Carboxylate-type palladium(II) complexes as soluble precursors for the preparation of carbon-supported Pd/C catalysts

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Abstract

Palladium-based carboxylate-type compounds were synthesized and used as precursors for the preparation of heterogeneous carbon-supported Pd/C catalysts. The selected compounds corresponded to the general formula $Pd(O_2CR)_2$, $Pd(O_2CR)_2L_2$ or $Pd(O_2CR)_2L'$, with $R = CH_3$, C_2H_5, or C_6H_5, L = pyridine or diethylamine, and L' = 2,2′-bipyridine or 1,10-phenanthroline. The precursors were characterized by means of FTIR and XPS. Thermogravimetric analyses allowed us to study the way they decompose under nitrogen: X-ray diffraction investigations indicated they were converted mainly into Pd metal and PdO. Pd/C catalysts were prepared by impregnation from solutions of these complexes in water, benzene or acetone, followed by thermal activation under nitrogen. Catalysts were engaged in the partial oxidation of glucose to gluconic acid and have been characterized by XRD and XPS before and after their use in the catalytic reaction. Catalysts prepared in benzene showed better performances and higher Pd dispersion on the surface than the catalysts prepared in water or acetone. Activity was also found to be enhanced by monomeric, instead of trimeric, structure of the precursor. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Carboxylates; Heterogeneous catalysis; Oxidation

1. Introduction

Palladium-based catalysts are known to be extremely useful in the field of partial oxidation reactions converting alcohols or aldehydes into carboxylic acids, in aqueous phase, particularly when the noble metal is associated with heavy post-transition metals acting as promoter elements [1–10]. The present work is performed within the frame of research looking for new preparation methods of bimetallic carbon-supported Pd–Bi catalysts. The synthesis of these bimetallic catalysts consists traditionally in a two-step procedure starting with the incorporation of Pd, and then Bi, on the support. As far as palladium is concerned, chloride or ammine Pd complexes are the most usual precursors used to introduce this metal in supported catalysts [3,6,7,11]. The present work deals more specifically with the involvement of impregnation procedures based upon carboxylate-type

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complexes to incorporate palladium in such catalysts.

A wide range of monometallic Pd/C catalysts were prepared in order to evaluate the influence of several parameters on the catalytic performances, namely, the nature of the solvent, the incorporation mode, and the nature and structure of the palladium precursor. Previous experiments carried out in our laboratory indicated that deposition of acetate-type precursors from a dispersion in *n*-heptane, followed by evaporation and thermal activation under nitrogen at 500°C gave rise to bimetallic Pd–Bi/C catalysts displaying the highest performances for the catalytic conversion of glucose to gluconic acid [10]. In the present work, palladium precursors were incorporated by impregnation after dissolution in an appropriate solvent. Because the homoleptic carboxylate complexes of Pd(II) are essentially insoluble in water, these compounds were used in organic medium, on one hand. On the other hand, heteroleptic complexes in which Pd is surrounded by a mixed coordination sphere made of carboxylates and N-bound ligands, which enhance the solubility in water, were also considered because they increase the interest from an industrial point of view. In addition, these compounds are free from heteroatoms like P, S, or halides which are known to cause catalyst deactivation.

In the first part of this work, palladium coordination compounds were synthesized and characterized: ligands are carboxylates (acetate, benzoate, propionate), eventually associated with diethylamine, pyridine (py), 2,2′-bipyridine (bpy), or 1,10-phenanthroline (phen). The molecular and crystal structures have been reported in the literature for most of these compounds [12–17]. Carboxylate ligands act as bidentates when they are alone, but their coordination mode switches to monodentate when additional N-containing ligands are incorporated. The latter impose a *trans* configuration when they are monodentate (L = py, Et_2NH), and a *cis* configuration when they are bidentate (L = bpy, phen). Interesting for the purpose of the
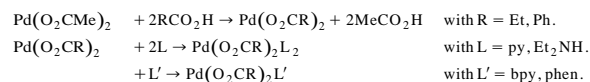
present work is the fact that the molecular structure of the homoleptic carboxylates in solution is known to depend upon the solvent nature and the temperature [18]. Whereas the solid state trimeric structures of Pd(II) acetate and propionate are reported to be preserved in benzene at 25°C, these compounds are converted into monomeric species in the same solvent when heated at 80°C. Pd(II) benzoate displays a different behaviour, keeping its trimeric structure in benzene throughout the whole temperature range. The other precursors used in this work are and remain monomeric in solution [19]. All the palladium complexes were characterized by FTIR, TGA and XPS.

In the second part, these complexes were used as precursors for the preparation of monometallic Pd/C catalysts, by impregnation, in various solvents and under different temperature conditions. Catalysts were engaged in the partial oxidation reaction of D-glucose to gluconic acid, and their catalytic performances were compared with those of catalysts prepared by dispersion in *n*-heptane. Catalysts were characterized before and after activation, and after reaction, to identify the parameters which are of special significance to explain their catalytic behaviour.

2. Experimental

2.1. Synthesis of the Pd(II) coordination compounds

The Pd(II) complexes were most usually obtained from diacetatopalladium(II), according to the following overall reaction scheme:

$$Pd(O_2CMe)_2 + 2RCO_2H \rightarrow Pd(O_2CR)_2 + 2MeCO_2H \quad \text{with } R = Et, Ph.$$
$$Pd(O_2CR)_2 + 2L \rightarrow Pd(O_2CR)_2L_2 \quad \text{with } L = py, Et_2NH.$$
$$+ L' \rightarrow Pd(O_2CR)_2L' \quad \text{with } L' = bpy, phen.$$

This scheme corresponds to a ligand substitution mechanism in which the N-coordinating ligands replace one of the oxygen atoms belonging to the bidentate carboxylate. All reagents

were used as commercially available, without any further purification. The complexes were obtained according to procedures slightly adapted from the literature [12,18]. Because these procedures were sometimes very cursorily described, some of them are described with more details below.

2.1.1. Diacetatobis(pyridine)palladium(II) (Pd(OAc)$_2$(py)$_2$) [18]

A 0.5-g diacetatopalladium (Acros) was dissolved into 20-ml pyridine (Merck, 98%) and heated at 80°C until complete dissolution. Crystallisation occurred after refrigeration in a NaCl/ice cooling mixture. The product was recrystallised in benzene (Fluka, > 99.5%) and dried in vacuo (yield: 20–50%).

2.1.2. Diacetatobis(diethylamine)palladium(II) (Pd(OAc)$_2$(Et$_2$NH)$_2$) [18]

A 0.5-g diacetatopalladium(II) (Acros) was dissolved into 10-ml diethylamine (UCB, min. 98%). After filtration and slow evaporation of the solution, the obtained product was recrystallised in petroleum ether (T_{eb}: 40–60°C) and dried in vacuo (yield: 45–70%).

2.1.3. Diacetato(2,2′-bipyridine)palladium(II) (Pd(OAc)$_2$(bpy))

Whereas problems were encountered with the literature procedure given in Ref. [18], the procedure described in Ref. [12] was shown to give more satisfactory results (yield: 85–98%).

2.1.4. Diacetato(1,10-phenanthroline)palladium(II) (Pd(OAc)$_2$(phen)) [12]

This complex was obtained in good yield (75–92%) following the same literature procedure.

2.1.5. Dipropionatopalladium(II) (Pd(prop)$_2$)

The product was obtained by dissolving 0.5 g diacetatopalladium(II) (Acros) into benzene (Fluka, > 99.5%). The solution was filtered after 1 h stirring. Propionic acid (5.28 ml) (Janssen, min. 99%) was then added, and the reaction

was allowed to proceed during one night. After removal of the solvent, the collected product was washed with acetone (Fluka, > 99.5%) and dried in vacuo (yield: 64–77%).

2.1.6. Dibenzoatopalladium(II) (Pd(OBz)$_2$) [18]

A 0.5-g diacetatopalladium(II) (Acros) was dissolved in 50-ml benzene (Fluka, > 99.5%) and stirred for 1 h, before filtering. After addition of 0.82 g benzoic acid (Merck), the solution was stirred further, then benzene was evaporated. The obtained powder was washed with acetone (Fluka, > 99.5%), dried and recrystallised in benzene. The compound was dried in vacuo (yield: 85%).

2.1.7. Dibenzoatobis(pyridine)palladium(II) (Pd(OBz)$_2$(py)$_2$) [18]

3 ml pyridine (Merck, 98%) was added to a solution of dibenzoatopalladium (0.13 g) in benzene (30 ml) (Fluka, > 99.5%). The obtained solid product was filtered off after 30 min, washed with ether and dried in vacuo (yield: 60%).

2.2. Catalyst preparation

Carbon SXplus (S_{BET} = 750 m^2 g^{-1}; particle size: 50–100 μm) supplied by Norit was used as support for all the catalyst preparations.

A monometallic Pd/C catalyst prepared by dispersion of diacetatopalladium(II) in *n*-heptane according to a standard procedure described elsewhere [10] was used as reference catalyst for comparative purposes. Other monometallic Pd/C catalysts were prepared by impregnation of synthesized palladium compounds in various solvents, selected as a function of the solubility of the Pd-based precursors and their structures in solution. All the preparations are listed in Table 1. The Pd content was in all cases 5 wt.% with respect to the final catalyst.

The catalysts prepared by impregnation were obtained according to the following procedure. The appropriate amount of palladium coordina-

Table 1
List of synthesized catalysts

Precursor[a]	Solvent	Temperature (K)	Catalysts[b]
$Pd(OAc)_2$	benzene	298	$Pd(OAc)_2[bz298]/C$
$Pd(OAc)_2$	benzene	353	$Pd(OAc)_2[bz353]/C$
$Pd(OBz)_2$	benzene	298	$Pd(OBz)_2[bz298]/C$
$Pd(OBz)_2$	benzene	353	$Pd(OBz)_2[bz353]/C$
$Pd(prop)_2$	benzene	298	$Pd(prop)_2[bz298]/C$
$Pd(OAc)_2(Et_2NH)_2$	water	298	$Pd(OAc)_2(Et_2NH)_2[w]/C$
$Pd(OAc)_2(py)_2$	water	298	$Pd(OAc)_2(py)_2[w]/C$
$Pd(OAc)_2(bpy)$	water	298	$Pd(OAc)_2(bpy)[w]/C$
$Pd(OAc)_2(phen)$	water	298	$Pd(OAc)_2(phen)[w]/C$
$Pd(OAc)_2(Et_2NH)_2$	acetone	298	$Pd(OAc)_2(Et_2NH)_2[ac]/C$

[a] OAc = acetate; OBz = benzoate; prop = propionate; py = pyridine; bpy = 2,2′-bipyridine; phen = 1,10-phenanthroline.
[b] bz = Benzene; w = water; ac = acetone; C is SXplus active carbon supplied by Norit (50–100 μm; 750 m^2/g).

tion compound was dissolved into the chosen solvent (to obtain a 1.2×10^{-2} mol/l solution). After heating the solution up to the desired temperature, the carbon support was incorporated into the flask. The resulting slurry was put in a water bath to keep temperature constant, and continuously stirred for 30 min. After slow evaporation of the solvent, the catalyst was dried in vacuo, then submitted to a thermal treatment under nitrogen, at 500°C, during 18 h, to induce degradation of the surrounding ligands.

2.3. Catalytic reaction

Reaction conditions were maintained constant throughout the whole series of tests. Adequate pH and temperature control were achieved to avoid deactivation by reactants, by-products or acid adsorption on the catalyst [8,20–22]. The reaction vessel was equipped with a mechanical stirrer (Heidolph RZR 2051), and a thermostatisation device which allowed to keep temperature constant at 50°C. D-glucose (72 g) (Acros, 99 + %) and 400-ml distilled water were poured into the flask. The monometallic catalyst (0.5 g) was then added, and oxygen was introduced at a flow of 0.4 l/min. The stirring rate was fixed at 1000 rpm. The reaction was free from diffusional limitations. pH control was ensured in the range 9.25–9.50 by an automatic

titration device (Metrohm, Stat Titrino 718) controlling the supply of a 5 mol/l solution of NaOH. Catalytic runs were performed during 4 h, then the reaction was stopped by interrupting the oxygen supply. Once filtered off from the reaction medium, the catalyst was washed with water, alcohol, and ether, then dried in vacuo. The catalysts were characterized by XRD and XPS, and the composition of the reaction medium was determined by ^{13}C NMR.

2.4. Instrumental analysis

Infrared spectra were measured on KBr pellets using a Perkin-Elmer 1710 FTIR spectrometer, in the range 4000–400 cm^{-1}.

Thermograms were recorded on a Setaram type 4325 device. Samples (10 mg) were heated from 20 to 500°C, under a nitrogen flow (heating rate: 10°C/min).

X-ray photoelectron spectra were recorded on a Fisons SSI-X-probe (SSX-100/206) spectrometer using the Al–K$_\alpha$ emission ($E = 1486.6$ eV). The energy scale was calibrated with respect to the Au 4f$_{7/2}$ line (84 eV). The energy of the C 1s component corresponding to the CH$_x$ hydrocarbon contamination, was fixed at 284.8 eV and used as internal reference. The analysis was based on the following photopeaks: Bi 4f$_{7/2}$, Pd 3d$_{5/2}$, C 1s, and N 1s. Analysis of the O 1s signal was omitted because

of the overlap with the Pd $3p_{3/2}$ photopeaks. Before analysis, samples were heated for several hours under vacuum, at 30°C.

Powder X-ray diffraction spectra were recorded on a Siemens D-5000 diffractometer, using the Cu–K$_\alpha$ radiation ($\lambda = 154.18$ pm). The samples were dispersed on quartz monocrystals purchased from Siemens.

^{13}C NMR spectra were recorded under standard conditions, on a Bruker AM500 spectrometer, equipped with an Aspect 3000 computer. A 5-mm ^{1}H probe was used. D_2O was used as internal lock signal, and methyl carbons from sodium 2,2-dimethyl-2-silapentane-5-sulfonate (DSS) as internal spectral reference.

3. Results

3.1. Characterization of the palladium coordination complexes

3.1.1. Infrared spectroscopy

Particular attention has been paid to the COO^- stretching bands, because the difference ($\Delta\nu = \nu_s - \nu_{as}$) between the wave number values associated with the symmetric and antisymmetric COO stretching modes are known to inform on the various coordination modes of the carboxylate ligands [23]. $\Delta\nu$-values below 150 cm^{-1} are indicative of symmetrically bound carboxylate ligands, i.e., bridging or chelating: this is the case in the homoleptic $M(O_2CR)_2$ complexes. Unidentate coordination causes the

antisymmetric stretching energy to increase, while that of the corresponding symmetric mode decreases, resulting in $\Delta\nu$-values above 200 cm^{-1}; this is observed in the heteroleptic complexes $M(O_2CR)_2L_2$, and $M(O_2CR)_2L'$. The experimental values measured in this work are presented in Table 2, which shows the general agreement with the rules mentioned above; these results agree with those reported in the literature [16,18].

3.1.2. Thermogravimetric analysis

TGA was implemented to provide information on the degradation patterns of these complexes when decomposed under nitrogen, to simulate the activation step occurring during the catalyst preparation. Decomposition temperatures of these compounds could be determined (Table 3). Thermal degradation residues were analysed by X-ray diffraction to check their nature: Pd metal and PdO were the only crys-

Table 3
TGA results

Compound[a]	$(\Delta m)_{theor}$ (%)		$(\Delta m)_{exp}$ (%)	T_{dec} (K)
	for PdO	for Pd		
Pd(OAc)$_2$(py)$_2$	67.9	72.0	69	475
Pd(OAc)$_2$(Et$_2$NH)$_2$	66.9	71.3	71	463
Pd(OAc)$_2$(bpy)	67.8	72.0	52	518
Pd(OAc)$_2$(phen)	69.7	73.7	40	525
Pd(prop)$_2$	51.5	57.8	58	510
Pd(OBz)$_2$	64.8	69.5	68	525
Pd(OBz)$_2$(py)$_2$	75.8	79.0	41	483
			31	583

[a]See footnote [a] in Table 1.

Table 2
IR characterization of the Pd-based precursors

Compound[a]	Coordination mode	$\Delta(\nu_{as} - \nu_s)$ theoretical (cm^{-1})	$\Delta(\nu_{as} - \nu_s)$ experimental (cm^{-1})
Pd(OAc)$_2$	bridging	< 150	174
Pd(OAc)$_2$(py)$_2$	unidentate	> 200	210–268
Pd(OAc)$_2$(Et$_2$NH)$_2$	unidentate	> 200	206
Pd(OAc)$_2$(bpy)	unidentate	> 200	261–305
Pd(OAc)$_2$(phen)	unidentate	> 200	311
Pd(prop)$_2$	bridging	< 150	172
Pd(OBz)$_2$	bridging	< 150	165
Pd(OBz)$_2$(py)$_2$	unidentate	> 200	260–278

[a]See footnote [a] in Table 1.

Table 4
XPS data of Pd(II) carboxylate-type precursors

		Assignment	Pd(OAc)$_2$(py)$_2$ [E_b (eV) (I_{rel} (%))]	Pd(OAc)$_2$(Et$_2$NH)$_2$ [E_b (eV) (I_{rel} (%))]	Pd(OAc)$_2$(bpy) [E_b (eV) (I_{rel} (%))]	Pd(OAc)$_2$(phen) [E_b (eV) (I_{rel}(%))]	Pd(prop)$_2$ [E_b (eV) (I_{rel} (%))]	Pd(OBz)$_2$ [E_b (eV) (I_{rel} (%))]	Pd(OBz)$_2$(py)$_2$ [E_b (eV) (I_{rel}(%))]
C 1s	C(I)	C–H	284.8 (65)	284.8 (60)	284.8 (47)	284.8 (65)	284.8 (64)	284.8 (84)	284.8 (74)
	C(II)	C–N	286.3 (3)	286.2 (10)	286.1 (25)	285.9 (11)	–	–	286.1 (8)
	C(III)	C=O	287.9 (13)	288.3 (11)	287.9 (13)	287.5 (7)	288.5 (22)	288.7 (5)	288.0 (6)
N 1s		N–Pd	399.8 (6)	399.7 (7)	399.9 (9)	399.8 (9)	–	–	400.2 (5)
Pd 3d$_{5/2}$		Pd(II)	337.7 (10)	337.9 (8)	337.9 (6)	337.8 (5)	338.3 (10)	338.4 (7)	338.1 (5)
C(I + II + III)/Pd(II)	theoretical		14	12	14	16	6	14	24
	experimental		8	10	15	15	8	12	17
N/Pd(II)	theoretical		2	2	2	2	–	–	2
	experimental		0.6	0.9	1.5	1.6	–	–	0.9

Table 5
XPS data of fresh and used catalysts

Catalyst[a]	Pd/C ($\times 100$)[b]		Pd(0)/Pd(II)	
	Fresh	Used	Fresh	Used
Pd(OAc)$_2$[bz298]/C	0.81	0.64	2.5	4.8
Pd(OAc)$_2$[bz353]/C	1.50	1.3	4.9	24
Pd(OBz)$_2$[bz298]/C	0.83	–	2.7	–
Pd(OBz)$_2$[bz353]/C	2.70	4.0	4.5	7.8
Pd(prop)$_2$[bz298]/C	0.59	–	2.9	–
Pd(OAc)$_2$(Et$_2$NH)$_2$[w]/C	0.28	0.32	8.3	5.4
Pd(OAc)$_2$(py)$_2$[w]/C	0.26	–	3.3	–
Pd(OAc)$_2$(phen)[w]/C	0.40	0.36	2.3	2.3
Pd(OAc)$_2$(Et$_2$NH)$_2$[ac]/C	0.35	0.33	4.4	3.1

[a]See footnote [a] in Table 1.
[b]Theoretical value based on stoichiometric composition is 0.59%.

talline phases detected. Mass losses calculated on the basis of this assumption were found to be in line with those observed during the TGA experiments (Table 3). Weight losses inferior to calculated values were at least partially interpreted as suggesting the presence of residual carbon.

3.1.3. X-ray photoelectron spectroscopy (XPS)

C 1s photoelectron spectra could be resolved into several components: hydrocarbon 'CH$_x$' fixed at 284.8 eV, sometimes accompanied by a 'C–N' component at 286 eV, and a COO component from carboxylic groups at 288 eV. Nitrogen N 1s spectra were made of a single peak appearing at 400 eV. The Pd spectra are indicative for the presence of two different oxidation states, Pd(0) and Pd(II). The experimental binding energies, relative intensities and some useful atomic intensity ratios are presented in Table 4.

It is a common characteristic of these Pd complexes to decompose partially when submitted to ultra-high vacuum and X-ray irradiation conditions: this accounts for the presence of Pd(0) in the spectra of the starting materials, and for the fact that the experimental atomic intensity ratios N/Pd and C/Pd are systematically below the theoretical values.

3.2. Characterization of the fresh catalysts

Catalysts were characterized by XRD and XPS, before and after their activation upon thermal degradation. *XRD*: diffraction lines characteristic of the used precursors were sometimes hardly observable in the spectra before degradation, this being probably due to the relative instability of these compounds. After activation, only metallic palladium was detected. *XPS* (Table 5): while the C 1s spectra consisted essentially in one line fixed at 284.8 eV, the Pd 3d spectra could be decomposed into two doublets corresponding to Pd(0) (335.7 and 340.9 eV) and Pd(II) (337.7 and 342.8 eV). Dispersion of palladium on the support was evaluated by comparing the experimental Pd/C atomic intensity ratio with the theoretical value corresponding to the overall catalyst composition, i.e., Pd/C = 0.59% (Table 5). All the catalysts prepared in benzene were found to behave favourably with respect to that point, and to display experimental intensity ratios which are in most cases, significantly larger than the theoretical value. This was clearly not the case for the catalysts

Table 6
Catalytic performances

Catalyst	Mean initial reaction rate[a] (10^{-5} mol/min)	Gluconic acid yield at $t = 4$ h Y_{GLU} (%)
Pd(OAc)$_2$[bz298]/C	5.3	2.3
Pd(OAc)$_2$[bz353]/C	15	7.3
Pd(OBz)$_2$[bz353]/C	11	4.3
Pd(OAc)$_2$(Et$_2$NH)$_2$[w]/C	4.0	1.9
Pd(OAc)$_2$(phen)[w]/C	3.0	1.3
Pd(OAc)$_2$(Et$_2$NH)$_2$[ac]/C	2.7	1.3
Pd/C reference	10	4.1

[a]Mean reaction rate calculated within the interval 10–30 min (expressed in moles of gluconic acid produced per minute).
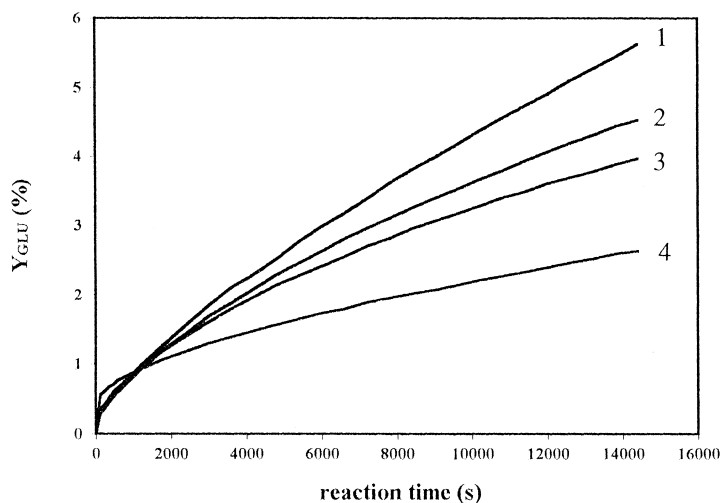
Fig. 1. Yield in gluconic acid (%) vs. reaction time for Pd/C catalysts prepared in benzene: (1) Pd(OAc)$_2$[bz353]/C, (2) Pd(OBz)$_2$[bz353]/C, (4) Pd(OAc)$_2$[bz298]/C and for a reference Pd/C catalyst (3).

impregnated in water or acetone, in which palladium seems to be poorly dispersed.

3.3. Catalytic results

3.3.1. Selectivity determination by ^{13}C NMR

In order to determine the selectivity in gluconic acid, which is the main partial oxidation product, reaction media were analysed by ^{13}C NMR at the end of the catalytic tests. The only detectable by-product was fructose, occasionally accompanied by an unidentified product which is not a carboxylic acid. Fructose results from the isomerization of glucose in alkaline medium [24] and is therefore, not to be considered as a catalytical product.

3.3.2. Catalytic performances

Because gluconic acid was the only carboxylic acid detected by NMR in the reaction products, the yield in gluconic acid was calculated directly from the NaOH consumption. The
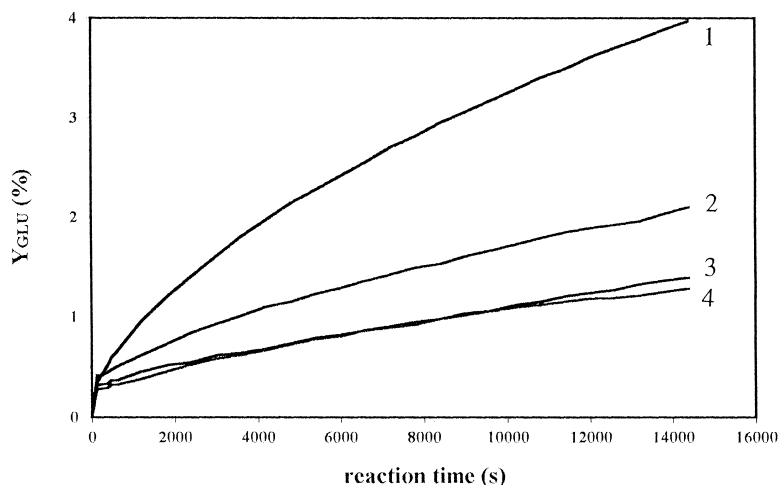

Fig. 2. Yield in gluconic acid (%) vs. reaction time for a reference Pd/C catalyst (1), and for catalysts prepared in water and acetone: (2) Pd(OAc)$_2$(Et$_2$NH)$_2$[w]/C, (3) Pd(OAc)$_2$(Et$_2$NH)$_2$[ac]/C, (4) Pd(OAc)$_2$(phen)[w]/C.

experimental results of the individual catalytic tests are described in Table 6, in the form of the mean initial reaction rate over the interval 10–30 min, and the yield in gluconic acid after 4 h. These data are illustrated in Figs. 1 and 2, in which they are presented as continuous curves because they actually correspond to 120 successive experimental points. The low absolute yields in gluconic acid obtained are typical of monometallic Pd/C catalysts and, as mentioned earlier, can be very significantly enhanced by incorporating promoting elements like Bi.

3.4. Characterization of the used catalysts

Metallic palladium was the only crystalline phase detected in the used catalysts by XRD, as in the case of the fresh catalysts. As indicated in Table 5, the experimental Pd/C atomic intensity ratios determined by XPS in the used catalysts behave similarly with those observed before their use, and remain above or below the theoretical value, according to the case. The reaction itself has thus, no significant influence on the catalyst nature or metal dispersion.

4. Discussion

4.1. Monometallic Pd / C catalysts prepared by impregnation in benzene (Fig. 1)

As already mentioned, diacetatopalladium(II) is trimeric in benzene solution at 25°C but monomeric at 80°C, while dibenzoatopalladium(II) remains trimeric when dissolved in this solvent throughout this temperature range. As shown in Fig. 1 and Table 6, it is the catalyst prepared by impregnation of diacetatopalladium(II) in benzene at 80°C that displayed the highest activity among the investigated series. The presence of a monomeric structure seems to allow better catalytic performances; this behaviour has to be related with the XPS data given in Table 5, indicating that this catalyst was also the one exhibiting the highest experi-

mental Pd/C ratio (about 4.5 times the theoretical value).

In addition, the precursor nature is suggested to influence the catalytic performances, as shown by comparing curves No. 2 and 4 in Fig. 1, corresponding to catalysts prepared by impregnation in benzene under conditions where both acetate and benzoate retain their trimeric structure.

The difference between the catalyst prepared from Pd(II) acetate by impregnation in benzene and the so-called reference Pd/C catalyst obtained from a dispersion in *n*-heptane is not so marked: one has obtained the best results by impregnation in benzene at 80°C.

4.2. Monometallic catalysts Pd / C prepared by impregnation in water or acetone (Fig. 2)

As indicated in Table 6 and illustrated in Fig. 2, catalysts prepared by impregnation in water or acetone exhibited most usually performances which are significantly lower than those of the reference catalyst prepared by a deposition procedure. These observations are once again to be associated with the fact that these catalysts were characterized by low Pd/C atomic ratios in XPS (and lower than the theoretical value), meaning that palladium was very poorly dispersed on the surface of these samples. This must be due to the influence of solvent on interactions between support and precursor. The comparison between $Pd(OAc)_2(Et_2NH)_2$/C catalysts prepared by impregnation in water or in acetone confirms that there is not only a precursor effect.

5. Conclusions

A wide series of carboxylate-type Pd(II) complexes were isolated and used as soluble precursors for the preparation of monometallic carbon-supported Pd/C catalysts: $Pd(OAc)_2$-$(Et_2NH)_2$, $Pd(OAc)_2(py)_2$, $Pd(OAc)_2(bpy)$, Pd-$(OAc)_2(phen)$, $Pd(prop)_2$, $Pd(OBz)_2$, and Pd-

(OBz)$_2$(py)$_2$. Their common characteristics are the ligand type, and the solubility in water or current organic solvents. XRD analyses of residues from TGA experiments indicated that these complexes degraded mainly into Pd metal and PdO when heated under nitrogen at 500°C.

Whereas the use of homoleptic carboxylates Pd(O$_2$CR)$_2$ was restricted for solubility reasons to impregnation procedures in benzene, partial substitution of carboxylates by N-bound ligands that remove the bidentate coordination, was shown to open new synthetic pathways for these catalysts, starting from solutions in water or acetone. Palladium dispersion on the support was evaluated by XPS and found to be more satisfactory for the catalysts prepared in benzene.

When these catalysts were engaged in the partial oxidation reaction of D-glucose into gluconic acid, in aqueous phase, by oxygen, the samples displaying the highest Pd dispersion were also observed to provide the highest catalytic performances in terms of yield in gluconic acid. Among several parameters that were found to influence the catalytic performances are the nature and structure of the coordination compound used as precursor. Conditions under which the carboxylate precursors are converted into monomeric species were shown to be favourable to the catalytic properties. In general, however, impregnation methods did not lead to outstanding improvements of the catalytic properties when comparing with those of a reference catalyst made by a deposition procedure from a dispersion of Pd(II) acetate in *n*-heptane.

Acknowledgements

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