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Bimetallic Bi–Pt, Ru–Pt and Ru–Pd and trimetallic catalysts for the selective oxidation of glyoxal into glyoxalic acid in aqueous phase

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Abstract

Various bi- and trimetallic associations have been tested as catalysts for the selective oxidation of glyoxal into glyoxalic acid in aqueous phase. All catalysts were supported on carbon and consisted of a noble metal (Pd or Pt) in association with a second (or third) metal acting as promoter (Ru or Bi). Out of all the possible combinations, some families of catalysts were selected as interesting candidates and a detailed kinetic study was undertaken, in order to determine the rate constant associated with the formation of glyoxalic acid. In particular, the BiPt/C catalysts gave very high activity, but low selectivity (due to over-oxidation to oxalic acid), the PdRu/C catalysts gave the highest yields in glyoxalic acid, but with long reaction times and a marked sensitivity to the preparation procedure, while the trimetallic catalysts gave high yields in relatively short periods of time.
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1. Introduction

In an era of increasing economical and environmental strain, conducting chemical transformations with high yield and selectivity in a benign medium is more than ever a priority. In this context, catalytic partial oxidations in aqueous phase present a high interest, because they can lead to the production of high added-value materials, with pharmaceutical and fine chemistry applications [1–4]. In the present study, we focus on the specific transformation of glyoxal into glyoxalic acid, a reaction that finds its justification in the various possible uses for the latter in the cosmetic, food and pharmaceutical industries [5,6], and in particular for the synthesis of vanillin [7,8]. Industrially, glyoxalic acid is currently produced by nitric acid oxidation of glyoxal or glycol [5]. The electrochemical oxidation of glyoxal [9], the electroreduction of oxalic acid [11,12], the simultaneous anodic oxidation of glyoxal and cathodic reduction of oxalic acid [13,14], or a chemo-enzymic route [10,15] have also been proposed for the synthesis of glyoxalic acid. The liquid phase heterogeneous catalytic oxidation of glyoxal is thus an attractive alternative, avoiding the use of stoichiometric amounts of acids, enzymes or high temperatures and pressures. Moreover, the catalysts, being heterogeneous, may be recovered and reused, with the additional advantages of low cost, simplicity of procedure, and negligible amounts of polluting effluents. However, due to the variety of by-products that can be formed (oxalic or formic acids by over-oxidation, glycolic acid by Cannizzaro dismutation depending only on the pH), conducting this catalytic oxidation selectively still represents a challenge for the chemist. The general scheme displayed in Fig. 1 shows the various products of glyoxal oxidation, and the way in which they are interconnected, based on our previous studies [16].

Glyoxal oxidation has already been tested with some heterogeneous catalysts, with monometallic [17] or bimetallic formulations [18,19], all based on a noble metal deposited on a carbonaceous support. The second metal (when used) usually is a heavy element that plays the role of a promoter. This is a widespread strategy in oxidation

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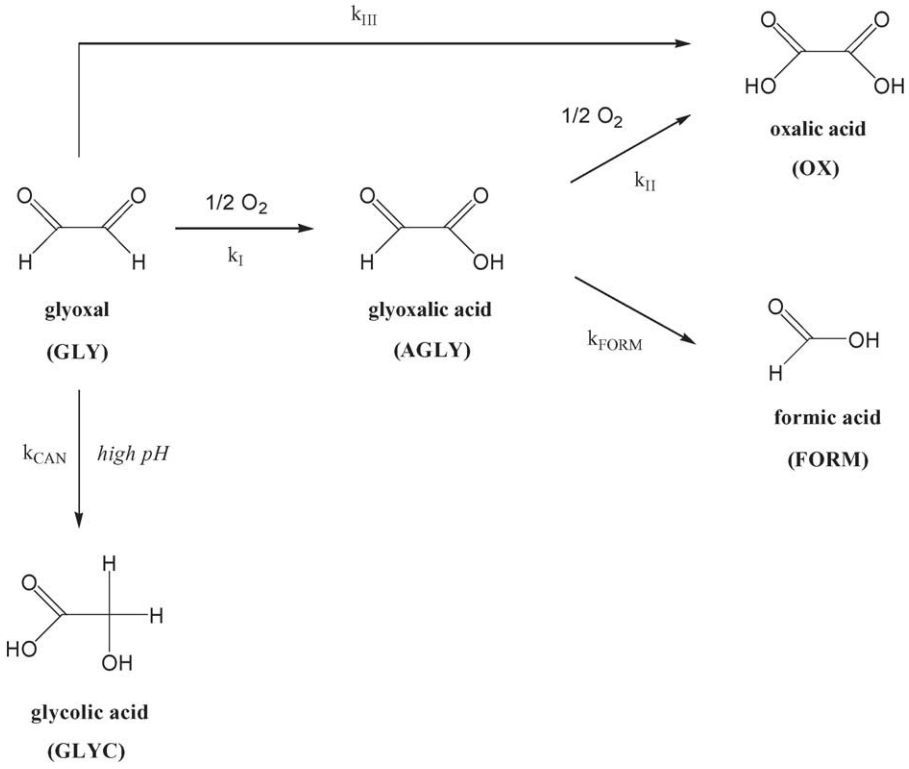

Fig. 1. Reaction scheme showing the possible by-products in the catalytic oxidation of glyoxal (note: the production of glycolic acid depends only on the pH by Cannizzaro dismutation and is thus truly homogeneous), and how the different rate constants are defined.

catalysts' preparation, with the promoter being responsible for major improvements in activity, selectivity and durability of the catalysts, without having a catalytic activity by itself [2–4]. In our group, the promoter effect of post-transition elements such as Bi or Pb have been studied for Pd/C catalysts used in glucose [20,21] or glyoxal [18,19] selective oxidation. For the latter, the most active catalysts so far were BiPd/C or PbPd/C, with the drawback of leaching of the promoter element (Bi or Pb) in the reaction mixture during catalytic use [19].

In consequence, there is a high scope for finding other combinations that would combine high activity and selectivity with high stability, in order to increase lifetime and reusability of the catalyst. Indeed, the presence of potentially toxic elements in solution is a major drawback of the current systems, especially when considering industrial applications on a larger scale. In this paper, we describe the results of a study that was focused on the introduction of ruthenium (as a promoting element) and/or platinum (as an active metal), in addition to Bi and/or Pd, in the catalysts' formulation, in order to improve the overall process of glyoxal selective oxidation into glyoxalic acid. Platinum was chosen on the basis of the screening effected with monometallic catalysts [17], where it was quoted as the most active metal for this reaction, and ruthenium was chosen by analogy with glucose oxidation [22], where it was found to play the role of a promoter without leaching in solution. It should also be noted that very few studies are devoted to the bimetallic association Ru–Pd in catalysis. Most reports are related to applications in hydrogenation and hydrotreatment [23–39], or electro-catalysis [40–42], and sophisticated preparation methods (for example Pd films deposited on Ru(0 0 1) surfaces [43] or Ru–Pd alloy membranes [44,45]). One recent paper deals with oxidation, and describes the use of a Ru–Pd/CeO_2 catalyst for the catalytic wet air oxidation of ammonia [46].

2. Experimental

2.1. Catalysts synthesis

All bimetallic (Bi–Pt, Ru–Pt and Ru–Pd) catalysts were synthesised from commercial monometallic catalysts M(5 wt.%)/C (Aldrich, M = Pt, Pd or Ru) by sonication with a chosen metallic precursor in *n*-heptane (Acros), followed by slow evaporation of the solvent and activation at 500 °C for 18 h under a nitrogen flow, as described previously [21]. Some catalysts were also activated under a mixture of 5% H_2 in Ar (18 h at 500 °C) or pure hydrogen (3 h at 300 °C) rather than nitrogen, but the activity was not improved. In some cases, the starting monometallic Pd(5 wt.%)/C catalyst was prepared by us, following the same method, using an activated carbon support of the type SX+ supplied by NORIT. For trimetallic catalysts, the third element was introduced similarly by dispersion in *n*-heptane

of the bimetallic (unactivated) catalyst in the presence of the metallic precursor of choice. The different precursors used are the following: $RuCl_3$ (Aldrich), $Pd(OAc)_2$ (Rocc), or BiO(OAc), the latter being obtained from Bi_2O_3 (Janssen Chimica), following a procedure reported earlier [21]. The total metal loading was 5 wt.% for the monometallic, 5–24 wt.% for the bimetallic and 10 wt.% for the trimetallic catalysts. The weight ratio of the two metals in the bimetallic catalysts was varied between 0.2 and 5, and is noted in the following manner: M*x*M′*y*/C, where *x*/*y* is the weight ratio M/M′ in the catalyst, and M is the metal incorporated in second position. Because the molar masses of Pd and Ru, on the one hand, and of Bi and Pt on the other hand, are very similar, the Pd/Ru and Bi/Pt wt. ratios also correspond roughly to molar ratios. This is not true for the other catalysts formulations.

2.2. Catalytic tests

All catalytic tests were performed in a glass double-walled reactor as described previously [18,19], with water circulation for thermostatisation at 38 °C, and under constant pH, fixed between 7.6 and 8.3 by an automatic titration device METROHM (718 STAT Titrino). The acids formed were neutralised continuously by addition of NaOH (Acros, 1 mol/L) or Na_2CO_3 (Merck, 0.5 mol/L). The oxidation was conducted with an air flow of 0.4 L/min, 100 mg of catalyst, and a stirring rate of 1000 rpm, starting from 400 ml of a solution of glyoxal (Acros, 0.1 mol/L). The products obtained were quantified by HPLC, using a TSP (Thermo Separation Products) device, equipped with a Spectra System UV 6000LP detector, on a Aminex Biorad HPX-87H column. The metal leaching (if any) was determined by atomic absorption analysis of the reaction filtrates, using a Perkin-Elmer 3110 spectrometer. Most of the catalytic tests were carried out three times, and the values quoted in the tables are average values. The results are expressed in terms of yields (*Y*, %) in each different product shown in Fig. 1, and in particular Y_{AGLY} = yield in glyoxalic acid, conversion (*X*, %) and selectivity (*S*, %), defined as follows:

$$Y = C_{\text{Product}}/C_{\text{GLY at } t=0} \quad \text{where } C = \text{concentration} \tag{1}$$

$$X_{GLY} = Y_{AGLY} + Y_{OX} + Y_{GLYC} + (Y_{FORM}/2) \tag{2}$$

$$S_{AGLY} = (Y_{AGLY}/X_{GLY})100 \tag{3}$$

When the yield in glycolic acid is neglected (because its formation is due to Cannizzaro dismutation, which depends only on the pH and thus not on the catalyst [16]), a corrected conversion (X^* = conversion without considering the Cannizzaro reaction, %) and corrected selectivity S^* (%) are used, as defined below:

$$X^*_{GLY} = Y_{AGLY} + Y_{OX} + (Y_{FORM}/2) \tag{4}$$

$$S^*_{AGLY} = (Y_{AGLY}/X^*_{GLY})100 \tag{5}$$

In the above-mentioned equations, the occurrence of total oxidation was not taken into consideration (formation of CO_2), but it is usually negligible and has been checked by comparison between the total amount of carboxylic acids determined by HPLC and the amount of base added in order to keep the pH constant. When the carbon balance is not 100%, the production of CO_2, carbonates and hydrogenocarbonates is suspected. In this case, the conversion as defined above is underestimated, and the selectivity is overestimated. However, this does not hinder the comparison in terms of glyoxalic acid production.

2.3. Catalysts characterisation

The catalysts were characterised by XRD before and after catalytic testing on a SIEMENS D-5000 diffractometer equipped with a copper source ($\lambda_{K\alpha}$ = 154.18 pm). The crystalline phases present in the samples were identified by comparison with the JCPDS database. The catalysts were analysed also by XPS before and after test, using a SSI-X-probe (SSX-100/206) FISONS spectrometer. The energy calibration was done with reference to the peak $Au4f_{7/2}$ at 84 eV, and the binding energies for the peaks obtained were corrected by shifting the C1s peak (hydrocarbon contamination + C–C,H peak of the carbon support) to 284.8 eV. The constraints used for the deconvolution of the XPS data are presented in Table 1. Given the superposition of the C1s and $Ru3d_{3/2}$ peaks, these constraints were particularly important in order to quantify ruthenium, and the following method was used: a Gaussian/Lorentzian (85/15) was placed at the position of the $Ru3d_{5/2}$ peak, which is visible on the right hand side (lower binding energy) of the C1s peak, and the contribution of the $Ru3d_{3/2}$ peak to subtract from the carbon component was calculated by reference to it by placing another Gaussian/Lorentzian (85/15) at 4.17 eV towards higher binding energy, and imposing an area ratio $Ru3d_{5/2}/Ru3d_{3/2}$ = 1.5 and a FWHM ratio of unity.

3. Results and discussion

3.1. Screening

Several bi- and trimetallic catalysts of variable compositions and ratios of the different metals were prepared from monometallic catalysts M(5 wt.%)/C (M = Pt, Pd or Ru) by adding ruthenium, palladium and/or bismuth from the following precursors: $RuCl_3$, $Pd(OAc)_2$, or BiO(OAc). All these catalysts were tested in glyoxal oxidation in ''standard'' conditions chosen for screening purpose, i.e. using 100 mg of catalyst for a duration of catalytic testing of 20 h. The complete products distribution and selectivity obtained with some representative catalysts is given in Table 2. Given that the total metal loading was variable, and the ratio between the two metals was also varied, the catalytic results need to be normalised with respect to the

Table 1
Constraints used for the quantitative analysis of the XPS results

Peaks considered		Intensity ratio	Δ (B − A) (eV)	FWHM ratio
A	B	A/B		
$Bi4f_{7/2}$	$Bi4f_{5/2}$	1.33	5.31	1
$Pt4f_{7/2}$	$Pt4f_{5/2}$	1.33	3.33	1
$Ru3d_{5/2}$	$Ru3d_{3/2}$	1.5	4.17	1
$Pd3d_{5/2}$	$Pd3d_{3/2}$	1.5	5.26	1
$Cl2p_{3/2}$	$Cl2p_{1/2}$	2	1.6	1

amount of active metal (Pd or Pt) in order to draw comparisons. The normalised results obtained for each different category of catalyst are reported in Table 3 and discussed below.

3.1.1. Monometallic catalysts

The results obtained here are in agreement with the literature [17]: both Ru/C and Bi/C catalysts showed no activity, while the Pd/C catalyst was active, but not as much as Pt/C. The corrected selectivity (S^*) of the Pd/C catalyst was higher than that of Pt/C because the latter was the only monometallic one leading to formation of formic acid as a by-product. The home-made monometallic Pd(5 wt.%)/C catalysts usually give a yield in glyoxalic acid that is about 2% after 20 h for 100 mg of catalyst [18,19]. However, small variations in the preparation conditions could lead to increased activity, with a maximum of 10% yield in glyoxalic acid after 20 h. In this paper, we have taken this maximum value, and normalised it, in order to compare with bi- and trimetallic catalysts.

3.1.2. Bimetallic catalysts BiPt/C

This bimetallic association was highly active (conversion × 3.5 compared to Pt/C), but not selective due to the production of important amounts of oxalic acid, regardless of the Bi/Pt ratio in the catalyst. It should be noted, however, that the incorporation of bismuth in a Pt/C catalyst had the beneficial effect of inhibiting the production of formic acid. Unfortunately, as with BiPd/C catalysts [19], we observed Bi leaching in solution (see Table 3, last column), a fact that greatly limits the practical use of such catalysts.

3.1.3. Bimetallic catalysts RuPt/C

The yields in glyoxalic acid obtained with RuPt/C catalysts were not improved when compared to the monometallic Pt/C, and ruthenium even seemed to play an inhibitor effect for platinum when comparing normalised data (Table 3). However, the corrected selectivity was improved thanks to a decrease in oxalic acid yield (from 3.90% after 20 h for Pt/C to 0.85–1.45% for the RuPt/C catalysts) and an inhibition of formic acid production.

3.1.4. Bimetallic catalysts RuPd/C and PdRu/C

These catalysts are very sensitive to the preparation method, which can shift the role of Ru from promoter to inhibitor of the Pd catalytic activity. For example, adding ruthenium on a pre-made Pd/C catalyst could lead to increased yields in glyoxalic acid for the Ru-rich catalysts (for example Ru3Pd1/C) when compared to the results obtained with the monometallic commercial Pd/C catalyst. However, when palladium is added on a Ru/C catalyst, the yield in glyoxalic acid is always inferior to the monometallic Pd/C case (after 20 h, see below for more accurate discussion of these results), but the conversion is sometimes higher. This is illustrated in Fig. 2. This figure also shows that the ratio Ru/Pd has a marked influence on the activity, with a clear maximum for Ru/Pd = 3. Ruthenium could thus be considered as a promoter for palladium, but under strict control of the preparation procedure. Moreover, there was no observable Ru or Pd leaching during catalytic use (see Table 3, last column), a major advantage when compared to Bi- or Pb-promoted catalysts.

3.1.5. Trimetallic catalysts

Three different trimetallic catalysts gave interesting results: Bi1Pd2Ru2/C (high activity, better than bimetallic formulations, but low corrected selectivity due to formic acid production) and Ru1Pd1Pt2/C or Pd1Ru1Pt2/C (lower

Table 2
Catalytic results for m_{CAT} = 100 mg, t = 20 h, showing the complete products distribution and the selectivity for some representative catalysts (com = commercial)

Catalyst	Precursors		Y_{AGLY} (%)	Y_{OX} (%)	Y_{FORM} (%)	Y_{GLYC} (%)	X_{GLY} (%)	S_{AGLY} (%)
Pt/C	Pt/C com	–	11.8	0.8	14.3	10.9	30.6	38.4
Ru/C	Ru/C com	–	–	–	–	13.0	13.0	–
Pd/C	$Pd(OAc)_2$	–	10.3	1.1	–	15.7	27.1	38.0
Bi1Pt1/C	BiO(OAc)	Pt/C com	6.2	58.2	7.0	14.1	82.0	7.6
Ru1Pt1/C[a]	$RuCl_3$	Pt/C com	13.2	1.0	–	11.7	25.9	51.0
Ru1Pd1/C	$RuCl_3$	Pd/C com	10.7	1.1	–	11.3	23.1	46.3
Pd1Ru1/C	$Pd(OAc)_2$	Ru/C com	6.3	0.5	4.0	10.1	18.9	33.3
Pd5Ru1/C	$Pd(OAc)_2$	Ru/C com	20.5	3.7	7.1	9.9	37.6	54.5
Bi1Pd2Ru2/C[b]	BiO(OAc)	$Pd(OAc)_2$	18.4	18.4	17.6	8.8	54.4	33.8
Ru1Pd1Pt2/C[c]	$RuCl_3$	$Pd(OAc)_2$	4.2	0.2	2.1	12.1	17.6	23.9
Pd1Ru1Pt2/C[c]	$Pd(OAc)_2$	$RuCl_3$	5.3	0.2	2.7	12.0	18.8	28.2

[a] Tested with m_{CAT} = 200 mg.
[b] Precursor 1 = Ru/C com.
[c] Precursor 1 = Pt/C com.

Table 3
Catalytic results for m_{CAT} = 100 mg, t = 20 h, normalised with respect to the amount of active metal (Pd or Pt) in the catalyst (com = commercial)

Catalyst	Precursors		$Y_{AGLY}/m_{Pt,Pd}$ (%/mg)	$X^*/m_{Pt,Pd}$ (%/mg)	S^* (%)	Y_{AGLY}/m_{tot} (%/mg)	Bi or Ru leaching (%)
Pt/C	Pt/C com	–	2.4	4.0	60.0	2.4	
Bi/C [18]	BiO(OAc)	–	–	–	–	0.2	3
Ru/C	Ru/C com	–	–	–	–	0.0	0
Pd/C	Pd/C com	–	1.9	2.1	90.4	1.9	
Pd/C	$Pd(OAc)_2$	–	2.1	2.3	91.3	2.1	
Bi1Pd1/C [18]	BiO(OAc)	$Pd(OAc)_2$	2.9	5.2	55.8	1.4	17
Bi3Pt1/C	BiO(OAc)	Pt/C com	2.0	13.8	14.5	0.5	22
Bi1Pt1/C	BiO(OAc)	Pt/C com	1.3	14.3	9.1	0.6	37
Bi1Pt3/C	BiO(OAc)	Pt/C com	1.9	12.9	14.7	1.4	47
Ru4Pt1/C[a]	$RuCl_3$	Pt/C com	1.3	1.4	92.8	0.3	0
Ru1Pt1/C[a]	$RuCl_3$	Pt/C com	1.4	1.5	93.3	0.7	0
Ru1Pt4/C[a]	$RuCl_3$	Pt/C com	2.0	2.2	90.9	1.6	0
Ru3Pd1/C	$RuCl_3$	Pd/C com	2.4	2.7	88.9	0.6	0
Ru1Pd1/C	$RuCl_3$	Pd/C com	2.2	2.5	88.0	1.1	0
Ru1Pd3/C	$RuCl_3$	Pd/C com	1.4	1.5	93.3	1.1	0
Ru1Pd4/C	$RuCl_3$	Pd/C com	0.8	0.9	88.9	0.6	0
Pd1Ru3/C	$Pd(OAc)_2$	Ru/C com	1.8	2.8	64.3	0.4	0
Pd1Ru1/C	$Pd(OAc)_2$	Ru/C com	1.3	1.8	72.2	0.7	0
Pd3Ru1/C	$Pd(OAc)_2$	Ru/C com	1.4	2.0	70.0	1.0	0
Pd5Ru1/C	$Pd(OAc)_2$	Ru/C com	1.0	1.4	71.4	0.8	0
Bi1Pd2Ru2/C[b]	BiO(OAc)	$Pd(OAc)_2$	4.0	11.4	35.1	1.6	Ru:0–Bi:3
Ru1Pd1Pt2/C[c]	$RuCl_3$	$Pd(OAc)_2$	0.6[d]	0.9[e]	66.7	0.4	0
Pd1Ru1Pt2/C[c]	$Pd(OAc)_2$	$RuCl_3$	0.8[d]	1.1[e]	72.7	0.6	0

[a] Tested with m_{CAT} = 200 mg.
[b] Precursor 1 = Ru/C com.
[c] Precursor 1 = Pt/C com.
[d] $Y_{AGLY}/m_{(Pt + Pd)}$ (%/mg)
[e] $X^*/m_{(Pt + Pd)}$ (%/mg)

activity but higher corrected selectivity). The performance of the former formulation in terms of yield in glyoxalic acid after 20 h of reaction is clearly the best so far, but with the drawback of still containing bismuth, with its associated leaching problem (see Table 3, last column), although more limited than in the bimetallic cases.

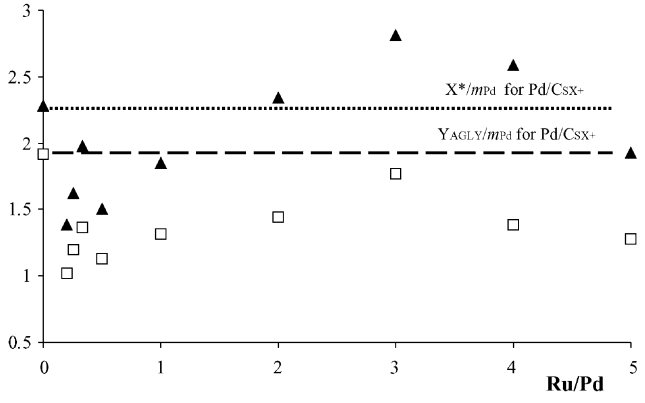

Fig. 2. Normalised (with respect to the amount of active metal in the catalyst) yield in glyoxalic acid Y_{AGLY}/m_{Pd} (%/mg) (□), and normalised corrected conversion X^*/m_{Pd} (%/mg) (▲), vs. Ru/Pd ratio in the Ru-Pd catalysts (m_{CAT} = 100 mg, t = 20 h). The dotted lines represent the normalised values of yield (- - -) and conversion (· · ·) obtained with the monometallic Pd/C catalyst (as reference).

3.2. Kinetics

The activity of some interesting catalysts was studied in more details by continuous sampling of the reaction mixture as a function of time. This has allowed us to draw kinetic plots, and to determine the period of time (hereafter called t_{max}) after which the maximum yield in glyoxalic acid is attained, before decreasing due to over-oxidation to oxalic acid (see Fig. 3). In some cases, the value of t_{max} was not determined, because the kinetic plot showed a slow increase of both glyoxalic and oxalic acids over time, without a clear maximum for the former, even after 72 h. In those cases, we

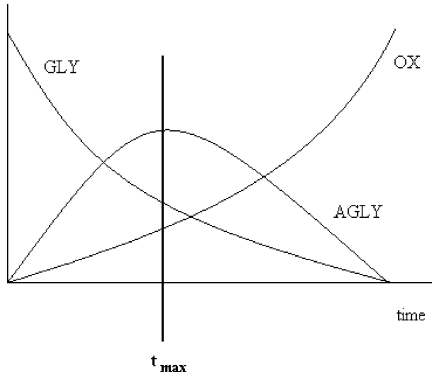

Fig. 3. Schematic kinetic plot showing how we define t_{max}.

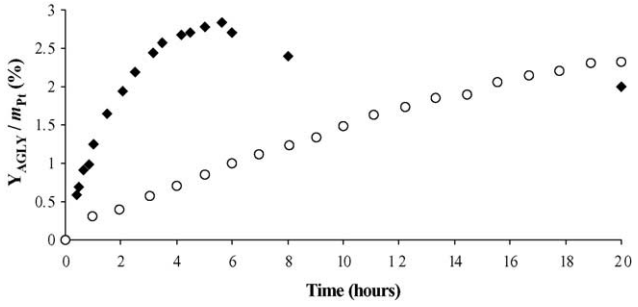

Fig. 4. Normalised (with respect to the amount of active metal in the catalyst) yields in glyoxalic acid vs. time, for the Pt/C (○) and Bi1Pt1/C (◆) catalysts.

assumed that t_{max} had not yet been attained and that the catalytic performance could be compared anyway, without the risk of underestimating the amounts of glyoxalic acid produced as it would happen after reaching t_{max}.

3.2.1. Catalysts BiPt/C

The promoting effect of bismuth is obvious when comparing the curves obtained for Pt/C and BiPt/C catalysts (Fig. 4). The maximum yield in glyoxalic acid is obtained after 5 h for the bimetallic catalyst, while it is not yet attained after 20 h for the monometallic Pt/C equivalent. It should be noted that a monometallic Bi/C catalyst is completely inactive for this reaction [18], thus we observe a synergetic effect between these two elements (Pt and Bi). However, the drawback of this high activity is the lack of selectivity as over-oxidation to oxalic acid occurs rapidly.

3.2.2. Catalysts RuPd/C and PdRu/C

The detailed analysis as a function of time allows precise comparisons between different catalysts to be carried out. For example, Fig. 5 shows two bimetallic Ru–Pd catalysts for which the order of incorporation of the metallic precursors on the support was varied, in comparison with a monometallic Pd/C catalyst. It can be seen from this graph that the three catalysts have very similar behaviours, indicating that: (i) for this particular Pd:Ru ratio, the ruthenium does not seem to play a promoter role, and (ii) the order of incorporation has no influence on the catalyst performance. However, when comparing the selectivities obtained with the bimetallic systems with the Pd/C case (see Table 2), striking differences are observed: the main trend is that formic acid production is increased when using the bimetallic catalysts. This is in agreement with the literature [17], which quotes high yields of formic acid formed with monometallic Ru/C catalysts.

Another example is shown in Fig. 6: the case of a PdRu/C catalyst where the Ru/Pd wt. ratio equals 1/5. It is striking that its behaviour over time is completely different from the above-mentioned cases, and this only by modifying the metal composition. By quantifying the different products obtained as a function of time, it is possible not only to determine t_{max} (optimal reaction time to maximise the yield in glyoxalic acid, here 27 h, see Fig. 6) but also the absolute value of Y_{AGLY} at this time, which also varies from one catalyst to the other (compare Figs. 4 and 6). When comparing the value of Y_{AGLY} obtained for the Pd5Ru1/C catalyst at t_{max} (27 h, see Fig. 6) with the value of Y_{AGLY} at 72 h for the Pd1Ru1/C catalyst (Fig. 5), it can be seen that, even if in the latter case t_{max} is not yet attained, the absolute amount of glyoxalic acid produced is higher.

The scheme presented in Fig. 1 is the result of detailed studies, where each acid produced has been separately engaged in catalytic tests (in similar conditions of concentration, temperature, etc.) in order to determine in which other product(s) it is further transformed [16]. With Ru–Pd systems, it is found that glyoxalic acid is oxidised into oxalic and formic acids, while glycolic, oxalic and formic acids do not react further. Fig. 1 also shows the different rate constants that can be associated with such a scheme. The direct transformation of glyoxal into oxalic acid (expressed by k_{III}) is neglected here because full kinetic treatment of the data obtained with BiPd/C catalysts showed

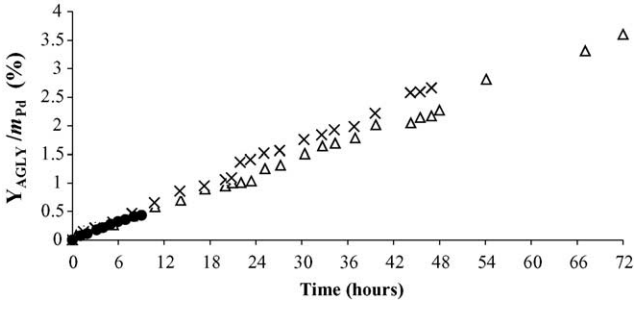

Fig. 5. Normalised (with respect to the amount of active metal in the catalyst) yields in glyoxalic acid vs. time, for the commercial Pd/C (●), bimetallic Pd1Ru1/C prepared from $Pd(OAc)_2$ and Ru/C commercial (△) and Ru1Pd1/C prepared from $RuCl_3$ and Pd/C commercial (×) catalysts.

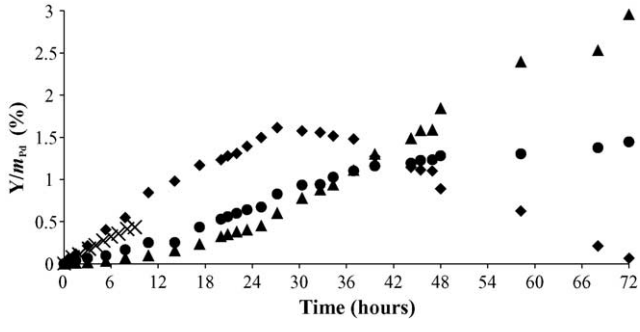

Fig. 6. Normalised (with respect to the amount of active metal in the catalyst) yields in glyoxalic (◆, Y_{AGLY}/m_{Pd}), oxalic (▲, Y_{OX}/m_{Pd}) and formic (●, Y_{FORM}/m_{Pd}) acids vs. time, for a Pd5Ru1/C catalyst prepared from $Pd(OAc)_2$ and Ru/C commercial, in comparison with the monometallic commercial Pd/C (×, Y_{AGLY}/m_{Pd}) catalyst.

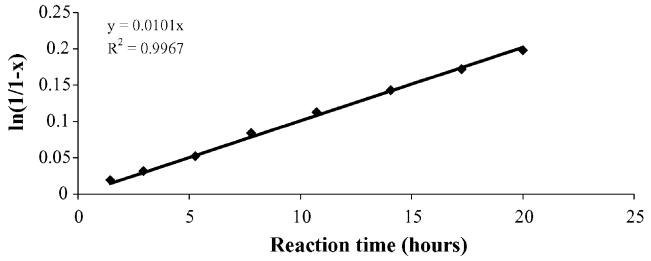

Fig. 7. Evolution of $\ln(1/1-x)$ as a function of time for the catalyst Pd1Ru1/C prepared from $Pd(OAc)_2$ and Ru/C commercial ($x = X_{GLY}/100$).

that this contribution was negligible [16], and because preliminary calculations for the catalysts presented here provided the same conclusion. Glycolic acid (with associated rate constant k_{CAN}) is produced without the aid of a catalyst and depends only of the pH in homogeneous phase [16]. It is thus of interest to determine k_I, in order to compare the different catalysts, knowing that the oxygen partial pressure and the mass of catalyst used have not been varied. A first-order kinetics with respect to glyoxal was obtained for the Ru–Pd catalysts (see Fig. 7 for a representative catalyst). This was also the case for the BiPd/C and PbPd/C catalysts [16]. The slope of the linear plot obtained gives the value of k_{exp}, according to the following equations [16]:

$$v = -d\,C_{GLY}/dt = k_{CAN}C_{GLY} + k_I C_{GLY} = k_{exp}C_{GLY} \quad (6)$$

with $k_{exp} = k_{CAN} + k_I$

$$\Rightarrow k_{exp}t = \ln(a/a-x)$$

with $a = C_{GLY}$ at $t = 0$ and $a - x = C_{GLY}$ at $t \neq 0$.

When taking $a = 1$, $x = X_{GLY}/100$.

In order to deduce k_I from k_{exp}, the following relations have been used [16]:

$$dC_{GLYC}/dt = k_{CAN}C_{GLY} \quad (7)$$

$$-dC_{GLY}/dt = (k_{CAN} + k_I)C_{GLY} \quad (8)$$

$$dC_{GLYC}/-dC_{GLY} = k_{CAN}/(k_{CAN} + k_I) \quad (9)$$

$$Y_{GLYC} = k_{CAN}/(k_{CAN} + k_I)X_{GLY} \quad (10)$$

From a graph of the yield in glycolic acid in function of glyoxal conversion, the value of $k_{CAN}/(k_{CAN} + k_I)$ can be obtained (being the slope of the linear plot obtained), and thus k_I is deduced from the relation $k_{exp} = k_{CAN} + k_I$. The results obtained for different catalysts are presented in Table 4. The values of k_{CAN} obtained are relatively constant, confirming the homogeneous nature of glycolic formation (independently from the catalyst), while the values of k_I vary a lot in function of the catalyst used, being much higher in the case of very active formulations. The values of k_I obtained with the Ru–Pd catalysts (ranging between 0.003 and 0.024 h^{-1}) are very similar to the values reported previously for MPd/C catalysts (ranging between 0.008 and 0.025 h^{-1}, M = Bi or Pb) [16].

3.3. Characterisation

The catalysts were characterised before and after test by XRD and XPS. The results are discussed below in corresponding sub-sections.

3.3.1. Powder X-ray diffraction

The phases detected at the surface of the carbon in all cases corresponded to the separated metallic phases, i.e. Pd, Ru, Pt and/or Bi. This is illustrated in Fig. 8 for a representative RuPd/C catalyst. In addition, in the case of bismuth-containing catalysts, Bi_2O_3 was also observed. No intermetallic or alloy phases were detected, in agreement with the phase diagrams for the Ru–Pd and Ru–Pt bimetallic associations [47], where there is nearly no zone of miscibility and no alloy described, but in contrast with the Bi–Pt phase diagram [47], which quotes several different possible intermetallics (such as α-Bi_2Pt or BiPt). The XRD patterns obtained after catalysis did not show any dramatic change in the supported phases occurring during catalytic use.

3.3.2. X-ray photoelectron spectroscopy

The oxidation states observed on the surface for each different metal were the following: Pt^0 and Pt^{II} for platinum, Pd^0 and Pd^{II} for palladium, Ru^{IV} for ruthenium, which becomes Ru^0 after addition of Pd, Bi^{III} before test and Bi^0 and Bi^{III} after test for bismuth. The catalysts derived from commercial ones all contained traces of Na, which tend to disappear after catalytic test, suggesting dissolution in the reaction mixture. In addition, the catalysts which did not contain traces of Na before test remain Na-free after test. Also for catalysts derived from commercial materials, the atomic intensity ratios M/C_{exp} are superior to the values calculated on the basis of the bulk composition (see Table 5),

Table 4
Rate constants determined for some representative catalysts

	Pt/C[a]	Pd/C[a]	Ru1Pd1/C[b]	Pd1Ru1/C[b]	Pd5Ru1/C[b]
$k_{exp} = (k_{CAN} + k_I)$ (h^{-1})	0.025	0.014	0.008	0.010	0.035
$k_{CAN}/(k_{CAN} + k_I)$	0.274	0.773	0.609	0.424	0.261
k_{CAN} (h^{-1})	0.007	0.011	0.005	0.004	0.009
k_I (h^{-1})	0.018	0.004	0.003	0.006	0.024

[a] pH control during catalytic reaction by addition of a solution of NaOH.
[b] pH control during catalytic reaction by addition of a solution of Na_2CO_3.

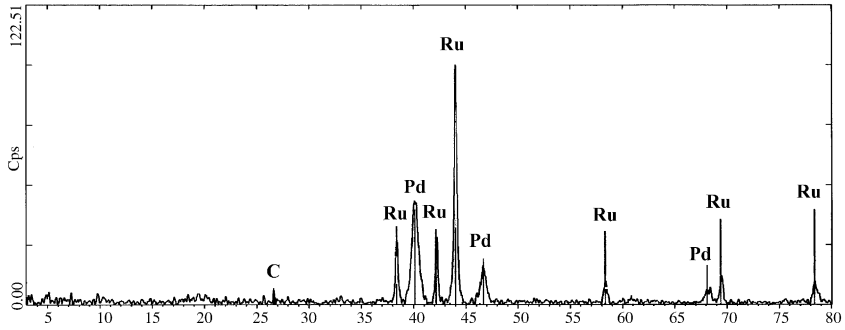

Fig. 8. Example of diffractogram obtained with a representative Ru1Pd1/C catalyst prepared from $RuCl_3$ and $Pd(OAc)_2$. The vertical lines correspond to the expected lines for the phases described (from the JCPDS database).

suggesting good dispersion of the active phase. These ratios stay relatively constant after test, demonstrating their stability. In bimetallic BiPt/C catalysts (Table 6), the experimental atomic intensity ratios Bi/Pt and Bi/C are superior to the calculated values (on the basis of bulk composition) before test, which suggests a surface enrichment in bismuth. This is in line with the surface free energy of Bi (γ_0^S(Bi) = 550 mJ/m^2) which is smaller than that of Pt (γ_0^S(Pt) = 2550 mJ/m^2) [48], and has been observed before for BiPd/C catalysts [20,21]. After catalyst use, the ratios Bi/Pt_{exp} (and Bi/C) become smaller that the Bi/Pt_{calc}, again in consistence with the fact that bismuth is leaching in solution. In bimetallic Ru–Pd catalysts (Table 5), the experimental ratios Ru/Pd are in general inferior to the calculated values, pointing towards an explanation in terms of surface enrichment in palladium. This again is in line with the values of surface free energies from the literature (γ_0^S(Pd) = 2100 mJ/m^2, γ_0^S(Ru) = 3050 mJ/m^2) [48]. The experimental Ru/C ratios, on the other hand, tend to be superior to the calculated values. The comparison of the two Ru–Pd catalysts prepared in a different order of incorporation for the two metals shows that the Pd/C ratios obtained are the same, confirming this effect of surface free energy. We also observed the presence of residual Cl on the surface if the metallic precursor(s) were chlorinated species, which tends to disappear after catalytic test, like Na, probably also by dissolution in the reaction medium. When looking at the Pd/C ratio for Ru–Pd catalysts in comparison with the corresponding monometallic Pd/C, one can conclude that Ru has a positive effect on the dispersion of palladium. This fact has already been quoted in the literature: for the combustion of methane over alumina-supported Pd catalysts prepared by incipient wetness impregnation, where it was noted that the addition of Ru increased the palladium dispersion and

Table 5
Atomic intensity ratios obtained by XPS for monometallic, Ru–Pd and RuPt/C catalysts: calc. = calculated values on the basis of bulk composition, exp. = experimental values (retrieved from XPS quantitative analysis), f = fresh catalyst (before catalytic test), t = tested (after catalytic reaction), com = commercial catalyst

Catalyst	Preparation		Pd,Pt/C (× 100)		Ru/C (× 100)		Ru/Pd,Pt	
			Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Pd/C	Commercial	f	0.59	2.19				
Pd/C	Home-made	f	0.59	0.67				
Pd/C		t	0.59	0.54				
Pt/C	Commercial	f	0.32	0.35				
Pt/C		t	0.32	0.35				
Ru/C	Commercial	f			0.62	2.53		
Ru/C		t			0.62	2.39		
Ru1Pd1/C	From Pd/C com	f	0.59	2.01	0.62	0.63	1.05	0.31
Ru1Pd1/C		t	0.59	0.96	0.62	0.52	1.05	0.54
Ru1Pd1/C	Home-made	f	0.59	1.03	0.62	0.81	1.05	0.78
Ru1Pd1/C		t	0.59	0.77	0.62	0.72	1.05	0.93
Pd1Ru1/C	Home-made	f	0.59	1.03	0.62	0.42	1.05	0.40
Pd1Ru1/C		t	0.59	1.00	0.62	0.48	1.05	0.48
Pd1Ru3/C	From Ru/C com	f	0.20	0.68	0.62	1.42	3.15	2.09
Pd1Ru3/C		t	0.20	0.65	0.62	1.46	3.15	2.26
Pd1Ru1/C	From Ru/C com	f	0.59	1.11	0.62	1.61	1.05	1.45
Pd1Ru1/C		t	0.59	1.20	0.62	1.65	1.05	1.38
Pd3Ru1/C	From Ru/C com	f	1.78	2.86	0.62	1.63	0.35	0.57
Pd3Ru1/C		t	1.78	2.98	0.62	1.69	0.35	0.57
Ru1Pt1/C	From Pt/C com	f	0.32	0.28	0.62	0.69	1.93	2.48
Ru1Pt1/C		t	0.32	0.33	0.62	0.30	1.93	0.91

Table 6
Atomic intensity ratios obtained by XPS for BiPt/C catalysts: calc. = calculated values on the basis of bulk composition, exp. = experimental values (retrieved from XPS quantitative analysis), f = fresh catalyst (before catalytic test), t = tested (after catalytic test)

Catalyst		Pt/C (× 100)		Bi/C (× 100)		Bi/Pt	
		Calc.	Exp.	Calc.	Exp.	Calc.	Exp.
Pt/C	f	0.32	0.35				
Pt/C	t	0.32	0.35				
Bi1Pt1/C	f	0.32	0.27	0.32	0.61	1	2.27
Bi1Pt1/C	t	0.32	0.43	0.32	0.26	1	0.61

poisoning resistance [23], in the case of Ru–Pd catalysts prepared by co-impregnation and characterised by temperature-programmed reduction (TPR) and wide-angle X-ray scattering (WAXS), where smaller Pd crystallite sizes were obtained in the presence of Ru [29], and for terephthalic acid hydropurification with carbon-supported Pd catalysts studied by XRD and electron microscopy (HREM), where the introduction of Ru increased the sintering stability and thus maintained a high dispersion of Pd even at high temperature [35].

3.4. Discussion

Given the complex reaction scheme (Fig. 1), the best way to compare the various catalysts prepared in this study is to consider the absolute value of yield in glyoxalic acid normalised with respect to the amount of active metal Pt or Pd (Y_{AGLY}/mPd,Pt) obtained at the optimum (t_{max}) (see Fig. 3). Some of these values are listed in Table 7 for commercial (com) catalysts, catalysts reported in the literature [17,18] or the catalysts described in this paper. The comparison between catalysts can thus be carried out at two levels: (i) on the position of t_{max} in time and (ii) on the value of glyoxalic acid yield and selectivity at this point. The addition of a second element to a monometallic catalyst might have an effect on one or both of these levels.

A kinetic effect on the position of t_{max} is observed when adding Bi or Ru to monometallic Pd/C or Pt/C catalysts: the amount of time required in order to reach t_{max} is clearly decreased with BiPt/C and increased with Ru–Pd catalysts. However, this is not the only effect, as the absolute value of Y_{AGLY} obtained at this time is variable (see above, comparison between Figs. 5 and 6 for Ru–Pd catalysts of different composition, giving different values of Y_{AGLY} at t_{max}). From Table 7, it is obvious that the trimetallic Bi1Pd2Ru2/C and the bimetallic Pd1Ru1/C catalysts display the best results so far, in comparison with the literature [17,18] and the other systems described in this paper. In the latter case, it is noteworthy that the value obtained (1.44 mol/g_{Pd}) is superior to that reported previously for BiPd/C catalysts (1.22 mol/g_{Pd}) [18], demonstrating the great promise of Ru as an alternative promoter for Bi, but only with a strict control of the preparation method and composition. Indeed, the Ru–Pd catalysts seem to be much more sensitive to the preparation procedure than the BiPd/C systems. This sensitivity to the preparation method had also been observed for RuPd/C catalysts used in glucose selective oxidation [22], where Ru was also found to play a promoter role. In addition, the value of 1.58 mol/g_{Pd} obtained for the trimetallic Bi1Pd2Ru2/C catalyst is not optimised, as t_{max} was not determined, but is already better than all the other systems, and better than a BiPdPt/C trimetallic system commercialised by Degussa (last line of Table 7).

The promoter role of Ru needs to be further investigated and its mechanisms elucidated, but it seems that it can be related to an effect on the Pd dispersion, in relation with the XPS results (see above). This would be in line with various reports of the literature, mentioning the role of ruthenium as a dispersing agent for Pd [23,29,35].

Table 7
Comparison of catalysts' performance in this work and in the literature [17,18] (com = commercial catalyst)

Catalyst	t_{max} (h)	$(Y_{AGLY})_{max}/m$Pd,Pt (mol/g)	Y_{AGLY}/mPd,Pt at t = 20 h (mol/g)[a]
Pt/C com	>20	0.93	
Bi1Pt1/C	5.6	1.14	
Pd/C com	>9	0.17	0.77
Pd/C home-made	–	–	0.82–0.95
Ru1Pd1/C[b]	>48	1.06	
Pd1Ru1/C[b]	>72	1.44	
Pd5Ru1/C[c]	27	0.64	
Ru3Pd1/C	–	–	0.97
Pd1Ru3/C	–	–	0.71
Bi1Pd2Ru2/C	–	–	1.58
Pt/C [17]	1.5	0.55	
Pd/C [17]	–	0.38	
Bi1Pd1/C [18]	24	1.22	
BiPdPt/C Degussa [18]	8	0.78	

[a] The positions of t_{max} were not determined for these catalysts (and therefore might be before or after 20 h).
[b] See Fig. 5.
[c] See Fig. 6.

4. Conclusion

In this paper, we have shown that alternative formulations than the previously described BiPd/C and PbPd/C catalysts [18,19] can be successfully applied to the selective oxidation of glyoxal in the liquid phase, without the problems of Pb or Bi leaching that were associated with these. The catalysts described here were based on bi-or trimetallic associations comprising Pd, Pt, Ru and/or Bi, supported on carbon. Synergetic effects were observed between some of these elements (i.e. bimetallic catalyst being more performant than each corresponding monometallic catalyst tested separately), with Bi and Ru playing promoter roles rather than being active metals for the reaction (no catalytic activity when used alone). From the results obtained, it can be concluded that the combination BiPt/C is not optimal, as it leads to a great activity (i.e. high conversions obtained at very short reaction times) but a low selectivity because of rapid over-oxidation to oxalic acid. The RuPt/C catalysts were all less active than the corresponding Pt/C. In contrast, the association Ru–Pd is much more promising, as it can give yields in glyoxalic acid (absolute value obtained at the optimum (t_{max})) that have never been obtained before. The limitations of this bimetallic association reside in greater reaction times, formic acid production and high sensitivity to the preparation method. However, it presents the great advantage of no metal leaching in solution. Finally, the trimetallic formulations seem to combine short reaction times with high glyoxalic acid yields, thanks to the additive effects of the three elements, yielding the best overall performance so far.

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