pd–Bi (<20% conversion) than for Pd–Bi on carbon (40% conversion), both being less resistant than monometallic Pt/C. Previous studies correlated the behavior of Pd- and

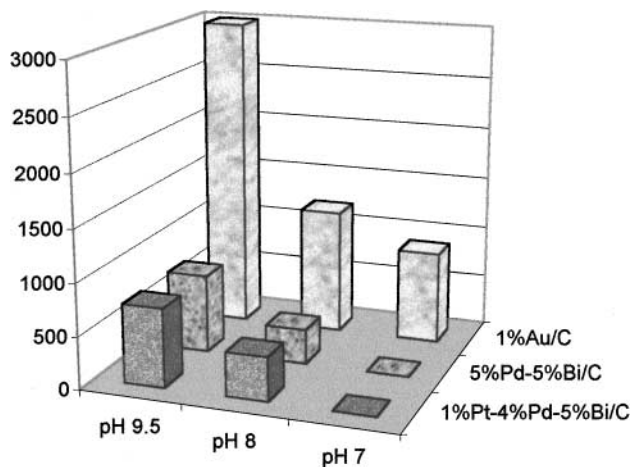


FIG. 2. TOF (h^{-1}) as a function of pH.

Pt-based catalysts with the poisoning effect of the formed gluconate, which becomes more evident as the pH decreases (13). Thus as the amount of free acid increases with decreasing pH, the poisoning of the Bi-doped catalysts was considered to be a temporary inhibition, related to the concentration of gluconic acid on the catalyst surface and, therefore, to the concentration of the acid in solution. This was in part confirmed by removing the solution from a deactivated catalyst and adding a fresh, acid-free solution of glucose: the activity was partially restored (80%), probably owing to the dilution of the adsorbed gluconic acid.

Gold on carbon, unlike the other tested catalysts, enabled a quantitative transformation of glucose even at pH 7. However, the TOF value was considerably lower than that at pH 9.5, partly because of the decrease in the reaction rate above 85 to 90% conversion.

Figure 2 shows the trend of the TOF values at different pH by using the three different catalysts (Au, Pt–Pd–Bi, Pd–Bi). Given that we report TOF values calculated at 30% conversion, but knowing that gold is unique in achieving total conversion at any pH, it can be seen that gold on carbon shows the lowest decrease in activity with decreasing pH.

Our study on glycol oxidation using Au/C had revealed the resistance of this catalyst to the poisoning by hydroxy carboxylate (16–18); thus, we first ascribed the decrease in the reaction rate above 85% conversion to a kinetic effect of the lower concentration of the reactant. Adding a new sample of glucose at the end of the reaction resulted in a kinetic profile identical to the first run. However, more detailed experiments of recycling (Figs. 3a–3c), carried out by removing the reacted solution and washing the catalyst with water before reusing it in the following run with a freshly prepared solution of glucose, showed a different behavior. In four runs, we observed a decrease in activity, the degree of which depended on the pH of the reaction ($\text{pH } 7 > \text{pH } 8 > \text{pH } 9.5$). Analyses on fresh and used cata-

lyst revealed a leaching of metal which was important at pH 7 (18%), whereas no leaching of metal was observed at pH 9.5. The diameter of the metal particle also increased (Table 1): when metal leaching increases, the particle size decreases. This behavior was explained by the dissolution and reprecipitation of the gold species. Since XPS analyses revealed only the presence of metallic gold, we assume that Au(I, III) species, which may be present, reduced, probably as a result of carbon or other reducing species.

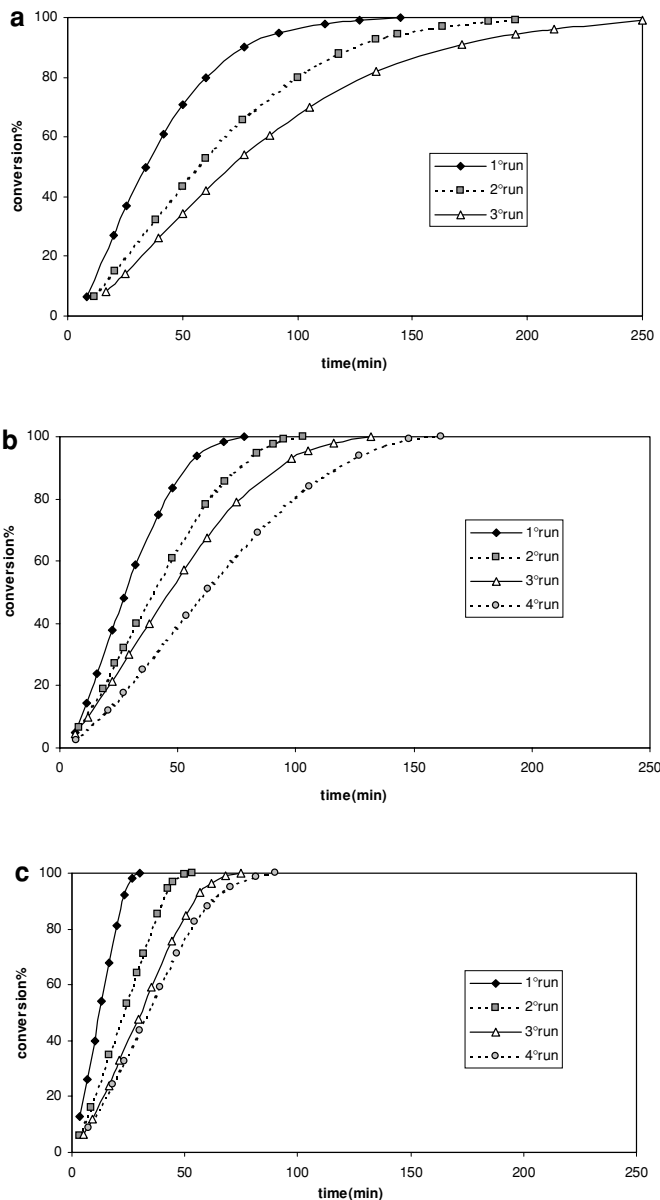


FIG. 3. Recycling tests under pH-controlled conditions using 1%Au/C. Reaction conditions as in Fig. 1. The catalyst was washed with distilled water every run and then used in a fresh glucose solution: (a) the pH was maintained at pH 7 by adding dropwise NaOH 0.3M; (b) the pH was maintained at 8 by adding dropwise NaOH 0.3M; (c) the pH was maintained at 9.5 by adding dropwise NaOH 0.3M.

TABLE 1
Data of Fresh and Used Au/C Catalyst

	Fresh	Used at pH 9.5 ^a	Used at pH 8 ^a	Used at pH 7 ^a
%Au [ICP]	0.89	0.89	0.81	0.73
d(nm) [XRPD]	4.42	5.85	5.71	5.26

^a Used in four runs (see Figs. 3a–3c) and washed with water every run.

3.2. Oxidation at Uncontrolled pH

As previously reported, platinum-based catalysts rapidly deactivate in the liquid-phase oxidation of glucose under uncontrolled pH (13, 23). Based on the observation that gold enables 100% conversion, even at neutral pH, we also tested the behavior of gold on carbon under uncontrolled pH.

Based on the assumption that gold on carbon does not suffer from oxygen poisoning, we used a closed vessel at an oxygen pressure of 300 kPa to increase oxygen dissolution, thus speeding up the reaction. As shown in Fig. 4, gold on carbon shows a lower reaction rate than under pH-controlled conditions, but it also enabled a quantitative transformation without controlling the pH. This led us to study the recycling of the catalyst under the same conditions (Fig. 5). Washing the catalyst with water in each cycle, after the third run we observed a decrease in activity which increased markedly upon recycling. ICP analysis failed to detect leaching of gold in a single reactant solution; leaching of gold was obvious, however, after considering the metal content following a few runs: 10% of the metal is lost in only two runs and about the 70% in six runs.

In order to reduce metal leaching we tentatively changed the treatment of the catalyst in the recycling step (Fig. 5). Nevertheless by operating both acidic or reductive washing we still obtained a strong deactivation of the catalyst, faster than when water was employed; thus we concluded that the loss of metal does not involve the treatment of the catalyst.

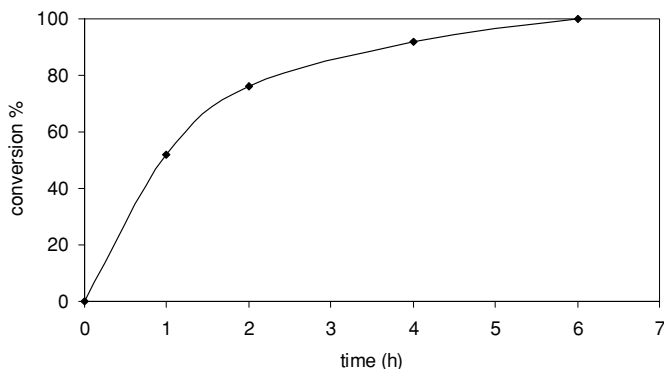


FIG. 4. Glucose oxidation at uncontrolled pH conditions using 1% Au/C catalyst. Reaction conditions: glucose 4 wt%; glucose/M = 1000; p_{O_2} = 300 kPa; T = 373 K.

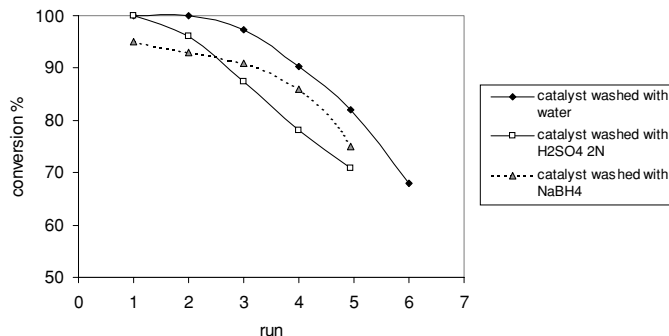


FIG. 5. Recycling tests at uncontrolled pH using 1% Au/C with different treatment. Reaction conditions: glucose 4 wt%; glucose/M = 1000; p_{O_2} = 300 kPa; T = 373 K; t_{react} = 6 h.

3.3. Selectivity of the Reaction

Using fresh catalysts based on gold or even on platinum/bismuth-modified metals, we obtained very high (>99%) selectivity to gluconate. Differences between gold and platinum-based catalysts were detected only by recycling, with gold always showing total selectivity.

We separated two contributions leading high selectivity: first, avoiding isomerization of glucose to fructose (obtainable by operating at a pH as low as possible) and, second, enhancing the oxidation rate of the aldehydic group with respect to the alcoholic group. In the case of gold, as stated above, the presence of a base is compulsory in alcohol oxidation. Thus the absence of oxidation in the alcoholic group, observed under acidic (uncontrolled pH) conditions, was not surprising. On the contrary, we expected that at controlled pH, especially when pH increases (9.5), the selectivity decreases since the oxidation of the alcoholic group also begins to become possible. It is difficult to detect real selectivity in glucose oxidation due to analytical limits. Thus, in a parallel experiment, we tested the competitive oxidation of an aldehyde (*n*-butanal) and a primary alcohol (*n*-propanol). We observed that aldehyde oxidation proceeds quicker than alcohol oxidation (Table 2) and, in the case of the Au/C catalyst, we confirmed the total inactivity of the Au/C catalyst toward alcohol oxidation. Moreover, the oxidation of the aldehyde is reported to proceed through an intermediate acetal form (10). Thus, we assumed that starting from the hemiacetal form, as in glucose, the aldehyde oxidation rate would be promoted, while that of the alcohol would remain the same. Considering that (i) at 100% conversion, i.e., in the absence of glucose, HPLC analyses excluded the presence of byproduct derived from alcohol oxidation (<1%), and the analysis by titration fitted with the presence of 100% acidic product, (ii) in the test on competitive oxidation of aldehydic and alcoholic groups only the aldehydic is oxidized, we can propose for glucose oxidation in the presence of Au/C a total selectivity to gluconic acid.

TABLE 2
Oxidation of *n*-Butanal/*n*-Propanol Mixture

Run	Catalyst	pH	Butyrate (mol%)	Propanoate (mol%)
1 ^a	1% Au/C	9.5	74	0
2 ^a	1% Pt-4% Pd-5% Bi/C	9.5	76	0
3 ^a	5% Pd-5% Bi/C	9.5	69	0
4 ^a	5% Pt/C	9.5	54	5
5 ^a	1% Au/C	8	63	0
6 ^a	1% Pt-4% Pd-5% Bi/C	8	70	0
7 ^a	5% Pd-5% Bi/C	8	57	0
8 ^a	5% Pt/C	8	36	2
9 ^b	1% Au/C	No control	63	0
10 ^b	1% Pt-4% Pd-5% Bi/C	No control	70	0
11 ^b	5% Pd-5% Bi/C	No control	70	13
12 ^b	5% Pt/C	No control	58	37

^a Reaction conditions: *n*-butanal/*n*-propanol (mol/mol) = 1; O₂ flow = 20 ml/min; *T* = 323 K; *t*_{react} = 1 h. The pH was maintained at the indicated constant value by dropping NaOH 0.3M.

^b Reaction conditions: *n*-butanal/*n*-propanol (mol/mol) = 1; pO₂ = 300 kPa; *T* = 363 K; *t*_{react} = 1 h.

4. CONCLUSION

The catalytic oxidation of D-glucose to D-gluconic acid remains an attractive target in industrial chemistry.

The present study showed that gold on carbon catalyst is a valid alternative to most of the investigated multimetallic catalysts based on palladium and/or platinum metals. Moreover, it was shown that gold has a unique property, i.e., it operates without the external control of pH, thus ensuring total conversion at all pH values. We already reported on the resistance of gold to oxygen poisoning (16–18) during alcohol oxidation, but gold is probably also less sensitive to chemical poisoning than was proven for platinum catalysts (13). Nevertheless, metal leaching was proved to be more consistent as pH decreased and corresponded to a gradual decrease in activity.

The high selectivity of the gold catalyst to D-gluconate is explained by considering (i) the large gap in the oxidation rate of the aldehydic and the alcoholic groups, (ii) the inertness toward oxidation of secondary alcoholic group, and (iii) the operative pH at which isomerization of glucose is avoided. Comparing gold with platinum or palladium on carbon catalysts, we conclude that bismuth must be involved to obtain good results in the cases of platinum-

or palladium-based catalysts, which, however, remain inferior to the results obtained with the monometallic gold catalyst.

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REFERENCES

- Kirk-Othmer, "Encyclopedia of Chemical Technology," 4th ed. Wiley, New York, 1993; Datta, R., in "Encyclopedia of Chemical Technology," Vol. 13, 4th ed. Wiley, New York, 1995.
- Johnson, Matthey and Co., Ltd., GB 1208101 (1970).
- Kawaken Fine Chemicals Co. Ltd., JP 8007230 (1980).
- Mitsui Toatsu Chemicals Inc., JP 7652121 (1976).
- Kawaken Fine Chemicals Co. Ltd./Kao Corp., JP 5872538 (1983).
- Asahi Chemical Industry Co. Ltd. DE-OS2936652 (1980).
- Kawaken Fine Chemicals Co. Ltd./Kao Corp., U.S. Patent 4,843,173 (1989).
- Degussa Aktiengesellschaft, U.S. Patent 5,132,452 (1992).
- For a review see also: Besson, M., and Gallezot, P., *Catal. Today* **57**, 127 (2000).
- Mallat, T., and Baiker, A., *Catal. Today* **19**, 247 (1994).
- Wenkin, M., Renard, C., Ruiz, P., Delmon, B., and Devillers, M., *Stud. Surf. Sci. Catal.* **110**, 517 (1997).
- Besson, M., Lahmer, F., Gallezot, P., Fuertes, P., and Fleche, G., *J. Catal.* **152**, 116 (1995).
- Abbadì, A., and van Bekkum, H., *Appl. Catal. A: General* **124**, 409 (1995).
- Bronnimann, C., Bodnar, Z., Hug, P., Mallat, T., and Baiker, A., *J. Catal.* **150**, 199 (1994).
- Wenkin, M., Touillaux, R., Ruiz, P., Belmon, B., and Devillers, M., *Appl. Catal. A: General* **148**, 181 (1996) and references cited therein.
- Prati, L., and Rossi, M., *Stud. Surf. Sci. Catal.* **110**, 509 (1997).
- Prati, L., and Rossi, M., *J. Catal.* **176**, 552 (1998).
- Bianchi, C., Porta, F., Prati, L., and Rossi, M., *Topics in Catal.* **13**, 231 (2000).
- Prati, L., and Martra, G., *Gold Bull.* **32**, 96 (1999).
- Coluccia, S., Martra, G., Porta, F., Prati, L., and Rossi, M., *Catal. Today* **61**, 165 (2000).
- Tsubota, S., Cunningham, D. A. H., Bando, Y., and Haruta, M., in "Preparation of Catalysts VI" (Studies on Surface Science and Catalysis) (G. Poncelet, J. Martens, B. Delmon, P. A. Jacobs, and P. Grange, Eds.), Vol. 91, p. 227. Elsevier, Amsterdam, 1995.
- Despeyroux, B. M., Deller, K., and Peldszus, E., in "New Developments in Selective Oxidation" (G. Centi and F. Trifirò, Eds.), p. 159. Elsevier, Amsterdam, 1990.
- Abbadì, A., and van Bekkum, H., *J. Mol. Catal. A: Chemical* **97**, 111 (1995).
- Abbadì, A., Makkee, M., Visscher, W., van Veen, J. A. R., and van Bekkum, H., *J. Carbohydr. Chem.* **12**, 573 (1993).