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Bismuth-promoted palladium catalysts for the selective oxidation of glyoxal into glyoxalic acid

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Abstract

The incorporation of bismuth in carbon-supported Pd-based catalysts is shown to increase significantly the catalytic activity in the selective oxidation of glyoxal into glyoxalic acid. Main side products are glycolic acid resulting from Cannizzaro dismutation and oxalic acid, generated by further oxidation of glyoxalic acid. Catalysts characterized by different Bi/Pd ratios (with Pd + Bi = 10 wt.%) were prepared according to various experimental procedures from two kinds of precursors, containing either inorganic (chloride, nitrate) or organic (acetate) ligands. The fresh and used catalysts were characterized by X-ray diffractometry and X-ray photoelectron spectroscopy. When comparing the time dependence of the performances of catalysts having the same overall composition (Bi/Pd = 0.5), bimetallic catalysts prepared from inorganic ligands or from acetate precursors exhibit comparable activities, while the selectivity towards glyoxalic acid remains higher for the acetate-type catalysts. In addition, the catalytic performances of Pd-Bi/C catalysts were found to be dependent upon the catalyst composition, those characterized by molar ratios Bi/Pd between 0.5 and 1.0 representing the most adequate compromise between high activity and high selectivity. Complementary experiments were also conducted on the second step of the oxidation scheme, i.e. oxidation of glyoxalic acid to oxalic acid. The behavior of the bimetallic Pd-Bi catalysts is also compared to that of a commercial trimetallic PdPtBi/C catalyst.

Keywords: Bismuth; Palladium catalysts; Glyoxalic acid

1. Introduction

Glyoxalic acid, OHC–COOH, is the simplest α-oxocarboxylic acid. It is implicated in several synthetic processes of primary importance and is potentially a useful starting material for the synthesis of many valuable fine chemicals, especially in flavor and cosmetic industries [1]. For instance, reaction with guaiacol produces vanillin by oxidative decarboxylation of the intermediate mandelic acid. At the industrial level, glyoxalic acid is produced by oxidation of glyoxal in aqueous solution with concentrated nitric acid at temperatures between 40 and 90°C. An alternative process is the anodic oxidation of glyoxal in a two-compartment electrolytic cell in the presence of chloride ions. Another interesting route is the use of noble metal-based catalysts able to oxidize selectively glyoxal into glyoxalic acid using air as oxidant. This reaction is reported in the literature to proceed near room temperature on various

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monometallic catalysts [2]. Pt/C catalysts exhibit by far the highest catalytic performances. Other group 8–10 metals (Ru, Rh, Pd, Ir) were found to be less active and also less selective than platinum, giving substantial amounts of glycolic and formic acids. The initial rates of glyoxalic acid formation were shown to increase with the redox potentials of these elements (Ru < Rh < Pd < Ir < Pt). The authors also propose a reactional scheme for the catalytic cycle of glyoxal oxidation in which the hydrated functional group of glyoxal dihydrate adsorbs on the metal surface and is oxidized via a dehydrogenation mechanism. In a second step, the adsorbed glyoxalic acid either desorbs from the metal surface or remains adsorbed via the other functional group of the molecule, and can be oxidized further into oxalic acid. Over-oxidation into this product is actually the most critical aspect. As shown by Gallezot et al. in studies comparing platinum catalysts prepared on various carbon supports [3], both a careful choice of adequate operating conditions and the tailoring of catalyst morphology are essential to preserve a high selectivity into glyoxalic acid. Simultaneously, the authors point out that in contrast with the glucose-to-gluconate oxidation, Pt was not poisoned by oxygen under the selected experimental conditions, and they relate this feature to the strong reducing properties of all reagents present (glyoxal, glyoxalic acid, and oxalic acid).

On the other hand, heavy post-transition elements are well known for displaying attractive properties as promoting elements in such noble metal-based catalysts. Numerous patents and papers have disclosed that the introduction of bismuth in Pt- or Pd-based catalysts significantly improves their catalytic performances for the selective oxidation of alcohols or aldehydes by molecular oxygen in aqueous solutions [4,5]. This effect has been investigated with great care in the selective oxidations of glucose into gluconic acid using Bi-promoted Pd/C catalysts [6,7], and has also been described in the oxidation of glycerol into dihydroxyacetone on Bi-promoted Pt/C catalysts [8]. The promoting effects of Bi, Pb, and Te in noble metal-based catalysts have also been compared for the conversion of 1,2-propanediol into lactic and pyruvic acid [9]. In general, the main role of these promoters is to avoid or reduce catalyst deactivation. In this way, they increase the overall catalytic efficiency, but sometimes also influence directly the selectivity towards given products. However, a non-equivocal interpretation of the actual origin of the promoting role of these elements on the catalytic activity of Pd- or Pt-based catalysts is still missing.

Account taken of the fact that Pd/C catalysts were shown to exhibit poorer catalytic performances than Pt/C catalysts for the selective oxidation of glyoxal to glyoxalic acid [2], the present work is dedicated to the promotion of Pd catalysts by bismuth. The main by-products of this process are (i) glycolic acid resulting from a competitive Cannizzaro reaction occurring in homogeneous phase and depending exclusively on the pH, and (ii) oxalic acid which is essentially generated by further oxidation of glyoxalic acid. The influence of the metallic precursors and the incorporation mode on the catalysts' properties were also investigated. By referring to a similar approach applied to the selective oxidation of glucose [6], catalysts prepared from carboxylate-type precursors were compared with those obtained according to a patented literature based on the use of classical inorganic compounds [10]. The behavior of the bimetallic Pd (5 wt.%)-Bi (5 wt.%) catalysts was also compared to that of a commercial carbon-supported trimetallic Pd (4 wt.%)-Pt (1 wt.%)-Bi (5 wt.%) catalyst supplied by Degussa. All the catalysts were systematically characterized by X-ray diffraction and X-ray photoelectron spectroscopy before and after their use in the catalytic tests.

Investigations were also undertaken to evidence the influence of Bi/Pd proportions on the catalytic activity. Catalysts characterized by different Bi/Pd molar ratios were therefore prepared. The presence of intermetallics was previously shown to be important to explain the properties of such catalysts [11,12]. The Bi/Pd ratios selected in this study are therefore those corresponding to the stoichiometry of some Bi/Pd intermetallics whose presence in the catalysts was suspected. Because the over-oxidation into oxalic acid is a critical aspect of this catalytic process, some complementary experiments on the oxidation of glyoxalic acid into oxalic acid were also carried out.

Moreover, partial dissolution of bismuth during the catalytic tests was clearly demonstrated by atomic absorption analysis of the reaction medium. A detailed investigation of the time dependence of the promoter

losses was carried out for the various Bi-promoted catalysts. The results of these experiments have been described in a recent paper devoted to the comparative stability of carbon-supported Pd-Bi and Pd-Pb bimetallic catalysts during their use in glyoxal oxidation [13]. Mainly glyoxal and glyoxylate were found to be among the main factors responsible for the promoter losses, this being due to their complexing properties.

2. Experimental

2.1. Preparation of catalysts

Activated carbon supplied by Norit (SXplus; $S_{BET} = 1000\,m^2\,g^{-1}$; particle size: 50–100 μm) was used as support. Carbon-supported Pd-Bi/C catalysts were prepared from two kinds of precursors, i.e. containing either inorganic or organic ligands of the acetate-type. Only one composition was used in the case of the inorganic ligands: it corresponds to a "standard" composition of 5 wt.% Bi and 5 wt.% Pd, namely almost exactly 1Bi:2Pd in molar ratio. Bimetallic catalysts characterized by different Bi/Pd molar ratios were also prepared from acetate precursors according to the same method as the standard catalysts. All these catalysts were characterized by an overall metal loading of Bi + Pd/catalyst equal to 10 wt.%. For comparative purposes, monometallic Bi (5 wt.%)/C and Pd (5 wt.%)/C catalysts were also prepared according to the acetate method.

2.1.1. Bimetallic catalysts prepared from inorganic precursors ("reference catalysts")

Reference catalysts prepared using a precipitation–deposition procedure described in a patented literature [8] are considered as "reference catalysts". They were obtained from aqueous solutions of Bi(III) nitrate pentahydrate and Pd(II) chloride. The formation of the active phase proceeded via in situ reduction of the precursor salts with formaldehyde at 80°C. This catalyst was noted as Ref.2Pd1Bi/C.

2.1.2. Catalysts prepared from acetate precursors

2.1.2.1. Monometallic Pd (5 wt.%)/C and Bi (5 wt.%)/C catalysts. For the preparation of the monometallic Pd (5 wt.%)/C and Bi (5 wt.%)/C catalysts, the corresponding acetate precursor (bismuth(III) oxoacetate, $BiO(O_2CCH_3)$), prepared according to a procedure described elsewhere [6]; Pd(II) acetate, $Pd_3(O_2CCH_3)_6$ purchased from Acros) was first dispersed in the presence of activated carbon in 150 ml *n*-heptane under ultrasonic stirring for 30 min. The hydrocarbon was then evaporated at room temperature under vacuum and the precursor deposited on the support was subsequently decomposed upon heating under nitrogen at 500°C during 18 h. These catalysts were noted in the following forms: Ac.Pd/C and Ac.Bi/C.

2.1.2.2. Bimetallic Pd-Bi/C catalysts. Carbon-supported bimetallic catalysts characterized by different Bi/Pd molar ratios (Bi/Pd = 0.33, 0.5, 1, and 2) were obtained by incorporating bismuth in a monometallic Pd/C catalyst prepared as described in Section 2.1.2.1. The non-activated Pd/C catalyst and the appropriate amount of bismuth oxoacetate were dispersed in *n*-heptane under ultrasonic stirring for 30 min. After evaporation of the hydrocarbon, the bimetallic catalyst was activated upon thermal heating under nitrogen at 500°C during 18 h. These catalysts are noted Ac.3Pd1Bi/C, Ac.2Pd1Bi/C, Ac.1Pd1Bi/C, and Ac.1Pd2Bi/C, where the numbers preceeding Pd and Bi refer to the relative molar composition.

2.2. Catalysts characterization techniques

2.2.1. X-ray diffractometry (XRD)

Powder X-ray diffraction patterns were obtained with a Siemens D-5000 diffractometer using the Cu Kα radiation (λ = 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 JCPDS data file.

2.2.2. X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed on a SSI-X-probe (SSX-100/206) spectrometer from FISONS, using the Al Kα 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 reference. The analyses of bismuth and palladium were based on the Bi $4f_{7/2}$ and Pd $3d_{5/2}$ photopeaks, respectively.

2.3. Reaction conditions and analytics

2.3.1. Catalytic tests

The catalytic tests were performed in a double-walled glass reactor with water circulation. The 400 ml of glyoxal solution ($0.1\,mol\,l^{-1}$) were heated in the reactor at 38°C. Reactions were carried out under constant stirring conditions (1000 rpm), ensured by a mechanical stirrer Heidolph RZR 2051. To limit the extent of glyoxal dismutation, the pH of the reaction mixture was kept at a constant value of 7.7. The produced carboxylic acids were therefore neutralized continuously by a 2 or 5 wt.% aqueous solution of sodium hydroxide, added by a Stat Titrino 718 from Metrohm. Air was bubbled through the solution at a constant flow rate of $0.4\,l\,min^{-1}$. A first series of "standard" measurements (reaction conditions A) was performed with 100 mg of catalyst during reaction times ranging between 0.5 and 24 h. Preliminary experiments demonstrated that the selected conditions correspond to a kinetic regime.

In order to determine the influence of the catalyst composition on the catalytic performances, further tests were carried out under the same conditions with catalysts characterized by different Bi/Pd molar ratios and by keeping the palladium weight constant ($m_{Pd} = 2$ mg). Depending on the Pd/Bi composition, the amounts of catalysts used in the catalytic tests were in the range 33–100 mg (reaction conditions B). Complementary experiments were also carried out under the same experimental conditions, but starting with glyoxalic acid instead of glyoxal. The initial concentration in glyoxalic acid ($0.122\,mol\,l^{-1}$) was selected as corresponding to the maximum concentration occurring in the standard experiments.

2.3.2. Analysis of the reaction medium

The nature of the reaction products was determined by high performance liquid chromatography (HPLC), using a liquid chromatograph TSP Spectra SERIES P200 coupled with a TSP Spectra System UV6000LP diode array detector. The different carboxylic acids were separated on a BioRad Aminex HPX-87H column heated at 60°C. The mobile phase was a $0.005\,mol\,l^{-1}$ sulfuric acid solution at a flow rate of $0.4\,ml\,min^{-1}$.

Bismuth losses from the catalysts in the reaction medium were measured by atomic absorption spectrometry after removal of the catalyst from the reaction mixture, washing, and subsequent concentration of the resulting filtrate. Analyses were performed on a Perkin-Elmer 3110 spectrometer equipped with an air–acetylene flame atomizer.

2.3.3. Expression of the catalytic results

Because the formation of glycolic acid only depends on the pH of the reaction mixture and is not related to the catalytic activity, we subtracted the corresponding amount of transformed glyoxal for the calculation of conversion and selectivity. Catalytic results were therefore expressed as yields in glyoxalic or oxalic acids (Y, %), glyoxal "corrected" conversion (X^*, %) and "corrected" selectivity in glyoxalic acid (S^*, %). These last two parameters were calculated from the following expressions:

$$X^*_{GLY} = Y_{AGLY} + Y_{OX}$$

$$S^*_{AGLY} = \frac{Y_{AGLY}}{X^*_{GLY}}$$

where GLY, AGLY, and OX refer to glyoxal, glyoxalic acid, and oxalic acid, respectively. This implies that there is no other by-product except glycolic acid. The only other detected product was formic acid, but its mean yield did actually never exceed 3% after 24 h.

3. Results and discussion

3.1. Catalytic results

Representative catalytical results collected under standard reaction conditions (denoted as A), with a constant catalyst mass (100 mg), are listed in Table 1. Yields in glyoxalic and oxalic acids are given for two different reaction times. Corrected conversion and corrected selectivity, as defined in Section 2.3.3, were also calculated after each catalytic test. The performances of the bimetallic Pd-Bi/C catalysts characterized by various compositions measured under reaction conditions B (constant Pd mass of 2 mg) are listed in Table 2.

Table 1
Catalytic results obtained with mono-, bi-, and trimetallic catalysts for two different reaction times under reaction conditions A (100 mg catalyst)[a]

Catalyst	$t = 6$ h				$t = 20$ h			
	Y_{AGLY} (%)	Y_{OX} (%)	X^*_{GLY} (%)	S^*_{AGLY} (%)	Y_{AGLY} (%)	Y_{OX} (%)	X^*_{GLY} (%)	S^*_{AGLY} (%)
Ac.Pd/C[b]	0.70	0.03	0.73	95.9	1.17	0.10	1.27	92.1
Ac.Bi/C[b]	0.55	0.03	0.58	94.8	1.09	0.02	1.11	98.2
Ref.2Pd1Bi/C[c]	6.0	3.0	9.0	66.7	9.1	14.1	23.2	39.3
PdPtBi/C[d]	9.1	7.6	16.7	54.5	0.7	29.9	30.6	2.4
Ac.1Pd2Bi/C[c]	5.2	2.1	7.3	71.5	10.7	7.8	18.5	57.8
Ac.1Pd1Bi/C[c]	9.0	2.6	11.6	77.5	15.4	12.7	28.1	54.8
Ac.2Pd1Bi/C[c]	5.6	1.7	7.3	77.0	14.4	11.4	25.8	55.8
Ac.3Pd1Bi/C[c]	4.4	0.7	5.1	85.9	16.3	9.1	25.4	64.1

[a] A 1% conversion/yield corresponds to 4×10^{-4} mol glyoxal/glyoxalic acid/oxalic acid.
[b] 5 wt.% Pd or Bi.
[c] 10 wt.% Pd + Bi; the numbers preceeding Pd and Bi refer to the relative molar composition.
[d] Pd (4 wt.%)-Pt (1 wt.%)-Bi (5 wt.%)/C catalyst supplied by Degussa.

3.1.1. Overall evolution of the composition of the reaction mixture in function of the reaction time

Preliminary experiments carried out with the support alone in the presence of air (blank tests) confirmed the absence of any catalytic activity under these conditions.

As already mentioned, experiments performed in the absence of any catalyst showed previously that the production of glycolic acid did not depend on the catalytic activity, but was exclusively related to the pH of the reaction medium. The yield in glycolic acid increases linearly with the reaction time and reaches 22% after 24 h. All the catalysts tested in the present work were found to display a similar overall evolution of the yields in glyoxalic (Y_{AGLY}) and oxalic (Y_{OX}) acids. Once air is admitted, glyoxal is oxidized essentially to glyoxalic acid. Then, after a certain time depending on the catalyst nature, over-oxidation of this first reaction product into oxalic acid occurs. Fig. 1a and b display the overall evolution of the yields in glyoxalic and oxalic acids with the reaction time for the Ac.2Pd1Bi/C catalyst and the trimetallic PdPtBi/C catalyst from Degussa, respectively.

3.1.2. Promoting effect of bismuth

Under the reaction conditions used for the present work, the monometallic Pd/C catalyst displays a very

Table 2
Influence of catalyst composition on the catalytic performances of Pd-Bi/C catalysts prepared from organic ligands[a]

	Catalytic performances	Catalysts			
		Ac.1Pd2Bi/C	Ac.1Pd1Bi/C	Ac.2Pd1Bi/C	Ac.3Pd1Bi/C
1	Bi/Pd molar ratio	2	1	0.5	0.33
2	Pd-Bi (wt.%)	2.0–8.0	3.4–6.6	5.0–5.0	6.0–4.0
3	m_{cat} (mg)	100	60	40	33.3
4	Y_{AGLY}[b] (%)	10.7	8.7	5.0	3.3
5	X^*_{GLY}[b] (%)	18.5	11.3	5.3	3.5
6	S^*_{AGLY} (%)	57.8	77.3	93.2	94.0
7	Y_{AGLY}/m_{cat}[b] (% mg^{-1})	0.11	0.15	0.12	0.10
8	X^*_{GLY}/m_{cat}[b] (% mg^{-1})	0.19	0.19	0.13	0.10
9	Bi losses (%)	14	11	18	4

[a] Reaction conditions B; 2 mg Pd; $t = 20$ h.
[b] A 1% conversion or yield corresponds to 4×10^{-4} mol glyoxal or glyoxalic acid.

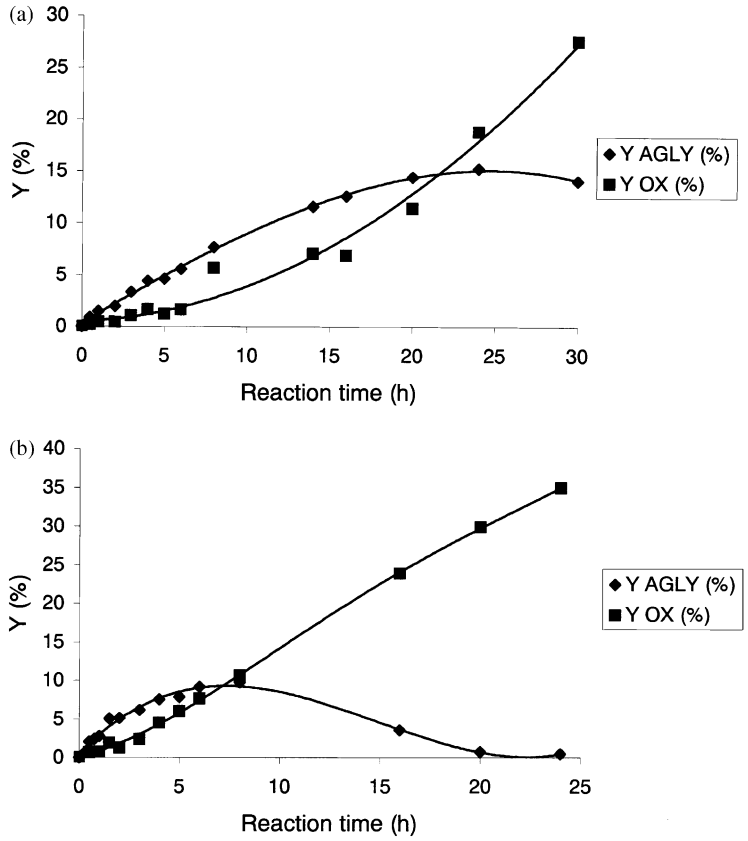

Fig. 1. Yields in glyoxalic and oxalic acids vs. reaction time for: (a) the Ac.2Pd1Bi/C catalyst; (b) the PdPtBi/C catalyst from Degussa (reaction conditions A).

low activity in glyoxal oxidation. This result differs from previous observations by Gallezot et al. [2], but cannot be directly compared with them. Although, the Pd contents are similar (5 wt.% Pd here versus 4 wt.% Pd in [2]), these catalysts have been obtained by different preparation procedures and are supported on carbons with different particle sizes (50–100 μm versus 0.1–1 μm in [2]) and BET specific surface areas (1000 $m^2 g^{-1}$ here versus 1400 $m^2 g^{-1}$ in [2]). In addition, the glyoxal-to-metal molar ratio is about five times higher in the present work ([GLY]/[M] = 850 instead of 177 in [2]), the other reaction parameters (temperature, pH) being the same. However, the present work clearly demonstrates that the incorporation of Bi in Pd-based catalysts drastically increases the catalytic activity with respect to the monometallic Pd/C catalyst prepared according to the same route. This promoter effect on the yield in glyoxalic acid is illustrated in Fig. 2 for the bimetallic Ac.2Pd1Bi/C catalyst.

Table 3 summarizes the optimal catalytic performances of this acetate-prepared and other

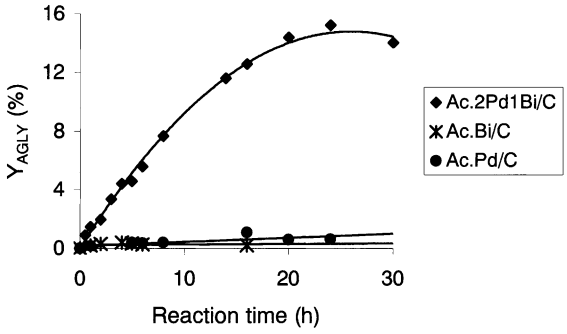

Fig. 2. Promoting effect on the yield in glyoxalic acid: comparison of mono- and bimetallic catalysts (reaction conditions A).

Table 3
Comparison of optimal performances of promoted and unpromoted Pd/C and Pt/C catalysts from this work and the literature[a]

Catalyst	$(Y_{AGLY})_{max}$ (%)	t_{max}[b] (h)	X^*_{GLY} at t_{max} (%)	S^*_{AGLY} at t_{max} (%)	$(Y_{AGLY})_{max}/m_{Pd/Pt}$ (mol g^{-1} metal)
This work[c]					
Ac.2Pd1Bi/C (5 wt.% Pd/5 wt.% Bi)	15.2	24	34.0	44.7	1.22
Ref.2Pd1Bi/C (5 wt.% Pd/5 wt.% Bi)	9.3	16	20.4	45.4	0.74
Pd (4 wt.%)-Pt (1 wt.%)-Bi (5 wt.%)/C (Degussa)	9.8	8	20.4	47.8	0.78
[2][d]					
Pd (4 wt.%)/C	23	–	62	37	0.38
Pt (4.2 wt.%)/C	60	1.5	~85	~70	0.55

[a] $T = 38°C$; pH = 7.7.
[b] Reaction time corresponding to the maximum yield in glyoxalic acid.
[c] Carbon support: $S_{BET} = 1000\,m^2\,g^{-1}$; particle size: 50–100 μm; [GLY]/[M] = 850.
[d] Carbon support: $S_{BET} = 1400\,m^2\,g^{-1}$; particle size: 0.1–1 μm; [GLY]/[M] = 177.

bimetallic catalysts, and compares them with those of the monometallic Pd/C and Pt/C catalysts described in [2]. The table reports the maximum yield in glyoxalic acid ever observed for each of the catalysts, and the corresponding values of corrected glyoxal conversion and selectivity in glyoxalic acid for the same reaction time, noted t_{max}. The last column refers to the maximum yield in glyoxalic acid normalized with respect to the mass of active metal (Pd or Pt). Although this comparison is only indicative due to the differences in the experimental parameters described above, it appears from the latter values that the promoted catalyst Ac.2Pd1Bi/C is about four times more efficient than the best monometallic catalyst reported so far for this reaction.

3.1.3. Influence of the preparation method and comparison with the Degussa catalyst

Fig. 3 compares the corrected conversions obtained for two different bimetallic Bi-Pd/C catalysts of the same composition (Bi/Pd = 0.5) and that of the commercial trimetallic catalyst containing also platinum. Bimetallic Bi-Pd/C catalysts prepared from inorganic ligands or according to the acetate route exhibit comparable activities in glyoxal oxidation. In both cases, the overall activity is rather constant with time, whereas the commercial trimetallic catalyst, which displays a higher activity at the early stage, deactivates already after 10 h operation. As far as selectivity is concerned (Fig. 4), the corrected selectivity towards glyoxalic acid remains significantly higher with time

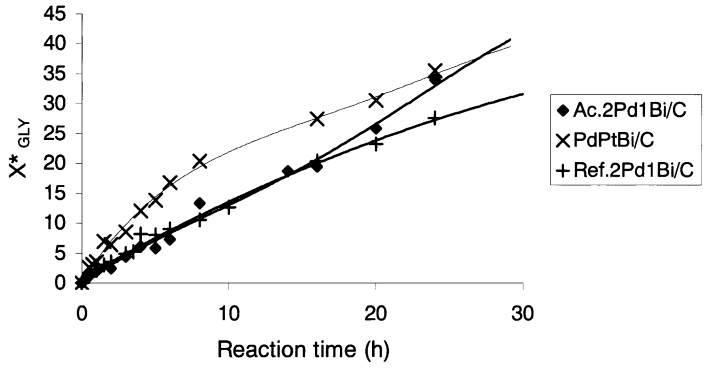

Fig. 3. Corrected glyoxal conversion rate vs. reaction time for multimetallic catalysts (reaction conditions A).

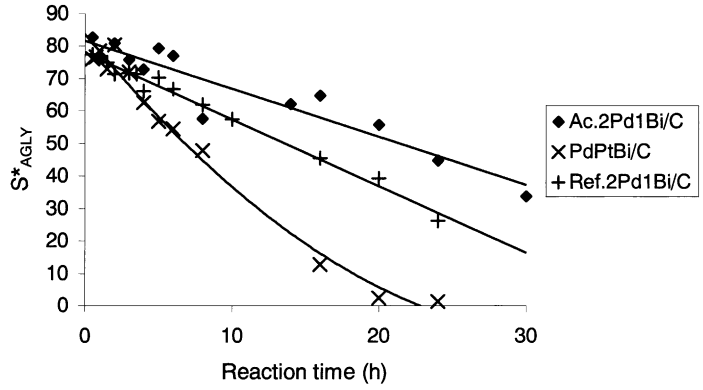

Fig. 4. Corrected selectivity towards glyoxalic acid vs. reaction time for multimetallic catalysts (reaction conditions A).

for the acetate-type catalyst. In the case of the Degussa catalyst, the selectivity towards glyoxalic acid drops severely after a few hours running and oxalic acid is finally found as the only product, leaving a 2% corrected selectivity in glyoxalic acid after 20 h. The optimal performances of these catalysts are also compared with those of monometallic Pd/C or Pt/C catalysts in Table 3. At the point where the maximum yield in glyoxalic acid is reached (t_{max}), all the three bimetallic and trimetallic catalysts investigated here are characterized by similar selectivities in glyoxalic acid (45–48%), but the acetate-prepared catalyst is clearly the most efficient one as the reaction proceeds further, because the over-oxidation into oxalic acid is delayed with respect to the other catalysts.

3.1.4. Influence of the catalyst composition in Pd-Bi bimetallic catalysts

The experiments performed with catalysts characterized by different Bi/Pd molar ratios show that, for a constant palladium mass (2 mg), Bi-rich catalysts present a higher catalytic activity (Table 2, rows 4 and 5). Conversely, the selectivity towards glyoxalic acid decreases when the Bi/Pd ratio increases (Table 2, row 6). The evolution of the corrected glyoxal conversion and selectivity towards glyoxalic acid observed for the different catalysts is described in Figs. 5 and 6, respectively. However, when the yield in glyoxalic acid or the glyoxal conversion are normalized with respect to the catalyst mass (Table 2, rows 7 and 8), it appears that the optimum combination of good activity

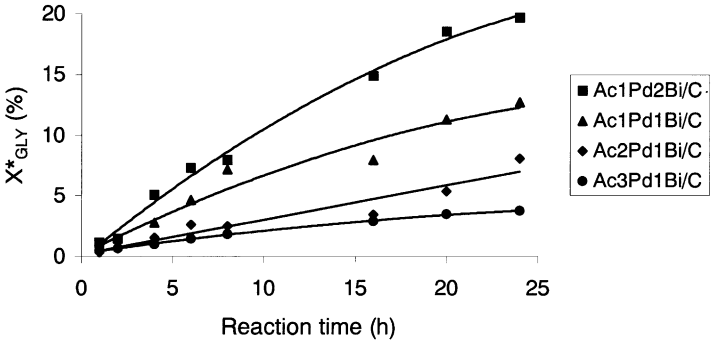

Fig. 5. Corrected glyoxal conversion vs. reaction time for various Bi/Pd compositions (reaction conditions B).

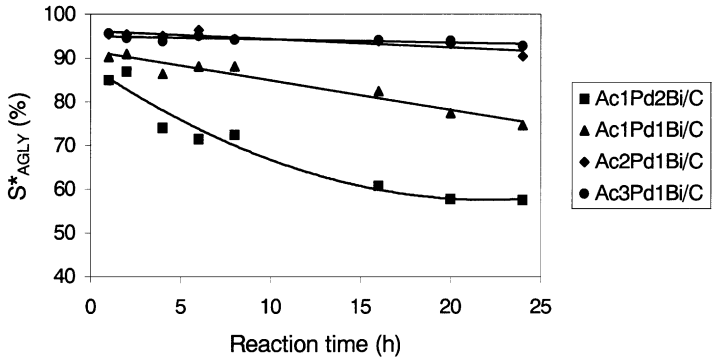

Fig. 6. Corrected selectivity towards glyoxylic acid vs. reaction time for various Bi/Pd compositions (reaction conditions B).

and selectivity towards glyoxalic acid occurs for the catalyst characterized by Bi/Pd equal to 1. Figs. 7 and 8 illustrate this behavior for the various catalyst compositions and different reaction times.

3.1.5. Oxidation of glyoxalic acid in oxalic acid

To provide a deeper insight in the differences in selectivity observed for the various bimetallic catalysts characterized by different Bi/Pd ratios, these catalysts were also engaged in complementary catalytic tests in which the starting reagent was glyoxalic acid instead of glyoxal (under reaction conditions B, with a constant Pd mass of 2 mg). The conversions in glyoxalic acid (X_{AGLY}) measured after 4, 8, and 24 h of operation are listed in Table 4. The two catalysts with the lowest Bi/Pd ratios (i.e. Ac.3Pd1Bi/C and Ac.2Pd1Bi/C) are

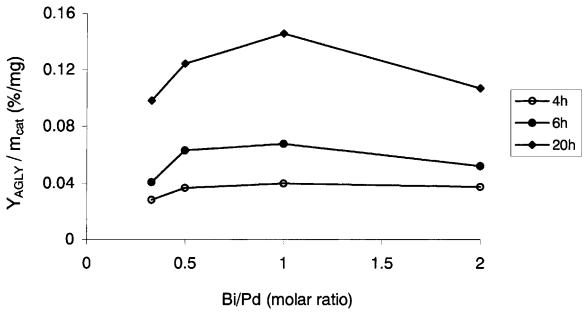

Fig. 8. Corrected selectivity towards glyoxylic acid normalized with respect to the catalyst mass vs. Bi/Pd molar ratio in acetate-type catalysts for various reaction times (reaction conditions B).

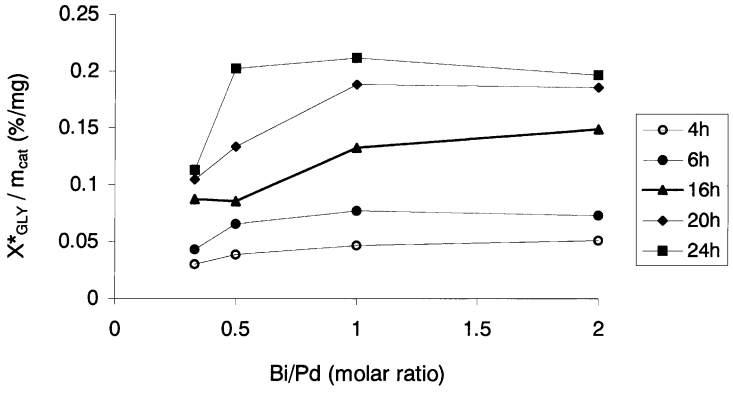

Fig. 7. Corrected glyoxal conversion normalized with respect to the catalyst mass vs. Bi/Pd molar ratio in acetate-type catalysts for various reaction times (reaction conditions B).

Table 4
Oxidation of glyoxalic acid into oxalic acid: conversion vs. time for different catalyst compositions (reaction conditions B)

Catalyst	X_{AGLY} (%)		
	$t = 4$ h	$t = 8$ h	$t = 24$ h
Ac.1Pd2Bi/C	59.3	91.6	99.7
Ac.1Pd1Bi/C	58.8	97.4	99.6
Ac.2Pd1Bi/C	59.9	75.6	99.5
Ac.3Pd1Bi/C	44.2	69.5	99.8

found to delay the conversion of glyoxalic acid into oxalic acid most efficiently. After 8 h of operation, conversions of about 70–75% are observed, whereas the Bi-richer compositions give already more than 90%. These results are in perfect agreement with the evolution of the corresponding values of corrected selectivity in glyoxalic acid illustrated in Fig. 6.

3.2. Stability of supported catalysts: time dependence of Bi losses

Like in many similar liquid phase processes, analyses by atomic absorption spectrometry showed that bismuth was steadily leached from the catalyst in the reaction medium during the catalytic tests. This behavior is usual for catalysts containing such a high amount of promoting element; as shown by Besson et al. in a study on glucose oxidation, there was no Bi leaching from Pd-Bi or Pt-Bi catalysts in which the promoter element was selectively deposited on the noble metal at low Bi loading (Bi/M = 0.1) [14]. Palladium concentrations were always below the analytical detection limit. Detailed investigations of the time dependence of Bi leaching were carried out with various Bi-Pd/C catalysts and were described elsewhere [10]. Fig. 9 allows to compare their behavior with that of the commercial trimetallic catalyst. It shows a regular increase of Bi losses from the bimetallic Pd-Bi/C catalysts with the reaction time. Losses are more important from Ac.2Pd1Bi/C than from the reference Ref.2Pd1Bi/C catalyst displaying the same composition. Promoting agent leaching is higher from the bimetallic (maximum 18% after 24 h) than from the monometallic (<5%) catalyst prepared from the same precursors according to the same method. However, Bi losses are much smaller from the Degussa catalyst and do not exceed 3%, establishing definitely the high stability of this catalyst under the present reaction conditions.

The extent of Bi leaching from different bimetallic catalysts prepared according to the acetate route and characterized by various Bi/Pd molar ratios has also been analyzed by atomic absorption spectrometry (Table 2, row 9). In all cases, Bi losses were relatively low and did not exceed 18% after 20 h of reaction.

In general, Bi losses are much lower in the glyoxal/glyoxalic acid process than when the same catalysts were involved in the glucose to gluconic acid reaction [4]; these marked differences noticed with respect to leaching when identical Pd-Bi/C catalysts are used in the two investigated oxidation processes suggest that the complexing properties of reactants and products play a crucial role in this phenomenon. In glucose oxidation, the positive influence of dissolved bismuth on the catalytic behavior was

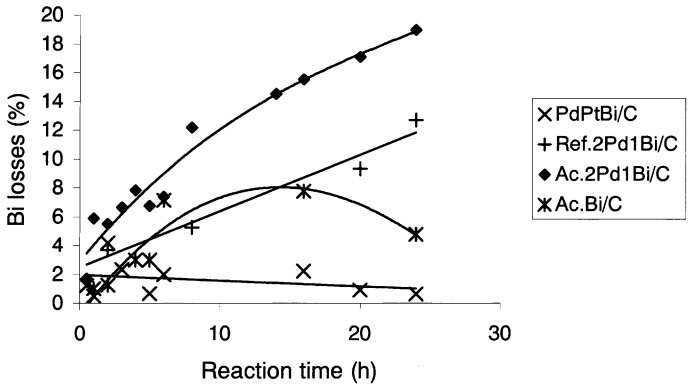

Fig. 9. Time dependence of Bi leaching vs. time for various mono-, bi-, and trimetallic catalysts.

demonstrated. In that case, arguments were based on the fact that the dissolved bismuth plays a role in the catalytic process. Addition of Bi^{3+} ions in the reaction medium improves the performances of monometallic Pd/C catalysts. However, it was shown that there was no simple relationship between the extent of Bi losses and the performances of the supported catalyst.

3.3. Characterization of supported catalysts

3.3.1. X-ray diffractometry

Fresh and used catalysts exhibit very similar XRD patterns. The diffractograms of the monometallic Pd/C catalyst and the Pd-Bi/C catalyst prepared from inorganic ligands indicated the presence of metallic Pd. In the monometallic Bi/C catalyst, metallic bismuth and minor amounts of Bi_2O_3 were detected. Bimetallic catalysts prepared from organic ligands are characterized by poorly resolved XRD data, suggesting an amorphous or microcrystalline structure in which the occurrence of one or several binary Bi_xPd_y alloys is however suspected. This interpretation was confirmed by the XRD analysis of the decomposition product of a mixture of Pd(II) acetate and Bi(III) oxoacetate submitted to the same treatment as the corresponding carbon-supported catalysts [4]; in this case, XRD patterns show unequivocally the presence of two intermetallics 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. Moreover, XRD characterization of the bimetallic Pb-Pd/C catalyst prepared from acetate precursors according to the same method has confirmed the presence of the intermetallic compound $PbPd_3$ [13].

3.3.2. X-ray photoelectron spectroscopy

The Bi 4f XPS spectra display two doublets which can be assigned to Bi(0) ($E_b = 158.4$ eV) and Bi(III) ($E_b = 160.1$ eV), respectively. The Pd 3d XPS spectra also display two doublets which correspond to Pd(0) ($E_b = 335.8$ eV) and Pd(II) ($E_b = 337.4$ eV).

Table 5 compares the experimental atomic intensity ratios with the theoretical values, i.e. those calculated from the overall catalyst composition. When Bi is concerned, the theoretical values reported for the used catalysts take into account the partial loss of promoting element during the catalytic test. The atomic intensity ratios Bi/Pd observed in fresh bimetallic catalysts are systematically higher than the theoretical values. A first possible interpretation of these results is related to the partial coverage of palladium by the promoting agent, a segregation effect which is in agreement with the lower surface energy of the latter.

Table 5
Atomic intensity ratios measured by XPS in fresh and used ($t = 24$ h) catalysts

Catalyst		Bi/Pd		Pd/C (× 100)		Bi/C (× 100)	
		Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
Ac.Pd/C	Fresh	–	–	0.59	1.24	–	–
	Used	–	–	0.59	1.13	–	–
Ac.Bi/C	Fresh	–	–	–	–	0.30	0.46
	Used	–	–	–	–	0.29	0.39
Ac.1Pd2Bi/C	Fresh	2.00	6.06	0.25	0.16	0.51	0.98
	Used	1.91	1.67	0.25	0.39	0.49	0.66
Ac.1Pd1Bi/C	Fresh	1.00	3.07	0.42	0.28	0.42	0.87
	Used	0.96	0.84	0.42	0.44	0.40	0.37
Ac.2Pd1Bi/C	Fresh	0.51	0.77	0.62	1.24	0.32	0.95
	Used	0.41	0.49	0.62	1.27	0.26	0.62
Ac.3Pd1Bi/C	Fresh	0.33	1.19	0.76	0.47	0.25	0.52
	Used	0.32	0.51	0.76	0.78	0.24	0.39
Ref.2Pd1Bi/C	Fresh	0.51	3.77	0.62	0.97	0.32	3.60
	Used	0.45	1.59	0.62	1.51	0.28	2.40
PdPtBi/C (Degussa)	Fresh	0.64	2.29	0.50	1.11	0.32	2.55
	Used	0.63	1.42	0.50	1.10	0.32	1.56

The fact that some experimental Pd/C ratios are lower than the theoretical values seems to strengthen this explanation. These values could also be interpreted as indicative for the presence of separate Bi-rich particles on the support, either in the metallic or the oxide form, that would lead to faster leaching than bimetallic particles in which Bi and Pd are alloyed. However, the detection by XPS of Bi(III) species at the surface cannot be used to support this explanation, because this oxidized state results most likely from surface contamination of the catalysts during their sampling and conditioning for the XPS analysis. Conversely, in tested catalysts, experimental ratios Pd/C and Bi/C are comparable or higher than the theoretical value (corrected for Bi leaching). These values indicate an adequate dispersion of these elements on the surface. The fact that the Bi/Pd and Bi/C ratios decrease in the used catalysts is in line with the leaching behavior.

4. Conclusions

The present work gives for the first time clear evidence that heavy post-transition elements like bismuth act as promoters of Pd-based catalysts in the selective conversion of glyoxal to glyoxalic acid. When comparing the time dependence of the performances of catalysts having the same overall composition (Bi/Pd = 0.5), bimetallic catalysts prepared from inorganic ligands or from acetate precursors exhibit comparable activities, while the selectivity towards glyoxalic acid remains higher for the acetate-type catalysts. At the point where the maximum yield in glyoxalic acid is reached, both bimetallic catalysts investigated here are characterized by similar selectivities in glyoxalic acid (45%), but the acetate-prepared catalyst is clearly the most efficient one at longer reaction times, because the over-oxidation into oxalic acid is delayed with respect to the other catalysts. Moreover, the catalytic performances of Pd-Bi/C catalysts were found to depend upon the composition of the catalyst, yield and selectivity into glyoxalic acid being simultaneously optimized for a composition characterized by molar ratios Bi/Pd between 0.5 and 1.0. Although, their initial activity is lower, the bimetallic catalysts investigated in this work display more attractive overall performances than a commercial trimetallic catalyst containing also platinum, which anticipates the formation of oxalic acid from the intermediate product.

Bismuth dissolves systematically from Bi/C and Pd-Bi/C catalysts during the catalytic operation. Previous investigations on the stability of such bimetallic Pd-Bi and Pd-Pb carbon-supported catalysts during their use in glyoxal oxidation indicated that both glyoxal and glyoxylate solutions seem to be among the main factors responsible for the promoter losses.

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