JOURNAL OF CATALYSIS 152, 116–121 (1995)

Catalytic Oxidation of Glucose on Bismuth-Promoted Palladium Catalysts

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Received May 3, 1994; revised September 1, 1994

Water solutions of glucose (1.66 mol liter^{-1}) were oxidized with air at 313 K on palladium catalysts supported on active charcoal. High gluconate yields (99.3%) were obtained in the presence of bismuth-promoted catalysis. Bismuth was deposited via a surface redox reaction on Pd/C catalysts containing 1- to 2-nm Pd particles. A STEM-EDX study showed that bismuth atoms are selectively and homogeneously deposited on the palladium particles. The catalyst can be recycled without loss of activity and selectivity. Bismuth was not leached from the catalyst during reaction and recycling. Bismuth adatoms prevent oxygen poisoning of the palladium surface by acting as a co-catalyst in the oxidative dehydrogenation mechanism. It was determined by calorimetric measurements that oxygen should adsorb preferentially on bismuth rather than on palladium. © 1995 Academic Press, Inc.

1. INTRODUCTION

Noble-metal-catalyzed oxidations with air of carbohydrates and derivatives have received increasing attention in the past few years (1, 2). In a number of cases, the selectivities of these catalytic processes can match those of enzymatic processes with the additional advantages of higher site–time yields and cleaner technologies. Thus, gluconic acid, used as a biodegradable chelating agent and as an intermediate in the food and pharmaceutical industries, is currently prepared by enzymatic oxidation of glucose (3). Catalytic oxidation on bimetallic Pd–Bi catalysts, which gives high gluconate yields even after many recycling operations (4, 5), might challenge the enzymatic process. A promoting effect of bismuth on the activity of Pd catalysts was also observed in lactose oxidation (6). Trimetallic Pt–Pd–Bi catalysts have been proposed (7), but the presence of platinum does not seem to bring further advantages. In the absence of bismuth, the activity and selectivity of palladium in glucose oxidation are much lower because catalysts deactivate. Thus in a previous investigation (8), we have shown that the smaller the particle size, the higher the deactivation as the reaction proceeds. This was attributed to oxygen poisoning of the metal surface which is particle size dependent because palladium particles smaller than 2 nm have a high affinity for oxygen. Oxygen poisoning of metal catalysts during oxidation of carbohydrates or alcohol has been documented earlier by groups at Eindhoven (9–11) and Delft (12–14). Strong adsorption of acids on the metal surface when the pH is not regulated (15, 16) and irreversible adsorption of reactants or by-products (17) are other causes of poisoning.

The present investigation was intended to enable a better understanding of the role of bismuth on the activity, selectivity, and stability of glucose oxidation catalysts where bismuth was deposited on small palladium particles by surface redox reactions.

2. EXPERIMENTAL

Catalyst Preparation

Pd/C catalysts were prepared by ion-exchange of an active charcoal (CECA 50S, 1400 m^2 g^{-1}). The support was washed with hot hydrochloric acid to eliminate mineral impurities. Then, it was oxidized with sodium hypochlorite solutions (3.5% active chlorine) at 300 K for 24 h to create exchangeable carboxylic acid groups. Ion exchange was performed by stirring the support for 15 h in an ammoniacal solution of $Pd(NH_3)_4Cl_2$ under nitrogen atmosphere. The suspension was filtered, washed with water until neutral, and dried overnight under an N_2 atmosphere at 373 K. Reduction was carried out in a glass cell under flowing hydrogen (250 ml min^{-1}) by heating at 1 K min^{-1} from 298 to 573 K and maintaining this temperature for 2 h. The powder was cooled to 300 K under argon and then contacted with air diluted with argon. The PdBi/C catalysts were prepared in the reaction vessel before the oxidation started. A suspension of the Pd/C catalyst in 300 ml of deionized water was heated at 313 K while nitrogen was bubbled through. After 20 min, 500 mmol of

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0021-9517/95 $6.00

D-glucose monohydrate was dissolved and the suspension was stirred for 10 min. A required volume of a hydrochloric acid solution of $BiONO_3$ (16.2 g liter^{-1} of Bi) was added dropwise to the suspension under continuous stirring. During all these operations nitrogen flow was maintained and the temperature was kept at 313 K.

Oxidative Procedure

Oxidations of glucose solutions (1.66 mol liter^{-1}) were performed in a thermostated glass reactor of 500 ml volume equipped with a stirrer, a gas supply system, an oxygen electrode, and a pH electrode. During the experiment, the acids formed were neutralized to maintain a constant pH in the reaction medium. This was achieved by addition of a 30% aqueous solution of sodium hydroxide with a pump under the control of a pH regulator (Radiometer). The oxygen concentration in the liquid phase was monitored with an oxygen sensor (Ingold and Radiometer). A scheme of the reactor is given in Fig. 1.

After preparation of the PdBi/C catalyst, the oxidation reaction was started in the same reaction vessel by switching from nitrogen to air. The reaction was conducted at 313 K, pH 9, stirring at 1200 rpm, and air was bubbled through at 1.5 liter min^{-1}. The consumption of alkali, the pH, and the oxygen concentration were recorded continuously. Samples of the reaction medium were taken after various time intervals and analyzed by HPLC on Aminex A27 and Q15S columns from Bio-Rad. Residual reducing carbohydrates were analyzed accurately by redox titration (Bertrand method) and by enzymatic titration (Boehringer–Mannheim). After reaction, catalysts were recycled by filtering the reaction mixture on a polyester filter (11-μm pores) to recover the catalyst powder, which was then washed with deionized water and reused as such.

Characterization of Catalysts

Catalysts were characterized after reaction, i.e., after filtering and washing the catalyst powder. The concentrations of palladium and bismuth in the catalysts were measured by atomic absorption spectroscopy after dissolving the solid. The concentration of bismuth in the reaction medium was determined by UV spectroscopy. The sizes of the metal particles were measured by high-resolution transmission electron microscopy (TEM) with a JEOL 100 CX microscope. TEM views were taken on ultramicrotome sections of the catalyst cut with a diamond knife after embedding in epoxy resin (Taab 812 resin kit). The compositions of individual metal particles were measured with a field-emission gun, scanning transmission electron microscope (STEM) VG HB 501 at a 1.5-nm spatial resolution on thin sections. Calorimetric data were obtained with a heat-flow microcalorimeter from Setaram.

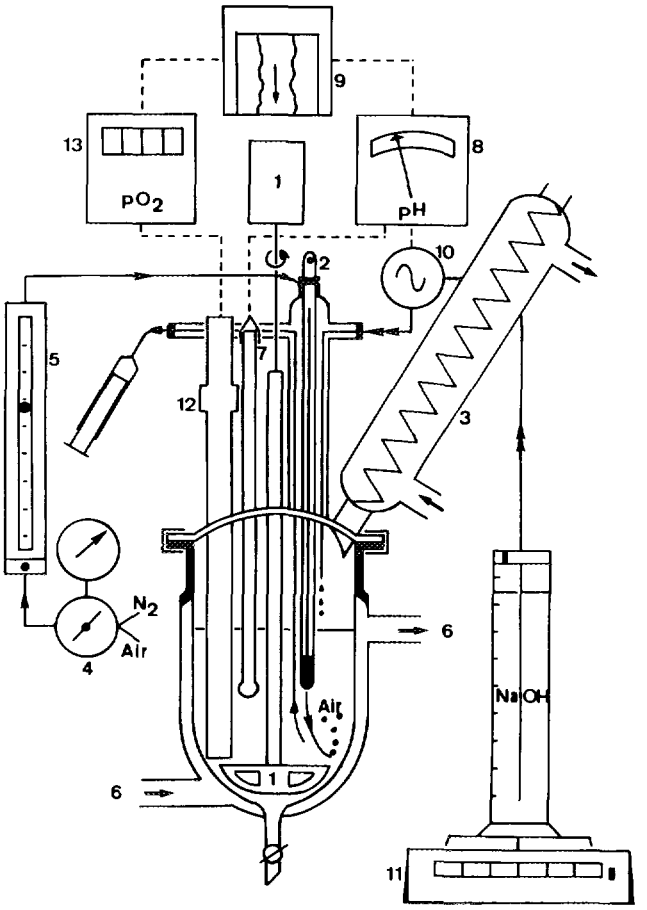

FIG. 1. Scheme of the reaction vessel and attachments. (1) Stirrer; (2) thermometer; (3) condenser; (4) air inlet; (5) flowmeter; (6) temperature regulator; (7) pH electrode; (8) pH-meter; (9) pen recorder; (10) pump; (11) scale; (12) O_2 electrode; (13) pO_2-meter.

Before measurements, the catalysts were evacuated and treated under hydrogen at 423 K for 2 h and then outgassed at 423 K for 2 h. The catalysts were contacted with small increments of oxygen, and the corresponding heats of adsorption were recorded.

3. RESULTS AND DISCUSSION

1. Bismuth Deposition on Palladium Particles

The palladium catalyst Pd/C prepared by ion exchange contains 4.7 wt% palladium. It was determined by TEM on ultramicrotome sections of the catalyst grains that the dispersion of the metal is similar to that found in previous studies (8, 15, 18), namely that palladium particles are in the size range 1–2.5 nm and are homogeneously distributed in the charcoal grains. This high dispersion of palladium and its stability to sintering was attributed to the interaction of the particles with the acidic functional groups present on the support.

TABLE 1

Product Distribution[a] after Successive Recyclings of PdBi/C

Run	Conversion (%)	Yield/mol%[b] 1	2	3	4	Selectivity (%)
1	99.6	99.4	<0.4	<0.4	0.2	99.8
2	99.7	98.9	<0.4	0.6	0.2	99.1
3	99.8	98.5	0.4	0.8	0.2	98.7
4	99.9	98.5	0.4	0.7	0.2	98.6
5	99.9	99.1	<0.4	0.6	0.2	99.2
Pd/C	82.6[c]	78.1	1.4	2.3	0.7	94.6

[a] After 155 min, T = 313 K, pH 9, [glucose]/[Pd] = 787, Bi/Pd = 0.1.
[b] 1, gluconate; 2, 2-ketogluconate; 3, 5-ketogluconate + glucarate; 4, fructose.
[c] After 24 h.

A PdBi/C catalyst prepared with an atomic ratio Bi/Pd = 0.1 by introducing the required amounts of $BiONO_3$ in the suspension of Pd/C in glucose solution was used in five successive glucose oxidation reactions with air. The reaction data given in Table 1 will be discussed in Section 3.2. The bismuth concentration was measured in the gluconate solutions after each reaction run, and bismuth was also analyzed in the catalyst after the fifth oxidation run. These measurements show that bismuth leakage, if any, would be less than 2 ppm during each reaction and the amount of bismuth measured on the catalyst was the same as that introduced initially in the solution. Therefore, bismuth is quantitatively fixed on the catalyst and remains fixed during the five oxidation reactions.

The local compositions of catalysts were measured by STEM-EDX analysis at a 1.5-nm spatial resolution on thin sections of the catalyst grains cut with an ultramicrotone. Bi/Pd ratios were measured either on microdomains encompassing a collection of particles or on nanodomains containing a single particle. Bismuth was never found as separate particles on the support; instead all the particles detected were found to be bimetallic. Analysis of sample areas containing 20–100 particles gives a ratio Bi/Pd = 0.1, similar to that of the overall composition. The ratios measured on individual particles range between 0.06 and 0.20, these fluctuations being partly due to the poor statistics of stored counts from the BiL and PdK X-ray emission lines because of the limited number of atoms present in single 2-nm particles. The STEM-EDX study gives clear evidence that bismuth atoms are selectively and homogeneously deposited on the palladium particles.

The homogeneous bismuth distribution is due to the low bismuth concentration (Bi/Pd (total) = 0.1, and given the high palladium dispersion, the ratio Bi/Pd (surface) does not exceed 0.15) and to the small size of the palladium particles well isolated from each other. A homogeneous distribution of bismuth was also reported by Mallat *et al.* (17) on small isolated platinum particles. However, the method of preparation is probably the main cause for the homogeneous bismuth deposition. Indeed, acidic $BiONO_3$ solutions were added to the slurry of Pd/C catalyst stirred in glucose solution in the absence of air; under these conditions the redox surface reaction

$$(PdH)_{surface} + BiO^+ \rightarrow (Pd\text{–}Bi)_{surface} + H_3O^+$$

should occur, where chemisorbed hydrogen comes from the dehydrogenation of glucose on the metal. It has been shown that at high pH, a continuous dehydrogenation of glucose occurs on platinum catalysts (19). Under the present conditions the dehydrogenation should stop when the surface is saturated with gluconic acid and hydrogen; therefore only limited amounts of bismuth adatoms can be loaded selectively on the metal surface.

2. *Reaction Data*

Activities of catalysts. Glucose oxidation reactions were conducted on catalysts with Bi/Pd = 0.1 or 0.2. Because the selectivity to gluconic acid is high (vide infra), the conversion can be conveniently measured from the amounts of sodium hydroxide added to the reaction medium to maintain a constant pH. Figure 2 gives the conversion as a function of time for the parent Pd/C catalyst and for a PdBi/C catalyst with Bi/Pd = 0.2. Glucose oxidation goes to completion within 130 min on PdBi/C whereas, as noted previously (8), the rate on Pd/C decreases with time and the conversion reaches a plateau which was attributed to a poisoning of the small palladium particles by chemisorbed oxygen.

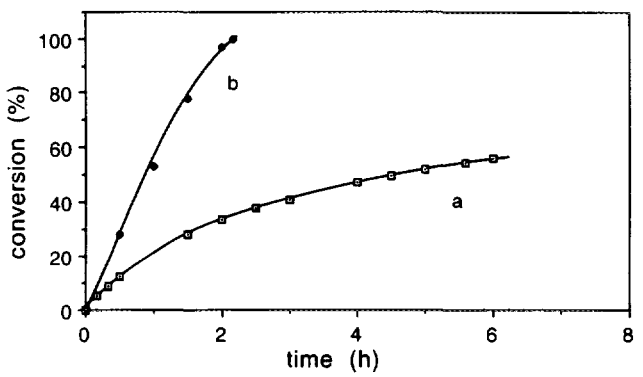

FIG. 2. Glucose conversion as a function of time for a catalytic ratio [glucose]/[Pd] = 787 (T = 313 K, pH 9). (a) 4.7 wt% Pd/C; (b) PdBi/C (Bi/Pd = 0.2).

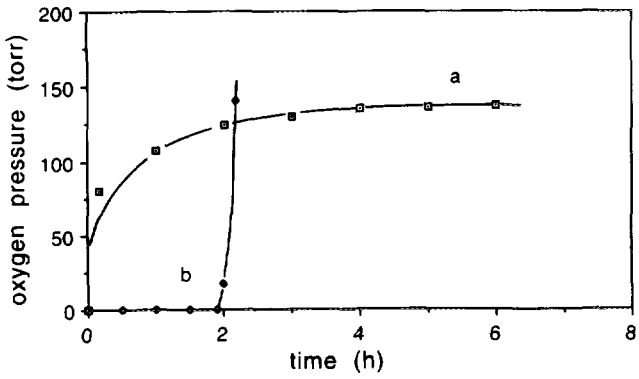

FIG. 3. Oxygen pressure in the liquid phase during glucose conversion. (a) Pd/C; (b) PdBi/C (Bi/Pd = 0.2).

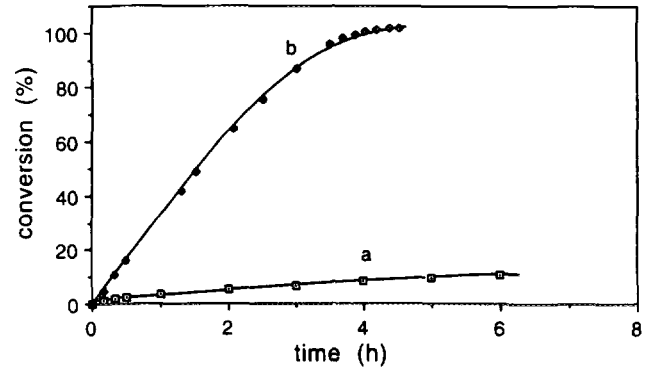

FIG. 5. Glucose conversion as a function of time for a catalytic ratio [glucose]/[Pd] = 3150. (a) Pd/C; (b) PdBi/C (Bi/Pd = 0.1).

With the catalytic ratio [glucose]/[palladium] = 787, the reaction rate on PdBi/C is not controlled by the kinetics on the metal surface; rather it is under mass transfer control. Indeed, the oxygen pressure in the reaction medium (Fig. 3) is 0 during the oxidation except at the very end of the reaction. Experiments were conducted with different masses of catalyst to confirm that the rate is under mass transfer control for [glucose]/[Pd] = 787. Figure 4 shows that surface chemical processes are significantly influencing the rate when the catalytic ratio is higher than 2000. To allow a better comparison between the activities of Pd/C and PdBi/C catalysts the oxidation reaction was conducted with a catalytic ratio [glucose]/[Pd] = 3150. Figure 5 shows that the difference in the activities of the two catalysts is much higher than that in the diffusion controlled regime (Fig. 2). These results show that the presence of bismuth atoms on the surface of palladium particles exerts a dramatic effect on catalyst activity; the interpretation of this effect will be discussed in Section 3.3.

Selectivity of catalysts. The product distribution given in Table 1 shows that after the first oxidation run the selectivity to gluconate is 99.8% at 99.6% conversion. The data on the parent Pd/C catalyst given for comparison indicate that without bismuth the catalyst is much less selective. This is due to the low activity of this catalyst, which favors parallel or successive reactions leading to unwanted products. Accordingly, the very active PdBi/C catalyst is also very selective, and it is remarkable that the primary alcohol function of gluconate is not oxidized into aldehyde or acid to yield guluronic or glucaric acids.

Stability of catalysts. The PdBi/C catalyst with Bi/Pd = 0.1 was used in five successive oxidation runs with a fresh charge of glucose solution. The five curves in Fig. 6 giving the conversion as a function of time are superimposable, which means that the catalyst can be recycled without appreciable loss of activity. The data given in Table 1 indicate that the gluconate yields remain very good even after the fifth oxidation run. However,

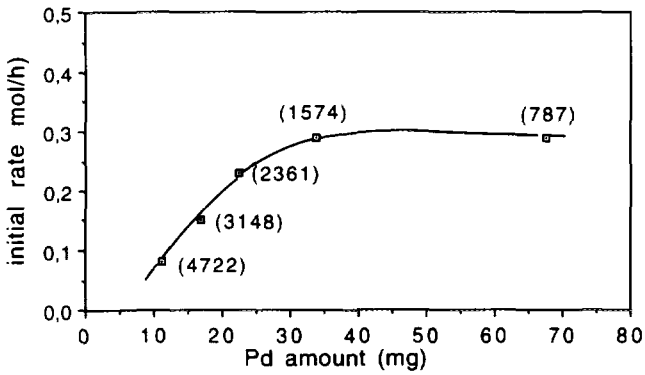

FIG. 4. Initial rates of glucose hydrogenation for PdBi/C (Bi/Pd = 0.1) as a function of the total amount of palladium (numbers in parentheses give the [glucose]/[Pd] ratios).

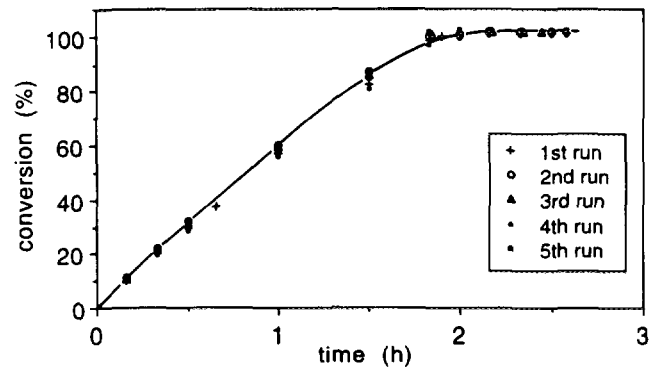

FIG. 6. Sodium hydroxide consumption as a function of time in five successive oxidation runs on PdBi/C (Bi/Pd = 0.1, [glucose]/[Pd] = 787, T = 313 K, pH 9).

under the present conditions, the reaction is under mass transfer control, and therefore a possible catalyst deactivation cannot be ruled out. The selectivity experiences a small drop in the second run, but this does not worsen in subsequent runs. This could be due to the formation during the first run of a product which remains adsorbed on the metal surface, modifying slightly the selectivity in subsequent oxidation runs. As mentioned above, no bismuth leakage was detected in the gluconate solution; therefore the PdBi/C catalysts prepared by the present method are very stable as far as the activity, selectivity, and catalyst composition are concerned.

3. *Role of Bismuth*

The deactivation of platinum-group metal catalysts used in the oxidation with air of oxygenates in water solutions is well documented. It is widely accepted that the metal surface of the working catalyst is partially covered by chemisorbed oxygen, and as the reaction proceeds the coverage increases and poisons the reaction. The oxygen coverage depends upon a number of factors such as the oxygen pressure in the liquid phase, including liquid in the catalyst pores (12, 13), or the redox potential of the organic substrate in connection with the redox potential of the metal (14, 15). In addition, the bonding strength of the organic substrate to the metal surface has to be considered; thus the absence of oxygen poisoning in the oxidation of 5-hydroxymethylfurfural on various noble metals (including ruthenium, the most prone to oxygen poisoning) was attributed to the strong bonding of the substrate via the π electron of the furan ring (20). The bonding strength of oxygen on the surface, which is particle size dependent (8, 21), is another parameter. Finally, the poisoning of the surface by irreversibly adsorbed substrates or reaction by-products can decrease the rate of reaction, thus favoring further deactivation by oxygen poisoning (17, 22). In view of the number of factors involved, the role of bismuth is not unambiguous. It has been suggested by Mallat *et al.* (22) that in the oxidation of cinnamyl alcohol on platinum that bismuth adatoms decrease the size of Pt ensembles and thus decrease the formation and irreversible adsorption of the substrate and by-products. However, these authors also consider that bismuth adatoms form new active centers which are oxidized more easily than platinum (17).

Our results can be also interpreted in terms of bismuth protecting palladium from overoxidation. Calorimetric measurements have been carried out to compare the adsorption of oxygen onto Pd/C and PdBi/C catalysts. Figure 7 gives the differential heats of adsorption of oxygen measured on these catalysts. The initial differential heats are the same for both catalysts (ca. 220 kJ/mol (O_2)), which means that at low coverage the affinity for oxygen

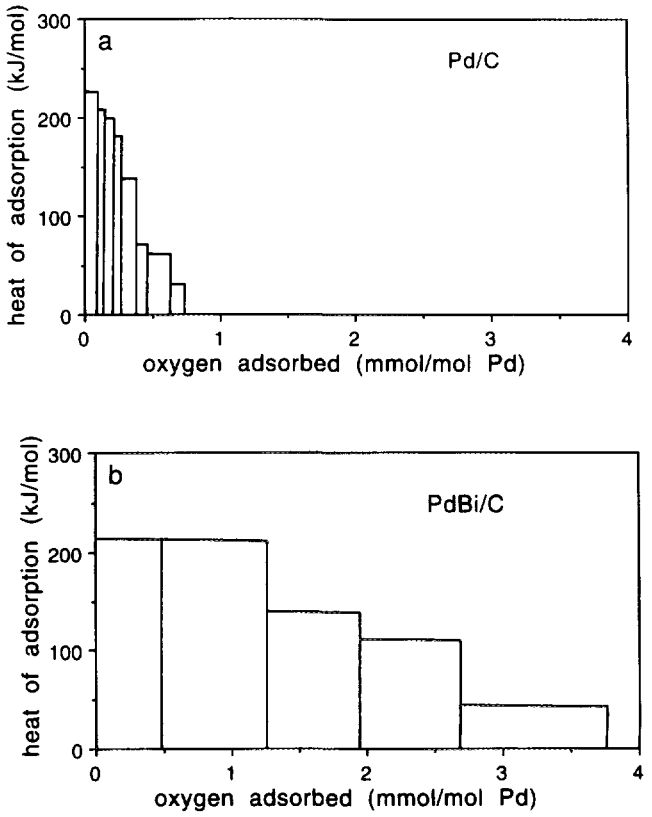

FIG. 7. Differential heat of adsorption measured by calorimetry. (a) Pd/C; (b) PdBi/C (Bi/Pd = 0.2).

is the same; however, for oxygen coverage higher than 5 to 10% the differential heats are much larger for PdBi/C, which means that oxygen adsorbs onto bismuth adatoms. The volume of oxygen adsorbed on PdBi/C (Bi/Pd = 0.2) is four times larger than that on Pd/C, and the integral heats of adsorption measured from the area under the curves are 229 and 68 kJ/mol (Pd), respectively. These differences correspond to an oxidation of bismuth from Bi^0 to a surface compound equivalent to Bi_2O_3.

We propose that glucose oxidation on PdBiC catalyst proceeds according to the oxidative dehydrogenation mechanism given in Fig. 8 where bismuth acts as a cocatalyst, avoiding the overoxidation of the palladium surface.

4. CONCLUSIONS

This study results in new data on the catalytic oxidation of glucose into gluconic acid. More specifically, the following points are highlighted.

1. Palladium–bismuth bimetallic catalysts are easily prepared by surface redox reaction in the liquid phase at room temperature. Starting from well-dispersed, palladium particles on active charcoal supports, bismuth at-

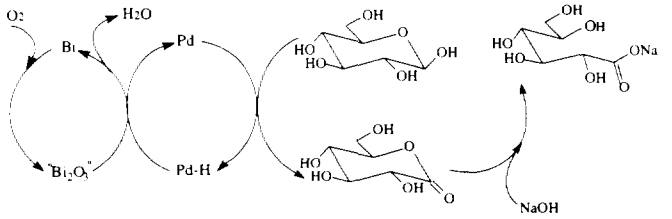

FIG. 8. Tentative scheme for the mechanism of glucose oxidation on PdBi catalyst.

oms are fixed selectively onto the surface of palladium particles, resulting in PdBi/C catalysts with a homogeneous bimetallic composition. The bismuth adatoms are strongly held on the surface since no bismuth leakage occurs during the oxidation of water solutions of glucose. The stability of catalysts toward bismuth leaching is mandatory in the production of gluconate used in the food and pharmaceutical industries.

2. From an industrial standpoint, PdBi/C is a very promising catalytic material for the production of gluconic acid from glucose by oxidation with air. The activity of palladium is so enhanced by bismuth adatoms that the reaction rates are rapidly limited by mass transfer of oxygen rather than by the activity of the catalyst. Gluconate yields as high as 99% are obtained even after several recyclings, and reducing sugars are the main residual impurities in the gluconate solution. Therefore the highly selective PdBi/C catalyst does not generate highly oxidized and cracked products, which probably also accounts for its high stability.

The catalytic oxidation presents the same advantages as the enzymatic oxidation, namely, a high selectivity and mild reaction conditions (oxidation with air at atmospheric pressure near room temperature). However, it presents two additional advantages, namely, (i) the possibility of conducting the oxidation in one step in a single reaction vessel, whereas the enzymatic route involves a multistep process with cumbersome installations, and (ii) a very high gluconate yield per catalyst mass. Moreover, the catalytic process is environmentally clean since it is conducted on recyclable catalysts and gives no noxious effluents nor side products.

3. From a more fundamental standpoint, the interpretation of the promoting effect of bismuth on the activity, selectivity, and stability of palladium is a challenging question. A definitive interpretation must await *in situ* studies on the precise location and oxidation state of bismuth atoms on the palladium surface. Studies by STM and AFM on model PdBi catalysts supported on graphite in the presence of glucose solution with or without air are planned. In the meantime, our whole set of data on Pd and PdBi catalysts suggests that oxygen poisoning is the main cause of deactivation and that bismuth, because of its higher affinity for oxygen, acts as a co-catalyst preventing the oxygen poisoning of palladium.

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