ELSEVIER

Applied Catalysis A: General 148 (1996) 181–199

APPLIED CATALYSIS A: GENERAL

Influence of metallic precursors on the properties of carbon-supported bismuth-promoted palladium catalysts for the selective oxidation of glucose to gluconic acid

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Received 2 May 1996; revised 21 June 1996; accepted 21 June 1996

Abstract

This work is devoted to the preparation of carbon-supported bismuth–palladium catalysts for the selective oxidation of glucose to gluconic acid, and to the understanding of the promoting role played by Bi in these catalysts. Catalysts were prepared according to various experimental procedures from two kinds of precursors, containing either classical inorganic ligands (chloride, nitrate) or organic ligands of the carboxylate-type: the acetates and derivatives of the pyrazine-2,3-dicarboxylic acid. Depending on the precursors used, the catalytic performances were found to be very different; catalysts prepared by deposition of acetate-type precursors display the highest activity. The incorporation of bismuth in the Pd/C catalysts was confirmed to increase drastically the catalytic activity. The catalysts were characterized before and after their use in the catalytic operation by XRD, XPS, BET and IR. Depending on the preparation procedure used, the presence of BiOCl, Bi_2O_3 and several Bi–Pd alloys in the bimetallic catalysts after the activation step was deduced from XRD studies. Partial dissolution of bismuth during the catalytic tests was demonstrated by atomic absorption analysis of the reaction medium and elaborate investigations were undertaken to understand the individual effects of the various constituents of the reaction mixture on the dissolution process. Monometallic Bi/C catalysts were found to lose significantly larger amounts of bismuth than bimetallic Pd–Bi/C catalysts. Both glucose and gluconate appear as

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PII S0926-860X(96)00231-1

responsible for the dissolution of the promoting element. Notwithstanding the increase in the conversion rate observed when two monometallic Pd/C and Bi/C catalysts were used simultaneously, it was shown that the promoting role of bismuth was not merely dictated by the presence of bismuth in solution.

Keywords: Bismuth; Palladium; Glucose; Gluconic acid; Selective oxidation

1. Introduction

Great interest has been recently paid to the promoting role of heavy post-transition elements like bismuth, lead or thallium in Pd- or Pt-based catalysts for the selective oxidation of alcohols into aldehydes and carboxylic acids with molecular oxygen in aqueous solutions. This effect has been investigated with great care in the oxidation of glucose or other monosaccharides [1–5], disaccharides like lactose [6] and in the partial liquid phase oxidation of alcohols or aldehydes in general [7–18]. Similar investigations dealt with the promoting role of adatoms in the electrooxidation of analogous substrates [19–25]. The promoting role of other post-transition elements like Te or transition metals like Co and Cd for the same kind of reactions has also been investigated [26,27].

The origin of the promoting role of bismuth on the activity of Pd or Pt is still a matter of discussion. Among various interpretations [28], the most currently mentioned refer to geometric blocking effects of active sites centered on Pd, to modifications of the adsorption properties of either hydrogen or the substrate on the catalyst, to the lowering of Pt metal corrosion in acidic media, to the stabilization of Pt or other oxide phases on the catalyst surface, and to the formation of complexes between the promoting element and reaction products displaying chelating properties.

We recently initiated a research programme dealing with the potential applicability of Bi^{III} coordination compounds as precursors for the incorporation of this element in bismuth oxide-based materials. This methodology was first applied to the preparation of bismuth molybdate-type heterogeneous catalysts for the selective gas phase oxidation of alkenes to aldehydes. Precursors used were various Bi^{III} carboxylate compounds that are incorporated in the future catalyst by deposition from a slurry where a hydrocarbon liquid is the suspension medium [29].

The present work deals with the preparation and characterization of carbon-supported bimetallic catalysts obtained according to several experimental procedures, and tested for their catalytic performances towards the selective reaction of molecular oxygen with glucose to form gluconic acid. The procedures based on the use of carboxylates as precursors are compared with the patented literature based on the use of classical inorganic compounds [30]. The influence of the carboxylate nature on the catalytical properties is also examined. Particular interest is paid to the losses of bismuth from the catalysts during the catalytic

tests and detailed investigations are carried out under various conditions to identify the different factors responsible for this process.

2. Experimental

2.1. Catalyst supports

Two different activated carbons supplied by Norit were used as supports in this study. They correspond to the trade names SXplus ($S_{BET} = 750\ m^2\ g^{-1}$) and PKDA 10X30 ($S_{BET} = 550\ m^2\ g^{-1}$) and are noted hereafter as C_{SX+} and C_0, respectively. Their selected particle size was in the range 0.1–0.2 mm.

2.2. Metallic precursors

Palladium acetate (Acros), palladium chloride (59 wt.-% Pd, Janssen), bismuth(III) nitrate pentahydrate (p.a., Fluka) and bismuth(III) oxide (99.9%, Janssen) were used as received.

Bismuth oxoacetate, $BiO(O_2CCH_3)$, was obtained by adding 5 ml glacial acetic acid (99.5%) to a suspension of 5 g of Bi_2O_3 in 100 ml acetone. The mixture was refluxed for 6 h, the precipitate was filtered, washed with acetone and ether, then air dried at room temperature.

A palladium(II) derivative of 2,3-pyrazinedicarboxylic acid (2,3-H_2pzdc), Pd(2,3-pzdc)$(NH_3)_2$ [31] was obtained according to a procedure described in the literature for the synthesis of the analogous derivative of 2,5-H_2pzdc [32]. The synthesis of the Bi^{III} compound, Bi(2,3-Hpzdc)$_3$, was developed in parallel with this work and will be described elsewhere [33].

2.3. Catalyst preparation

2.3.1. Catalysts prepared from carboxylate precursors

The mono- and bimetallic catalysts were prepared by deposition from a suspension of carboxylate particles in n-heptane chosen as an inert organic solvent.

2.3.1.1. Monometallic Pd / C catalysts (5 wt.-%). Palladium carboxylates were dispersed in the presence of 7.2 g of the activated carbon in 250 ml n-heptane under ultrasonic stirring for 30 min. The hydrocarbon was evaporated very slowly at room temperature under vacuum and the precursor deposited on the support was decomposed upon heating under nitrogen at 773 K during 18 h. These catalysts are noted in the following form: (Ac.Pd/C_{SX+}), (Ac.Pd/C_0), (pzdc.Pd/C_{SX+}) and (pzdc.Pd/C_0), depending on the carboxylate precursor,

acetate (Ac) or 2,3-pyrazinedicarboxylate (pzdc), and the active carbon support used.

2.3.1.2. Monometallic Bi / C catalysts (5 or 10 wt.-%). Monometallic catalysts containing only the promoting element were prepared according to the same procedure as the monometallic Pd/C catalysts, starting with the bismuth oxoacetate as precursor. These catalysts were noted in the following form: (Ac.Bi/C_{SX+}) and (Ac.Bi/C_0)

2.3.1.3. Bimetallic Pd(5 wt.-%)–Bi(5 wt.-%) / C catalysts. Carbon-supported bimetallic Pd–Bi/C catalysts were obtained by incorporating bismuth in a monometallic Pd/C catalyst prepared as described above. The non-activated Pd/C catalyst and the appropriate amount of bismuth carboxylate were dispersed in n-heptane under ultrasonic stirring for 30 min. After slow evaporation of the solvent, the catalyst was activated by thermal decomposition of the precursors upon heating under nitrogen at 773 K during 18 h. The obtained catalysts were described as: (Ac.PdBi/C_{SX+}), (Ac.PdBi/C_0), (pzdc.PdBi/C_{SX+}) and (pzdc.PdBi/C_0), depending on the carboxylate precursor, acetate (Ac), or 2,3-pyrazinedicarboxylate (pzdc), and the active carbon support, C_{SX+} or PKDA (noted C_0).

2.3.2. Reference catalysts prepared from inorganic precursors

Reference catalysts prepared from aqueous solutions of Bi^{III} nitrate pentahydrate and Pd^{II} chloride precursors were obtained from a precipitation–deposition procedure according to a patented literature [30]. The formation of the active phase proceeds via in situ reduction of the precursor salts with formaldehyde at 80°C. These catalysts are noted as (ref.PdBi/C_{SX+}) and (ref.PdBi/C_0), respectively.

2.3.3. Catalysts prepared from metals

Other mono- and bimetallic catalysts supported on carbon SXplus were also prepared according to the deposition procedure described in Section 2.3.1., from metallic palladium (Janssen, 99.99%) and metallic bismuth (Janssen, 99.999%) (catalysts noted (Pd/C_{SX+}) and (PdBi/C_{SX+}), and from previously decomposed palladium acetate (in Pd) or bismuth oxoacetate (in Bi + Bi_2O_3), all dispersed in heptane. The latter monometallic catalysts are noted ((Ac.Pd)$_d$/C_{SX+}) and ((Ac.Bi)$_d$/C_{SX+}), and the corresponding bimetallic catalyst is noted ((Ac.Pd)$_d$(Ac.Bi)$_d$/C_{SX+}). After evaporation of the solvent they were just dried under vacuum at 313 K.

To evaluate the proper influence of other Bi-containing phases, another catalyst was prepared in two steps from Pd acetate deposited on carbon, then activated as previously described, loaded afterwards with bismuth oxochloride, BiOCl, or bismuth(III) oxide, Bi_2O_3, according to the same deposition proce-

dure in n-heptane. These catalysts are noted ($(Ac.Pd/C_{SX+})_d$–BiOCl) and ($(Ac.Pd/C_{SX+})_d$–Bi_2O_3).

2.4. Catalytic measurements

2.4.1. Reactor vessel

The selective oxidation of D-glucose into gluconic acid was selected as catalytic test reaction. The reactions were carried out at atmospheric pressure in a 600 ml flat bottom double-sided glass reactor. The temperature was controlled through water circulation. Constant thorough mixing of the reaction medium was ensured by a mechanical stirrer (Heidolph RZR 2051).

The pH of the reaction mixture was measured continuously by a combined glass-reference electrode (Beckman model 39843) coupled with a pH meter/controller (Metrohm, Stat Titrino 718). To maintain a constant pH (9.25–9.45) in the reaction mixture during operation, the sugar-derived carboxylic acids formed were neutralized by adding a 20 or 40 wt.-% aqueous solution of sodium hydroxide. The base consumption was recorded in function of time.

2.4.2. Standard oxidation procedure

The glucose solution (72 g glucose (99 + %, Acros) in 400 ml) was heated in the reactor to 50°C. Once the temperature was stabilized, the catalyst was added to the solution and the oxidation reaction started by introducing oxygen (flow rate: 0.4 l min^{-1}) in the stirred (1000 rpm) slurry. Two different catalyst masses were used for these experiments and the corresponding reaction conditions were denoted as A (0.054 g) or B (1.08 g). Preliminary experiments with various catalyst masses and stirring rates were performed to search for diffusional limitations. The glucose conversion and yield in gluconic acid were found to be dependent upon the catalyst mass in the range 50–200 mg. Measurements carried out under conditions A with various stirring rates in the range 1000–1800 rpm confirmed the absence of diffusional limitations in this case; conditions B gave rise to mass transfer limitations. The catalytic tests were interrupted after 4 h, and the catalyst was removed from the reaction mixture by filtration. The filtrate was then analyzed by HPLC, ^{13}C-NMR and atomic absorption spectrometry. The catalyst was washed with water, dried under vacuum and analyzed by XPS and XRD.

2.4.3. Analysis of the reaction products

The composition of the reaction mixture was determined by high performance liquid chromatography and ^{13}C-NMR analysis.

2.4.3.1. High performance liquid chromatography (HPLC). Routine analysis of the various products was performed with a liquid chromatograph Perkin-Elmer

series 3B coupled with a variable wavelength Perkin-Elmer UV detector, type LC75. The reaction products were separated on a BioRad Aminex HPX-87H column thermostated at 45°C (injected volume: 20 μl). The mobile phase, degassed by helium bubbling, was a 0.5 mmol/l sulphuric acid solution; the flow rate was 0.4 l/min with a column pressure of 3.6 MPa.

Because the retention times of glucose and gluconic acid are very similar under the selected experimental conditions, two different detection wavelengths were used to determine the composition of the reaction mixture: 200 and 240 nm. Glucose does not absorb significantly at 240 nm, and the integrated surface area provides a measurement of the gluconic acid concentration. Glucose concentrations are estimated from a second assay at 200 nm, by subtracting the calculated contribution of gluconic acid. Because this data treatment is severely affected by significant sensitivity differences between these two components, this procedure was, however, restricted to situations where the yield in gluconic acid was low.

2.4.3.2. NMR spectroscopy. The ^{13}C-NMR spectra were measured under standard conditions on a Bruker AM500 spectrometer equipped with a computer Aspect 3000, using a 5 mm ^{1}H probe at 25°C. D_2O solvent was used as an internal deuterium lock signal with the methyl carbons of sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal spectral reference.

2.4.3.3. Atomic absorption. The bismuth and palladium losses from the catalysts in the reaction mixture during the catalytic tests were determined by analyzing the collected filtrates by atomic absorption spectrometry using a spectrometer Perkin Elmer 3110 equipped with a flame atomizer.

2.4.4. Expression of the catalytic results

Catalytic results are expressed as conversion (X, %), yields (Y, %) and selectivities (S, %). Because the ^{13}C-NMR analyses showed that gluconic acid was the only carboxylic acid generated in the reaction medium, the yields in gluconic acid were calculated directly from the NaOH consumption. The main side product is fructose due to isomerisation in the presence of oxygen. The fructose/gluconic acid and fructose/glucose molar ratios were determined by ^{13}C-NMR. The fructose yields were calculated from the expression:

$$Y_{\text{gluconicacid}}(\%) \cdot \left(n_{\text{fructose}}/n_{\text{gluconic acid}}\right)$$

2.5. Catalyst characterization techniques

2.5.1. Specific surface area measurements (BET)

BET specific surface area measurements were carried out on a Micrometrics ASAP 2000 apparatus using N_2 at 77 K. Samples were previously outgassed under vacuum at 150°C.

2.5.2. X-ray diffractometry (XRD)

Powder X-ray diffraction patterns were obtained with a Siemens D-5000 diffractometer using the copper Kα radiation ($\lambda = 154.18$ pm). The samples were analyzed after deposition on a quartz monocrystal sample-holder supplied by Siemens. The crystalline phases were identified by reference to the ASTM data files.

2.5.3. X-ray induced photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy was performed on a SSI-X-probe (SSX-100/206) spectrometer from FISONS, using the Al-K_α radiation ($E = 1486.6$ eV). The energy scale was calibrated by taking the Au $4f_{7/2}$ binding energy at 84 eV. The C 1s binding energy of contamination carbon set at 284.8 eV was used as internal standard value. The analysis of bismuth and palladium were based on the Bi $4f_{7/2}$ and Pd $3d_{5/2}$ photopeaks. The intensity ratios $I(Bi_{4f7/2})/I(Bi_{4f5/2})$ and $I(Pd_{3d5/2})/I(Pd_{3d3/2})$ were fixed at 1.33 and 1.5 respectively.

2.5.4. Infra-red spectroscopy (IR)

IR spectra were obtained with a Perkin Elmer FT-IR spectrometer, model 1710. Samples were analyzed in the form of KBr disks (0.8 wt.-% carbon) pelletized under a pressure of 8 tons cm^{-2}. Spectra were recorded with background correction in the wavenumber range 4000–400 cm^{-1}, the number of scans being fixed at 300.

3. Results

3.1. Characterization of fresh catalysts

3.1.1. Infra-red spectroscopy

Fig. 1a and b present the FT-IR spectra of two non-activated bimetallic catalysts supported on PKDA-type carbon support. In both cases, the presence of lines that are characteristic of the two concerned precursors, Pd acetate and Bi oxoacetate in Fig. 1a, the Pd and Bi derivatives of 2,3-pyrazinedicarboxylic acid in Fig. 1b, clearly demonstrates that the precursors remain unchanged after their deposition on the support. For instance, Fig. 1b shows the characteristic peaks of the pyrazinedicarboxylato derivatives of palladium(II) (1129, 1295 and 1317 cm^{-1}) and bismuth(III) (1720 and 1735 cm^{-1}).

3.1.2. BET specific surface area measurements

The surface area measurements showed that deposition of the precursors on the support caused a decrease in surface area, followed by an increase after their thermal decomposition.

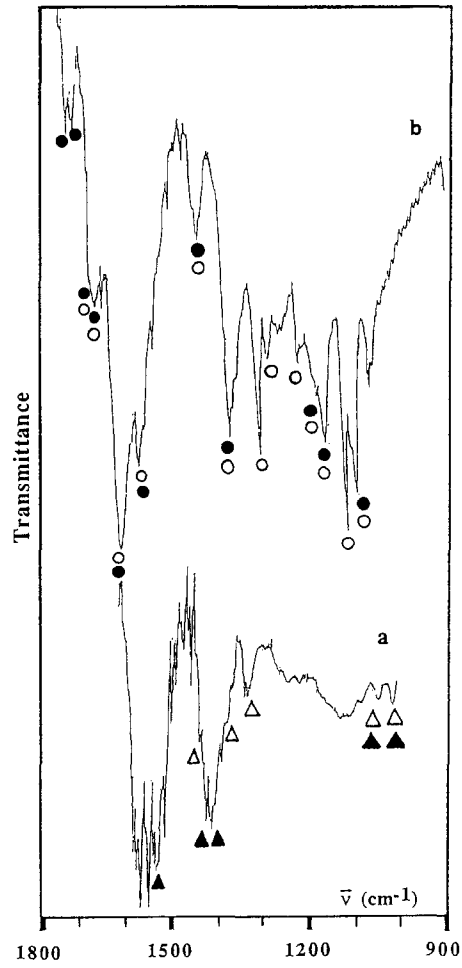

Fig. 1. Infrared spectra of non-activated Pd–Bi/C_0 catalysts made from (a) Pd^{II} acetate (△) and Bi^{III} oxoacetate (▲) and (b) Pd^{II} (○) and Bi^{III} (●) derivatives of pyrazine- 2,3-dicarboxylic acid.

3.1.3. XPS results

Representative XPS results are listed in Table 1, together with data concerning used catalysts. No significant variations in bismuth or palladium binding energies are observed between the samples prepared with different supports, or between data collected before or after performing the catalytic tests. The binding energy values associated with the Bi $4f_{7/2}$ photopeak lie in the range 156.6–158.1 eV for Bi^0 and 159–160.1 eV for Bi^{3+}, and for the Pd $3d_{5/2}$ line, in the range 335.5–336.3 eV for Pd^0 and 336.3–338.1 eV for Pd^{2+}. The values characterizing bismuth and palladium are similar or slightly higher than the literature data. According to Bertolini et al. [34], who reported the correlation existing between the particle size of a Pd supported catalyst and the positive shift in the binding energy, the abnormally high values for the binding energy of

Pd in $(Ac.Pd/C_{SX+})_f$ and $(Ac.PdBi/C_{SX+})_f$ catalysts could be explained by the small size of the particles.

After incorporation of the Bi-containing precursor in a non-activated monometallic Pd/C catalyst, the theoretical Bi/Pd intensity ratio amounts to 0.52. The fact that the experimental Bi/Pd ratios observed in the fresh activated catalysts are higher than this value is in agreement with the sequential incorporation of Pd first, then Bi on the surface of the support. These data clearly indicate partial coverage of Pd by Bi. The theoretical intensity ratios Pd/C and Bi/C in the bimetallic catalysts are 0.62 and 0.32%, respectively. The experimental values of these ratios in the fresh catalysts are higher and can be interpreted as indicatory of well dispersed Pd and Bi on the surface, especially in the case of the $(Ac.PdBi/C_0)_d$ catalyst. More reliable measurements of metal dispersion by other methods like chemisorption were not accessible in these bimetallic catalysts because of the possible interference problems between the various metal species present on the surface. Electron microscopy studies were found to lack sensitivity to provide a confident interpretation.

3.1.4. XRD

Metallic palladium was observed in all the monometallic Pd/C catalysts. Bismuth oxochloride, BiOCl, was almost systematically detected in the diffractograms of catalysts prepared from inorganic precursors. Most other bimetallic catalysts are characterized by poorly resolved XRD spectra, suggesting an amorphous or microcrystalline structure. The formation of one or several binary Pd_xBi_y alloys in these supported catalysts was, however, suspected in most of

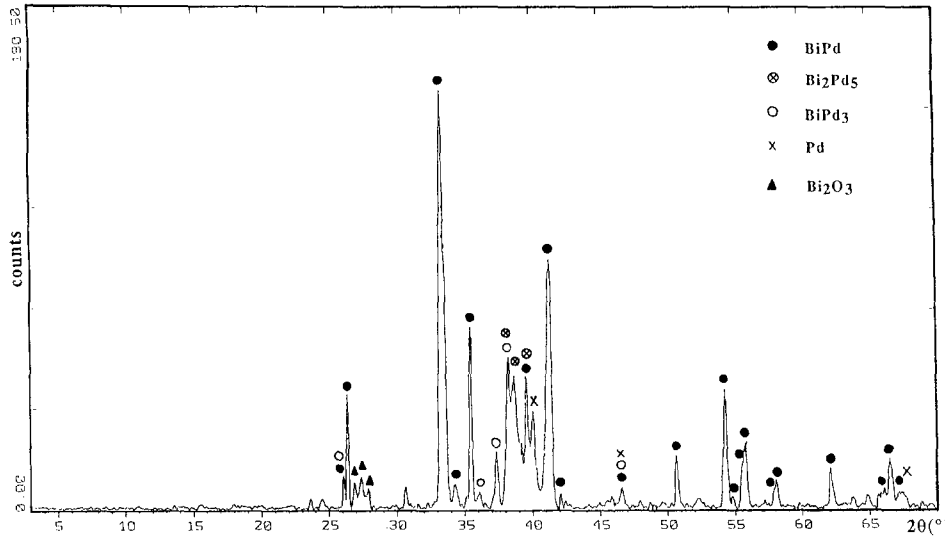

Fig. 2. X-ray diffraction pattern of the decomposition products of a mixture of Pd^{II} acetate and Bi^{III} oxoacetate heated under nitrogen at 773 K during 18 h.

Table 1
XPS atomic intensity ratios in fresh (activated and non-activated) and used catalysts [b]

Catalyst [a] Precursor(s)/ Support	Non-activated			Activated, fresh			Used			Reference number of the catalytic test [c]
	Bi/Pd	Pd/C ×100	Bi/C ×100	Bi/Pd	Pd/C ×100	Bi/C ×100	Bi/Pd	Pd/C ×100	Bi/C ×100	
Ac.PdBi/C_0	0.47	3.86	1.83	0.75	4.0	3.3	0.4	2.9	1.4	19
Ac.Pd/C_0	–	3.24	–		2.46	–	–	2.30	–	20
Ac.Bi/C_0	–	–	2.0		–	0.13	–	–	0.6	21
Ac.PdBi/C_0	0.47	3.86	1.83	0.75	4.0	3.3	0.36	3.0	1.1	22
pzdc.Pd/C_0	–	n.d.	–	–	0.10	–	–	0.22	–	23
pzdc.PdBi/C_0	–	n.d.	–	1.2	0.30	0.51	0.33	0.61	0.17	24
ref.PdBi/C_0	–	–	–	0.9	1.44	1.29	0.53	1.6	0.8	25
Ac.Pd/C_{SX+}	–	1.21	–	–	1.06	–	–	1.00	–	26
Ac.PdBi/C_{SX+}	0.62	1.21	0.75	0.74	0.87	0.65	0.45	1.04	0.47	28
pzdc.PdBi/C_{SX+}	1.24	0.25	0.31	1.90	0.10	0.26	0.40	0.20	0.08	29
ref.PdBi/C_{SX+}	–	–	–	1.42	0.99	1.41	0.80	1.00	0.80	30
$(Ac.Pd)_d$ /C_{SX+}	–	1.06	–	–	–	–	–	0.20	–	31
$(Ac.Pd)_d(Ac.Bi)_d$ / C_{SX+}	0.2	0.30	0.06	–	–	–	0.12	0.17	0.02	32
$(Ac.Pd/C_{SX+})_d$– BiOCl	–	–	–	0.50	0.84	0.40	0.17	0.83	0.14	33
Ac.Bi(5%)/C_{SX+}	–	–	0.60	–	–	0.16	–	–	–	–
Pd–Pt–Bi/C Degussa	–	–	–	–	–	–	0.75	1.4	1.1	37

[a] Precursors: Ac = acetate; pzdc = 2,3-pyrazinedicarboxylate; ref = inorganic precursors (patented procedure [28]).[b] n.d. = not detected.[c] See Table 3.

them; this interpretation was confirmed by the XRD investigations of the corresponding unsupported catalyst, prepared from the same Bi- and Pd-containing precursors according to the same experimental procedure. Fig. 2 presents the X-ray diffraction pattern of the decomposition products of a mixture of Pd^{II} acetate and Bi^{III} oxoacetate submitted to the same treatment as the corresponding carbon-supported catalysts. It shows unequivocally the presence of two binary alloys with the compositions BiPd and $BiPd_3$. Small amounts of Pd metal and Bi^{III} oxide are simultaneously detected, and another phase is present, which corresponds most probably to Bi_2Pd_5. Although the latter phase was not mentioned initially in the phase diagram of the binary Bi–Pd system [35], Bi_2Pd_5 was shown to be generated from a phase transformation of $Pd_{31}Bi_{12}$ below 550°C [36]. In our case, the coexistence of two major Bi–Pd alloys, one Bi-rich phase (BiPd) and one Pd-rich phase ($BiPd_3$), is in line with the nominal composition of the catalysts used in the present work, which corresponds to the atomic ratio Bi/Pd of 1/2. Although the presence of intermetallic compounds Bi_xPd_y in these catalysts remains debatable, their possible role in the catalytic properties is outside the scope of the present work and has been investigated separately [37].

3.2. Characterization of used catalysts

3.2.1. XRD and XPS

Apart from the relative decrease of diffraction lines assigned to BiOCl in the so-called reference catalysts, the XRD spectra of used catalysts display only very minor changes when compared to those of fresh catalysts. In the photoelectron spectra (Table 1), the decrease in the Bi/Pd and Bi/C ratios after the catalytic test suggest a loss of bismuth from the catalyst during the oxidation reaction. The changes in the Pd/C ratios are less clear and this behaviour could result from concomitant factors like dissolution of Bi covering Pd, redispersion of Pd during the catalytic tests, and/or presence of carbon deposits on Pd. Apart from this overall trend, there is no other specific comment on the XPS data listed in Table 1.

3.2.2. Atomic absorption

Partial dissolution of bismuth during catalytic operation was clearly demonstrated by performing atomic absorption analysis of the collected reaction mixtures after the catalytic tests (see last column of Table 3). This phenomenon is well-known in the literature and has been mentioned several times in the case of Bi- or Pb-based catalysts [5,38,39]. In contrast with bismuth, dissolution of palladium, which has been observed after much longer reaction times during partial oxidation of 2-methylphenoxyethanol to 2-methylphenoxyacetic acid [40], was never detected under the present experimental conditions. According to previous work, the oxidation and subsequent selective dissolution of bismuth from Bi–Pd carbon-supported catalysts is in line with the strong interaction between adsorbed Bi and palladium, and results in the fact that dissolution is restricted to Bi adsorbed on carbon rather than on Pd [5].

Dissolution of the active metals can be enhanced by an increase of the pH [28] or by the presence of complexing agents in the solution. In our case, the influence of the pH can be minimized because, owing to an adequate control, pH variations in the reaction medium are restricted to 0.1 pH unit around the standard value (9.35). The production of gluconate ions is, however, a matter of concern, because gluconic acid is known as being a good chelating agent for heavy metals and, for instance, lead(II) gluconate has been isolated and structurally characterized [41,42]. Reference to the chelating properties of sugar acids has been made to explain dissolution of Bi in the conversion of sorbose to 2-keto-L-gluconic acid [5], and to account for the absence of Bi losses in the oxidation of cinnamyl alcohol to cinnamaldehyde [43].

To improve our understanding of these phenomena, we looked more carefully at the effects of various parameters, with the objective of finding the factors that affect the propensity of bismuth to dissolve from the catalyst into the solution. The results of these experiments are described in Table 2. Measurements were carried out on bimetallic PdBi/C and monometallic Bi/C catalysts prepared

Table 2
Influence of the composition of the reaction medium and the experimental conditions on Bi dissolution

Test No.	Catalyst [a] Precursor(s)/Support	Reaction medium [b]	Atmosphere	Relative Bi losses (%)
1	Ac.PdBi/C_{SX+}	glucose	N_2	< 24
2	Ac.PdBi/C_{SX+}	glucose	O_2	33
3	Ac.PdBi/C_{SX+}	glucose	Air	33
4	Ac.PdBi/C_{SX+}	gluconate	N_2	33
5	Ac.PdBi/C_{SX+}	gluconate	O_2	24
6	Ac.PdBi/C_{SX+}	gluconate	Air	13
7	Ac.PdBi/C_{SX+}	–	N_2	< 20
8	Ac.PdBi/C_{SX+}	–	O_2	< 20
9	Ac.PdBi/C_{SX+}	–	Air	< 20
10	Ac.Bi/C_{SX+}	glucose	N_2	68
11	Ac.Bi/C_{SX+}	glucose	O_2	78
12	Ac.Bi/C_{SX+}	glucose	Air	76
13	Ac.Bi/C_{SX+}	gluconate	N_2	70–75
14	Ac.Bi/C_{SX+}	gluconate	O_2	66
15	Ac.Bi/C_{SX+}	gluconate	Air	60
16	Ac.Bi/C_{SX+}	–	N_2	< 10
17	Ac.Bi/C_{SX+}	–	O_2	< 10
18	Ac.Bi/C_{SX+}	–	Air	< 10

[a] Ac = acetate; C_{SX+} = Norit SXplus activated carbon.[b] Glucose or gluconate concentration is 1 mol/l.

from acetate precursors and supported on C_{SX+}, in different experimental conditions, i.e. in the presence of glucose and/or gluconate or neither of them, under an oxygen or nitrogen or ambient air atmosphere. Gluconate was introduced as the sodium salt to simulate the usual reaction medium. Because of the small catalyst masses used in the catalytic tests, bismuth concentrations were sometimes found below the analytical detection limit (1 mg/l); further concentration of the reaction filtrates was not possible due to the high viscosity of these sugar-rich solutions.

In the absence of glucose and gluconate (tests 7 to 9 and 16 to 18), bismuth losses are below the analytical detection limit and tests 8 and 17 confirm that neither the standard pH value, nor the presence of oxygen alone are responsible for the dissolution. In the presence of glucose and/or gluconate, bismuth losses are always much more extensive from the monometallic Bi/C than from the bimetallic PdBi/C catalysts. After 4 h running, these losses reach the considerable value of 60 to 80% in the monometallic catalysts (tests 10–15). In a bimetallic catalyst, the same loss is observed only after one day of operation, as shown in Fig. 3. This curve illustrates the time dependence of bismuth dissolution in the reaction medium from a standard PdBi/C catalyst in the usual reaction conditions, and shows that dissolution of the promoting element takes place progressively over a relatively long period of time.

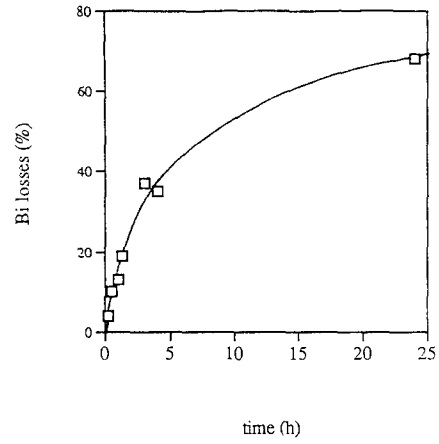

Fig. 3. Time dependence of bismuth dissolution from a bimetallic (Ac.PdBi/C_{SX+}) catalyst under the reaction conditions A (see text).

To separate the respective contributions of glucose and gluconate in the dissolution process, experiments were carried out with glucose as only starting reagent under a nitrogen atmosphere to prevent gluconate formation in the reaction medium and compared with those in which gluconate was the only starting reagent. As shown by comparing tests 1–4 and 10–13, there is a small increase of Bi dissolution in the presence of gluconate ions but the presence of glucose is sufficient to cause dissolution of the promoting element.

3.3. Catalytic results

Representative catalytical results are listed in Table 3 for two different sets of experimental conditions. Yields in gluconic acid are given at three different reaction times: 20 min, 1 h and 4 h. Yield values normalized with respect to the palladium mass were also calculated at the end of the catalytic tests. The last column on the right characterizes the extent of bismuth dissolution in the reactant mixture after 4 h running, in percents of initial Bi loading on the catalyst.

3.3.1. Influence of bismuth

We first checked that no catalytic activity was observed under blank conditions, i.e. with the support alone in the presence of oxygen. Although the Bi/C catalysts (tests 21 and 27) show no catalytic activity under the selected conditions, the incorporation of bismuth in the Pd/C drastically increases the glucose conversion, as seen from the comparison between tests 20–22 and 26–28 in the case of the acetate precursor, and 23–24 in the case of the pyrazinecarboxylates. This synergetic effect between both metals on the yield in gluconic acid is illustrated in Fig. 4 in the acetate case for catalysts supported on

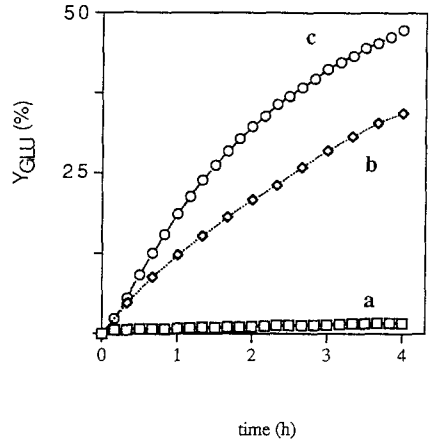

Fig. 4. Oxidation of glucose to gluconic acid in the presence of (a) the monometallic (Ac.Pd/C_{SX+}) catalyst, (b) the mixture of two monometallic catalysts (Ac.Pd/C_{SX+})+(Ac.Bi/C_{SX+}) and (c) bimetallic (Ac.PdBi/C_{SX+}) catalyst (reaction conditions A).

C_{SX+} (compare curves a and c). The comparison between the results of tests 19 and 28, carried out under the same reaction conditions, confirms that the catalyst with the highest specific surface area is the most active one.

In the presence of mono- or bimetallic catalysts, the only side product is always fructose, which appears with a yield lower than 4% under the standard reaction conditions. It should, however, be noted that fructose also appears in the reactant mixture in the absence of catalyst, at a somewhat higher amount of 10%. If one restricts the discussion to the production of carboxylic acids, there is consequently no significant influence of bismuth on the selectivity in gluconic acid, which remains very high in all cases.

Since bismuth was shown to dissolve, it seemed worth investigating whether the synergetic effects resulted from the association of Bi and Pd in the starting PdBi/C catalyst, or whether they could be observed also when the promoting element was introduced independently in the surrounding solution. As shown by runs 35a and b, glucose conversion was significantly enhanced when two monometallic Pd/C and Bi/C catalysts were used together in the reactant mixture, suggesting that it was not necessary to incorporate bismuth in the form of a bimetallic catalyst PdBi/C to improve the catalytic behaviour. One of these experiments (no. 35a) is illustrated in Fig. 4 (curve b) and corresponds to a test for which the total amount of active metals Pd + Bi is the same as for the experiment with the bimetallic PdBi/C catalyst (no. 28). The observed improvement of the catalytic activity in tests 35a and b might therefore be explained by re-deposition of Bi on the monometallic Pd/C catalyst during operation. To validate this statement, two additional experiments were performed (36a and b). In the first one (36a), a monometallic Bi(10 wt.-%)/C catalyst made from oxoacetate was employed under reaction conditions A, resulting in zero activity

Table 3
Catalytic results

Test No.	Catalyst [a] Precursor(s)/Support	Reaction conditions [b]	Y_{GLU} [c]			Y_{GLU}/m_{Pd}	Bi losses [d]
			$t = 20$ min (%)	$t = 2$ h (%)	$t = 4$ h (%)	$t = 4$ h (% · mg^{-1})	(%)
19	Ac.PdBi/C_0	A	2.8	21.4	41.4	15.33	–
20	Ac.Pd/C_0	B	3.1	10.3	15.3	0.28	–
21	Ac.Bi/C_0	B	0	0	0	–	–
22	Ac.PdBi/C_0	B	16	96.4	~ 100	1.85	–
23	pzdc.Pd/C_0	B	2.5	18.0	29.3	0.54	–
24	pzdc.PdBiC_0	B	80	53.5	76.4	1.41	–
25	ref.PdBi/C_0	B	21.3	86.4	~ 100	1.85	–
26	Ac.Pd/C_{SX+}	A	0	0.6	1.1	0.41	–
27	Ac.Bi(10%)/C_{SX+}	A	0	0	0	–	78
28	Ac.PdBi/C_{SX+}	A	5.5	32.3	47.3	17.52	33
29	pzdc.PdBi/$_{SX+}$	A	1.4	5.5	9.4	3.48	–
30	ref.PdBi/C_{SX+}	A	5.6	36.0	58.0	21.48	13
31	$(Ac.Pd)_d$ /C_{SX+}	A	0	0	0.2	0.07	–
32	$(Ac.Pd)_d(Ac.Bi)_d$ /C_{SX+}	A	0	0	0.1	0.04	24
33	(Ac.Pd/C_{SX+})–BiOCl	A	2.3	15.1	27.1	10.04	70
34	(Ac.Pd/C_{SX+})–Bi_2O_3	A	1.3	8.8	22	8.15	18–33
35a	(Ac.Pd/C_{SX+}) + (Ac.Bi/C_{SX+})	A [e,f]	4.8	20.9	34.4	12.74	–
35b	(Ac.Pd/C_{SX+}) + (Ac.Bi/C_{SX+})	A [f]	1.3	6.2	11.3	8.37	–
36a	Ac.Pd/C_{SX+}	A [g]	0.5	1.2	2.5	0.93	–
36b	Ac.Pd/C_{SX+}	A [h]	1.0	2.7	5.6	2.07	[h]
37	Pd–Pt–Bi/C Degussa	A [i]	6.1	30.6	41.5	19.2	10

[a] Precursors: Ac = acetate, pzdc = 2,3-pyrazinedicarboxylate; ref = inorganic precursors (patented procedure [28]). Support: C_0 = Norit PKDA-10x30; C_{SX+} = Norit SXplus. [b] Reaction conditions A: 0.054 g catalyst; B: 1.08 g catalyst (mass transfer control). [c] Yield in gluconic acid. [d] After 4 h running. [e] 108 mg catalyst. [f] Pd(2.5 wt.%)–Bi(2.5 wt.%) [g] In the presence of 3.78 mg dissolved Bi. [h] In the presence of 2.7 mg Bi metal in suspension; 16% of initial Bi was dissolved after 4 h. [i] Pd(4 wt.%)–Pt(1 wt.%)–Bi(5 wt.%).

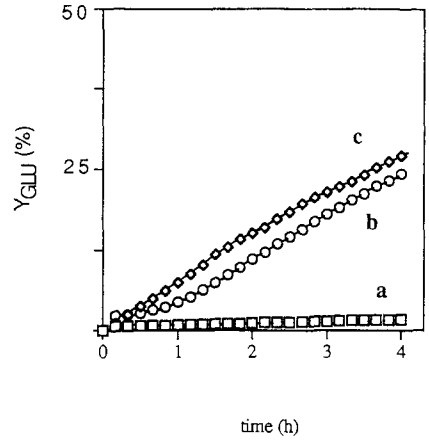

Fig. 5. Oxidation of glucose to gluconic acid in the presence of (a) the monometallic (Ac.Pd/C_{SX+}) catalyst, (b) the monometallic (Ac.Pd/C_{SX+}) catalyst mixed with Bi_2O_3 and (c) the monometallic (Ac.Pd/C_{SX+}) catalyst mixed with BiOCl (reaction conditions A).

and dissolution of 68% of the initial Bi loading; afterwards, the catalyst was removed from the reaction medium and replaced by a monometallic Ac.Pd/C_{SX+}. The yield in gluconic acid was found to be negligible after 4 h running. The mere presence of dissolved Bi in the reaction mixture is therefore not a sufficient condition to allow the reaction to proceed. In the second one (36b), an identical Ac.Pd/C_{SX+} catalyst was put in presence of powder Bi metal under the reaction conditions A; although the conversion in gluconic acid remains very low, this system was, however, more efficient than the previous one.

Because BiOCl was found in all catalysts prepared by the inorganic route, a similar experiment has been carried out by adding this compound to a monometallic Pd/C catalyst (test 33). The obtained curve is presented in Fig. 5 together with a related experiment using Bi_2O_3 (test 34) and in both cases, the same positive effect on the conversion rate can be observed. Consequently, the formation of BiOCl in the so-called reference catalysts cannot be considered as inhibiting the catalytic activity.

3.3.2. Influence of the precursors and the incorporation procedure

Two different carboxylate-type compounds were used as precursors for the incorporation of the two metals on the support according to the same experimental procedure based on deposition from a slurry in n-heptane. The catalysts made from acetate precursors (tests 22–28) were found to display better performances than those made from pyrazine–dicarboxylate compounds (tests 24–29), and their behaviour was roughly similar to that of the reference catalysts prepared by the inorganic route in water (tests 25–30).

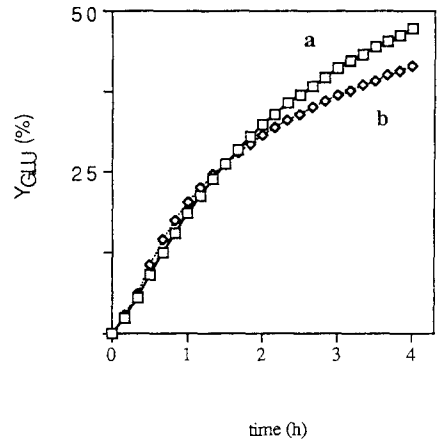

Fig. 6. Comparison of the catalytic performances of (a) the bimetallic catalyst (Ac.PdBi/C_{SX+}) made from the acetate route and (b) the commercial trimetallic catalyst Pd–Pt–Bi/C from Degussa.

Experiments clearly showed that the in situ generation of the active phase was critical for the behaviour of the catalysts, as indicated by the measurements performed with mono- or bimetallic catalysts Pd/C_{SX+} and PdBi/C_{SX+} obtained from a suspension of metallic Pd and Bi in heptane, which result in zero conversion at the end of the standard reaction test. The same behaviour was observed for catalysts made from previously decomposed acetates incorporated afterwards on the support (tests 31–32). The interaction between the support and the metallic precursors during the activation step seems therefore to be a critical aspect for achieving satisfactory catalytical properties.

Fig. 6 compares the performance curve of the best catalyst of the present work with that of a commercial trimetallic Pd(4 wt.-%)–Pt(1 wt.-%)–Bi(5 wt.-%)/C catalyst from Degussa (test 37). Despite the additional presence of Pt in this catalyst, its catalytical behaviour is less satisfactory because it deactivates more easily after the first running hour.

Complementary experiments are in progress to provide a deeper insight into the relationship between the dissolution process and the occurrence of synergetic effects in these catalysts, and to evaluate the role of the various Bi–Pd alloys detected in them.

4. Conclusions

It is possible to improve the catalytic activity of bimetallic Pd–Bi systems by choosing appropriate compounds as catalyst precursors which incorporate both metals (promoter and active metal) on the support. The catalysts made from the acetate precursors display better performances than those made from the pyrazine-2,3-dicarboxylato compounds. Their catalytical behaviours are also better

than those of a commercial trimetallic Pd(4%)–Pt(1%)–Bi(5%)/C, which deactivates more easily despite the presence of platinum in the catalyst.

The in situ generation of the active phase from precursors is critical for the behaviour of the catalyst, as demonstrated by the absence of any catalytic activity when bimetallic catalysts are obtained from a suspension of metallic palladium and bismuth or from a suspension of previously decomposed acetates.

The XPS results indicate a partial coverage of palladium by bismuth and a decrease of the Bi/Pd and Bi/C ratios after the test. This observation is in line with the dissolution of the promoting element during the oxidation reaction. The different phases identified by X-ray diffraction on the surface of the bimetallic catalysts after the activation step are Pd metal, various Pd–Bi alloys and, depending on the preparation procedure, Bi_2O_3 and BiOCl.

Bismuth dissolves systematically from Pd–Bi/C and Bi/C catalysts during the catalytic operation; the bismuth losses are always larger from the monometallic Bi/C than from the bimetallic PdBi/C catalysts. Glucose and gluconate in solution seem to be the factors responsible for catalyst leaching, since no dissolution occurs in the absence of these products even under an oxygen flow.

Bismuth was confirmed to drastically improve the catalytic activity of a Pd/C catalyst in the oxidation of glucose to gluconic acid. A direct association of bismuth with palladium, e.g. in the form of a bimetallic catalyst, is not required for achieving this improvement, as shown by the enhancement of glucose conversion when two monometallic catalysts Pd/C and Bi/C are engaged together in a catalytic test. Nevertheless, the poor performances of a carbon-supported palladium catalyst in the presence of bismuth in solution prove that the presence of dissolved bismuth in the reaction medium is not a sufficient condition to improve the catalytic activity. The present results suggest that Bi and Pd atoms associated in a given stoichiometric ratio might be responsible for the enhancement of catalytic activity. One could suspect that this association involves an adsorbed organic species, probably glucose, gluconic acid, or some other oxygenated species derived from them, possibly in the form of a bismuth complex on the surface of palladium.

Acknowledgements

The authors greatly acknowledge financial support from the Belgian National Fund for Scientific Research (F.N.R.S., Brussels) for the programme concerning the selective oxidation of glucose. The authors are grateful to NORIT for supplying the carbon support, to Mr. F. Delaruelle and J.F. Statsijns for their technical assistance in various parts of this work, and to the F.R.I.A, Brussels and the Catholic University of Louvain for the fellowships allotted to M.W.

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