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On the role of ruthenium associated with Pd and/or Bi in carbon-supported catalysts for the partial oxidation of glucose

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Abstract

The role of ruthenium when associated with Pd and/or Bi in carbon-supported catalysts for the selective oxidation of D-glucose in aqueous phase was investigated. It was found that ruthenium does not have an activity by itself, but acts as a "promoter" for the catalytic activity of monometallic Pd/C catalysts. Catalysts containing bismuth in association with ruthenium displayed a catalytic activity only when the temperature was raised above 60 °C, but to produce essentially glucuronic and oxalic acid. When incorporated into bimetallic Pd-Bi/C catalysts, Ru was shown to exert a slightly inhibitory effect on the production of gluconic acid. In contrast with Bi, which was found to leach as in previous studies, no significant Ru leaching was observed under the reaction conditions.

Keywords: Glucose oxidation; Ruthenium; Palladium; Bismuth; Bimetallic catalysts

1. Introduction

Using renewable sources as feedstock is easily justified by increasing economical and environmental pressures on the chemical industry. In particular, carbohydrates are indicated as raw material, given their wide availability and high degree of complexity. However, few chemo-catalytic processes starting from sugars are effectively used in the chemical industry, most industrial processes making use of sugars involving fermentation or enzymatic steps. This is due to the lack of efficient and reliable catalytic methods at the industrial scale to transform "basic" carbohydrates into more valuable derivatives, the main problems being associated with the rapid deactivation of the catalysts used in the transformations. Nevertheless, it has been shown that a wide range of chemicals that might be of interest for the fine chemistry or pharmaceutical industries might be produced from sugars [1]. Hence, the need for further research in the area. In order to reduce costs and waste to a minimum, all transformations should ideally be performed catalytically, in water (the ideal "benign" medium to carry out chemical reactions), with the highest selectivity possible, and the catalysts should be recoverable and reusable.

Various researchers have investigated the catalytic oxidation of poly-ols and carbohydrates in aqueous medium using molecular oxygen or air [2–5]. The ideal catalytic system for such transformations is a precious metal such as palladium or platinum, supported on carbon. In our group, a great deal of research in recent years has been focused on the partial oxidation

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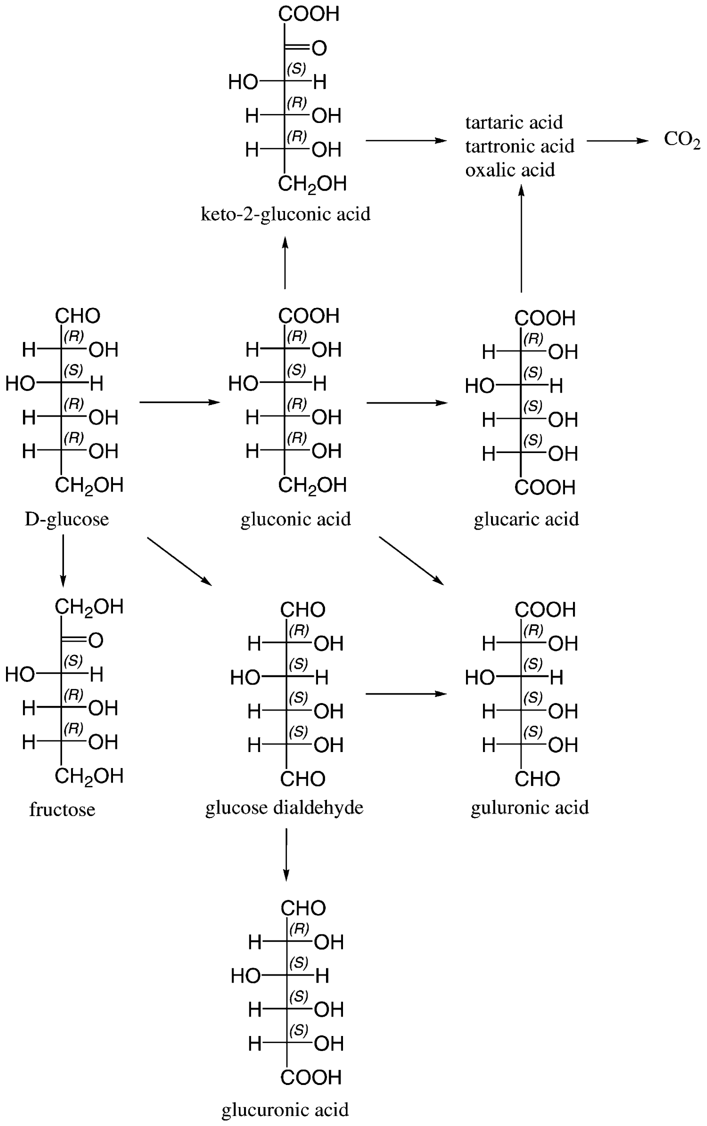
of glucose into gluconic acid, using carbon-supported Pd-Bi catalysts [6–10]. This particular transformation has been widely studied by other groups, [2–5] using Pd- or Pt-based catalysts. The interest for the reaction lies in the fact that gluconic acid is a biodegradable chelating agent and a key intermediate for foodstuffs and pharmaceuticals [11]. It is well known, from the results emanating from the various research groups working in the field, that bismuth acts as a promoter for the catalytic activity of palladium and retards the catalyst deactivation [10,12]. Some more specific aspects of the catalytic process using the Pd-Bi/C formulation have been addressed in detail in our group, such as the question of certain Pd-Bi intermetallic compounds playing a key role for the catalyst efficiency [7]. The catalytic activity was also related to the presence of Bi in the catalytic medium, most probably as a soluble glucose and/or gluconate complex. This association in solution and at the surface of the catalysts was assumed to be the key element in the overall



Scheme 1. Possible products of oxidation of D-glucose.

mechanism of the catalytic process, in relation with the systematic leaching of Bi during the operation [8,9]. In addition, the nature of the Pd coordination compound used as catalyst precursor was shown to have an influence on the catalytic activity and selectivity [13].

Here, we wish to report on the use of ruthenium as an additive for Bi and/or Pd carbon-supported catalysts for the partial oxidation of glucose in water (see Scheme 1), and on the influence of the preparation method and the nature of the Ru precursor on the catalysts performance. There have been so far few reports on the use of bimetallic heterogeneous Pd-Ru catalysts in catalytic oxidation. Catalysts prepared by the deposition of ruthenium and palladium on a variety of supports, such as alumina [14,15], silica [16,17], titania [15,18], MCM-41 [19] and carbon [20] have been reported, and were used mainly in hydrogenation applications. Some authors have investigated the use of Ru-Pd materials as electro-catalysts [21–23] and bimetallic Ru-Pd colloids stabilized by PVP polymers were used as catalysts for the selective hydrogenation of nitroaromatics to the corresponding aromatic amines [24–27]. Finally, catalysis was also performed with Pd films deposited on Ru(0 0 1) surfaces [28] or with Pd–Ru alloy membranes [29].

2. Experimental

2.1. *Preparation of the catalysts*

All the manipulations were performed on the open bench, without any precaution to exclude air. Bi(III) oxoacetate ($BiO(O_2CCH_3)$) was obtained according to a procedure described previously [6], starting from Bi_2O_3 [Janssen Chimica]. The solvents were standard laboratory grade solvents. The carbon support used in all cases is C SX+ ($S_{BET} = 750\,m^2/g$, particle size = 50–100 μm) supplied by Norit. If not specified, the catalysts were loaded with 5 wt.% of each metal. A commercial Ru (5 wt.%)/C catalyst was also purchased from Aldrich for comparison purpose.

Three different methods were used to load the metal(s) onto the carbon support. The metallic complexes used varied according to the preparation procedure and several different ruthenium precursors were envisaged in the case of method 2 (see Table 1).

2.1.1. *Method 1: co-impregnation—based on a patent by Saïto et al. [30]*

The carbon was suspended in a HCl solution of Bi(III) nitrate ($Bi(NO_3)_3{\cdot}5H_2O$) and a HCl solution of $RuCl_3$ [Johnson Matthey] was added dropwise. The metallic complexes were then reduced in situ by formalin at 80 °C.

2.1.2. *Method 2: deposition*

This method has been described previously [6]: the insoluble metallic precursors are deposited successively on the support from slurries in *n*-heptane [Acros] after sonication. Whereas Bi(III) oxoacetate and Pd(II) acetate [Acros] were always used as Bi and Pd precursors, Ru was introduced from three different precursors: Ru(III) trichloride [Janssens], Ru(III) trisacetylacetonate ($Ru(acac)_3$) [Aldrich], or triruthениumdodecacarbonyl ($Ru_3(CO)_{12}$) [Aldrich]. The catalyst is then activated by heating in a tubular oven at 500 °C for 18 h under a flow of nitrogen.

2.1.3. *Method 3: impregnation/deposition*

Ruthenium was introduced on the support by impregnation from a HCl solution of $RuCl_3$ [Johnson Matthey], and palladium was added subsequently by deposition from a suspension of Pd(II) acetate in

Table 1
Precursors used in the preparation of the catalysts

Preparation method	Bi precursor	Pd precursor	Ru precursor
Method 1: co-impregnation	$Bi(NO_3)_3{\cdot}5H_2O$	–	$RuCl_3$
Method 2: deposition	BiO(OAc)	$Pd(OAc)_2$	$RuCl_3$
	Same	Same	$Ru_3(CO)_{12}$
	Same	Same	$Ru(acac)_3$
Method 3: impregnation (Ru)/deposition (Pd)	–	$Pd(OAc)_2$	$RuCl_3$

OAc, acetate; acac, acetylacetonate (2,4-pentanedionate).

heptane as described earlier. The activation was also performed thermally at 500 °C for 18 h under a nitrogen flow.

The ruthenium precursor and method used are indicated in square brackets throughout the text, figures and tables (abbreviations used: co-impregnation = co-imp; deposition = dep; impregnation = imp; commercial = com). The metal indicated as first in the catalyst formulation was introduced first during the preparation. The catalyst Pd-$RuCl_3$/C was made by deposition of palladium(II) acetate and reduction in the tubular oven, followed by deposition of $RuCl_3$ from heptane with no additional reduction treatment, i.e. the ruthenium in that particular catalyst was exclusively present as "$RuCl_3$".

2.2. Catalytic tests

A double-wall glass reactor was equipped with a mechanical stirrer (Heidolph RZR 2051) and a device to keep the water flow in the external compartment at a constant temperature (50 °C if not specified otherwise). D-glucose (72 g) [Acros] and distilled water (400 ml) were introduced in the reactor (internal compartment), and the catalyst (0.5 g for mono- and bimetallic catalysts, 54 mg for trimetallic catalysts) was then added. Oxygen was introduced at a flow of 0.4 l/min and the stirring rate was fixed at 1000 rpm. The pH was kept constant in the range 9.25–9.50 with an automatic titration device (Metrohm, Stat Titrino 718) controlling the addition of a 5 mol/l solution of NaOH. The catalytic reactions were stopped after 4 h by interrupting the oxygen supply. The reaction medium was then filtered in order to recover the catalyst, which was washed with water, ethanol and ether and then dried in vacuo.

The catalysts before and after reaction were characterized by powder X-ray diffraction (XRD) and XPS, and the composition of the reaction medium after 4 h was determined either by HPLC or by ^{13}C NMR. The stability of the catalysts under reaction conditions was evaluated by determining the occurrence of solubilized bismuth or ruthenium by atomic absorption spectroscopy. The amount of acids produced during the catalytic reaction was deduced from the volume of NaOH consumed. When gluconic acid was the only acid formed, the yield in this product could be directly calculated from the volume of NaOH.

2.3. Instrumentation

X-ray photoelectron spectroscopy was performed on a SSX-100/206 spectrometer from Surface Science Instruments (USA) using a monochromatized Al X-ray source ($E_{K\alpha} = 1486.6$ eV). The energy scale was calibrated with respect to the Au $4f_{7/2}$ peak of a standard gold sample fixed at 83.98 eV. The binding energies were calculated with respect to the C–(C, H) component of the C 1s peak of hydrocarbon contamination fixed at 284.8 eV. The analysis was based on the following photopeaks: C 1s, Bi $4f_{7/2}$, Pd $3d_{5/2}$, Ru 3d, Ru 3p and Cl 2p. Molar fractions were calculated using peak areas normalized on the basis of acquisition parameters and sensitivity factors provided by the manufacturer. The peaks were deconvoluted by using the manufacturer S-probe least-square fitting routine with a gaussian/lorentzian ratio of 85/15 and after subtraction of a non linear baseline. The Ru 3d peak overlapping the C 1s peak, the Ru analysis was based on the Ru 3p peak, and the Ru 3d–C 1s band was decomposed by fixing the (Ru $3d_{5/2}$)/(Ru $3d_{3/2}$) ratio at 1.5. The O 1s peak was not recorded because of the overlap with the Pd $3p_{3/2}$ peak. For improving the vacuum, the samples were heated at 30 °C for several hours in the spectrometer introduction chamber before analysis.

Powder XRD was carried out on a Siemens D-5000 diffractometer, using the Cu Kα radiation ($\lambda = 154.18$ pm). The samples were dispersed on quartz monocrystals purchased from Siemens.

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

The presence of bismuth or ruthenium in the reaction media was detected by atomic absorption on a Perkin-Elmer 3110 spectrometer. The calibrations were done with standard solutions in the concentration range 2–20 mg/l.

The HPLC analyses were performed with a liquid chromatograph Perkin-Elmer series 3B coupled with UV-detector, type LC75. The reaction products were separated on a BioRad Aminex HPX-87H column thermostated at 45 °C. H_2SO_4 0.005 mol/l was used as the mobile phase at a fixed flux of 0.4 l/min. The products were detected at 200 nm. Retention times (min) under these conditions were: 8.6 for glucuronic acid, 9.6 for oxalic acid, 13.1 for glucose and gluconic acid, and 14.3 for fructose.

3. Results and discussion

Three different methods were used to prepare the ruthenium-containing catalysts. The first one was adapted from a patent from Saïto et al. [30] and involves the co-impregnation of nitrate/chloride salts of the metals on the support from an acidic solution, followed by in situ chemical reduction with formalin. The second method consists of successive depositions of the metallic precursors from slurries in *n*-heptane, followed by activation at 500 °C under N_2, while the third one is a combined impregnation/deposition procedure (impregnation of the Ru precursor from a HCl solution followed by deposition of the second metal from a suspension in heptane) followed by the same heat treatment to activate the catalyst. The metallic precursors used are summarized in Table 1.

Monometallic Ru/C and RuO_2/C catalysts were prepared by the various methods described earlier, and they all displayed very little or no catalytic activity. However, when ruthenium was added to Bi/C or Pd/C catalysts, the activity increased markedly. The performance of the Ru-Bi/C catalysts was poor at 50 °C, but we noted a temperature effect, and at 70 °C high yields of glucuronic and oxalic acids were produced directly from glucose (see Scheme 1). Unfortunately, as the activity increased, the selectivity towards a single product of oxidation decreased. The preparation method had a clear influence on the catalyst's activity (Fig. 1). The most active catalyst was the one prepared from a suspension of $RuCl_3$ in heptane. It is interesting to point out that the catalyst in which the two metals are incorporated successively from suspensions in heptane is more efficient than the one prepared by co-impregnation from the same precursors, although the overall dispersion of both metals is much higher in the latter case, as indicated by the atomic intensity ratios Ru/C and Bi/C measured by XPS (Table 4). In the best catalyst, the experimental Ru/Bi ratio is the closest to the theoretical value calculated from the bulk composition.

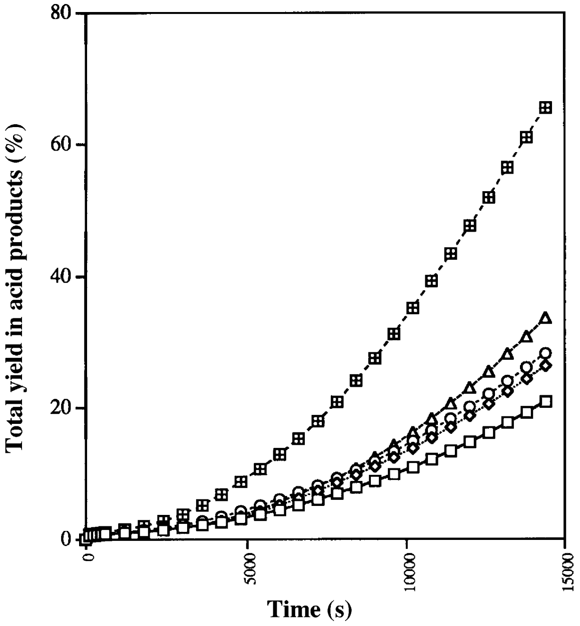


Fig. 1. Catalytic performances of bimetallic Ru-Bi/C catalysts at 70 °C: total yield in acid products vs. reaction time. (□) No catalyst, (◇) carbon alone, (○) Ru[$Ru_3(CO)_{12}$, dep]-Bi/C, (△) Ru[$RuCl_3$, co-imp]-Bi/C, (⊞) Ru[$RuCl_3$, dep]-Bi/C.

Bimetallic Ru-Pd/C catalysts, on the other hand, were active and selective for the oxidation of glucose to gluconic acid and more so than any monometallic Ru/C or Pd/C catalyst (Table 2), indicating a synergetic effect between the two metals. The only by-product detected by ^{13}C NMR was fructose, so the yield in gluconic acid could directly be deduced from the volume of NaOH added by the automatic titration device attached to the catalytic reactor. It should be noted that fructose is produced homogeneously, as a result of local increases in pH in the reaction mixture. We also tested the Ru-Pd/C materials before reduction treatment, and, as expected, they did not display any catalytic activity. Similarly, when ruthenium was introduced as RuO_2, the activity was cancelled. The influences of the preparation method and metallic precursors were investigated, and it was found that better results are obtained when Pd is incorporated before Ru (compare catalysts #4 and 5 in Table 2). The most active catalysts were prepared from $RuCl_3$ by methods 2 or 3 (deposition or impregnation/deposition procedures—see catalysts #2, 4 and 6 in Table 2). Powder XRD characterization of the catalysts demonstrated that some residual $RuCl_3$ was

Table 2
^{13}C NMR analysis of the reaction media after catalytic tests

	Catalyst[a]	Glucose conversion, X (%)	Yield		Selectivity in gluconic acid, S_{GLU} (%)
			Gluconic acid, Y_{GLU} (%)	Fructose, Y_{FRU} (%)	
1	Ru[com]/C	12.0	0.6	11.4	4.7
2	Pd-Ru[Ru(acac)$_3$, dep]/C	9.0	5.4	3.6	59.9
3	Pd-RuCl$_3$/C	7.7	1.3	6.4	16.4
4	Pd-Ru[RuCl$_3$, dep]/C	27.6	23.2	4.4	84.0
5	Ru[RuCl$_3$, dep]-Pd/C	14.5	3.4	11.1	23.5
6	Ru[RuCl$_3$, imp]-Pd/C	28.6	26.0	2.6	90.9
7	Pd-Ru[RuCl$_3$, dep]/C (Ru = 10 wt.%)	21.6	16.7	4.9	77.2
8	Pd-Ru[RuCl$_3$, dep]/C (Ru = 2.5 wt.%)	17.9	13.1	4.8	72.9
9	Pd-Ru[RuCl$_3$, dep]/C (Ru = 1.7 wt.%)	19.8	15.9	3.9	80.0
10	Ru[com]-Pd-Bi (2:2:1)/C (4.5 wt.% in each metal)	44.1	36.2	7.9	81.9
11	Ru[RuCl$_3$, dep]-Pd-Bi (2:2:1)/C (4.5 wt.% in each metal)	38.2	33.5	4.7	87.7
12	Ru[RuCl$_3$, dep]-Pd-Bi (1:1:1)/C (2.6 wt.% Ru and Pd, 5 wt.% Bi)	26.0	21.5	4.5	82.6

[a] 5 wt.% in each metal, unless otherwise stated.

present on the activated catalysts prepared from this precursor, and chlorine was also detected by XPS. This points towards a possible promoting role of Cl$^-$, an argument that has been used in the literature in several instances [31].

We then prepared a whole series of Pd-Ru/C catalysts from RuCl$_3$ by deposition with different ratios of the two metals. In a first experiment, the amount of palladium was kept constant at 5 wt.%, and the amount of ruthenium was varied between 0 and 10 wt.% (Fig. 2). The catalytic activity was found to be strongly affected by the amount of ruthenium present: the best catalyst in terms of activity contained the two metals in a 1:1 (w/w) ratio (molar ratio Ru/Pd = 1.05). The selectivity remained essentially constant throughout the whole series (Table 2). In a second set of experiments, the total amount of metals (Ru+Pd) was kept constant at 10 wt.%, but the ratio Pd:Ru was varied (Fig. 3). The influence of the Pd-Ru composition was strongly marked, the best results being obtained with catalysts containing the two metals in a 1:1 or 1:2 (w/w) ratio. When the Ru/Pd ratio was increased further (Pd:Ru 1:3 w/w ratio), the catalytic activity decreased markedly and even felt below that of a monometallic Pd/C catalyst. Both sets of results obtained when varying the palladium to ruthenium ratio are summarized in Fig. 4,

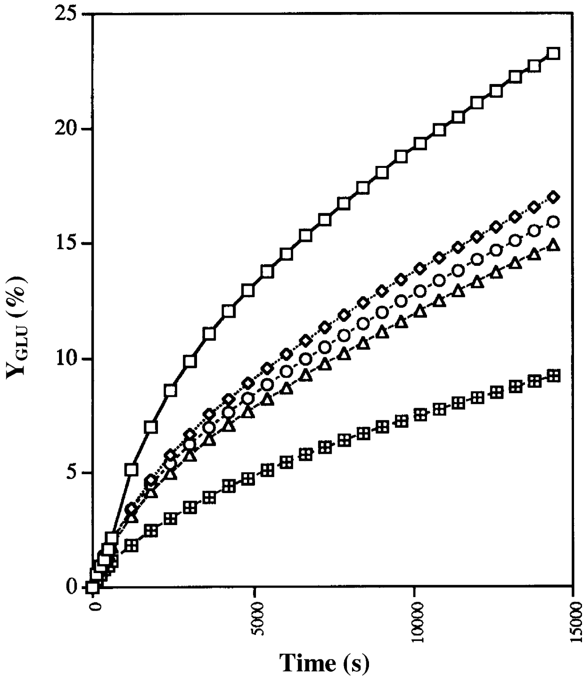


Fig. 2. Catalytic performances of Pd-Ru[RuCl$_3$, dep]/C catalysts (Pd = 5 wt.% and Ru = 0–10 wt.%) at 50 °C: yield in gluconic acid vs. reaction time. Ru wt.% (molar ratio Ru/Pd): (⊞) 0% (0), (○) 1.7% (0.35), (△) 2.5% (0.53), (□) 5% (1.05), (◇) 10% (2.1).

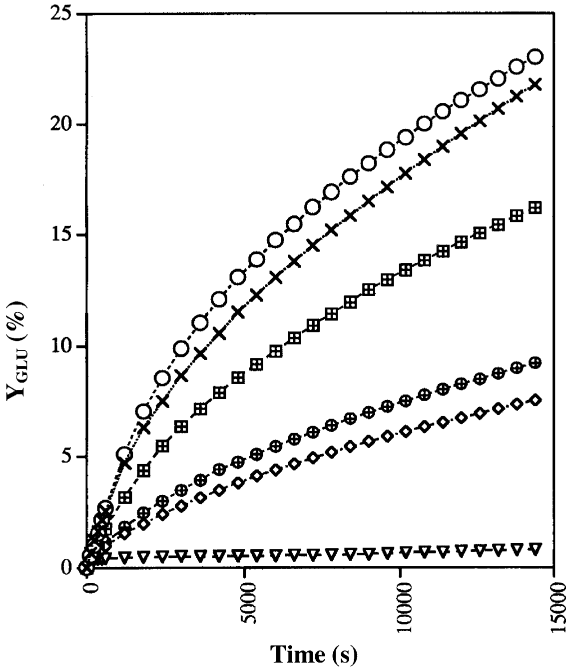


Fig. 3. Catalytic performances of Pd-Ru[$RuCl_3$, dep]/C catalysts (Pd + Ru = 10 wt.%) at 50 °C: yield in gluconic acid vs. reaction time. Catalysts (molar ratio Ru/Pd): (⊕) Pd/C, (▽) Ru/C, (⊞) Pd2-Ru1/C (0.53), (×) Pd1-Ru1/C (1.05), (○) Pd1-Ru2/C (2.10), (◇) Pd1-Ru3/C (3.16).

Table 3
Normalized catalytic performance of bimetallic Pd-Ru/C and trimetallic Pd-Ru-Bi/C catalysts

Catalyst	Y_{GLU}/m_{cat} (%/mg)	Y_{GLU}/m_{Pd} (%/mg)
Previous results [6,8]		
Pd/C	0.02	0.41
Pd-Bi/C	0.65–1.07	15.3–21.5
Pd-Pt-Bi/C (Degussa)	0.77	19.2
This work		
Ru-Pd/C	0.05	1.0
Ru-Pd-Bi/C 1:1:1 (mol)	0.40	15.3
Ru-Pd-Bi/C 2:2:1 (mol)	0.62–0.67	13.7–14.8

$[Glucose]_0 = 1$ mol/l, $T = 50$ °C, $t = 4$ h, kinetic regime, identical experimental conditions.

from which the maximum activity corresponding to a Ru/Pd (w/w) ratio between 1 and 2 can clearly be seen. The promoting influence of ruthenium in bimetallic Pd-Ru/C catalysts appears more significantly when comparing the catalytic performances after their normalization with respect to the amount of catalyst or Pd metal involved (Table 3). The bimetallic Pd-Ru catalyst is about 2.5 times more efficient than the monometallic Pd/C catalyst, but this promotion effect of Ru is definitely smaller than that of bismuth. A promoting role has already been attributed to ruthenium

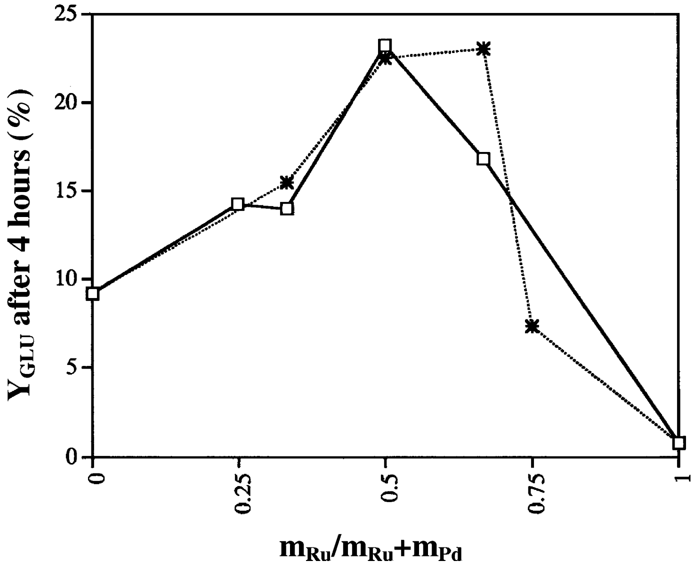


Fig. 4. Catalytic performances of bimetallic Pd-Ru/C catalysts at 50 °C: yield in gluconic acid after 4 h vs. catalyst composition. (□) Pd = 5 wt.%, Ru = x wt.%; (✱) Pd + Ru = 10 wt.%.

in other catalytic studies reported in the literature [32] in applications such as Fischer–Tropsch, hydrodesulphurization of dibenzothiophene, hydrocarbonylation of methanol, and electrooxidation of CO. In particular, the synergistic effects observed in the liquid phase hydrogenation of benzene with Ru-Pd catalysts were interpreted in terms of dilution of Ru ensembles by Pd atoms, increasing thereby the resistance to self-poisoning of the active surface [17]. Similarly, but in a reverse way, TPR and wide-angle X-ray scattering experiments on carbon-supported Pd-Ru catalysts concluded on the role of ruthenium as dispersing agent to increase the Pd dispersion in Pd/C catalysts [19]. When referring to the surface characteristics of our bimetallic Pd-Ru/C catalysts (Table 4), no clear correlation between the catalytic performance and the metal dispersion, as measured by the XPS Ru/C or Pd/C atomic intensity ratios, could be detected. In the fresh catalysts, the Ru/Pd ratio was always smaller than the theoretical value, indicating thereby a relative surface enrichment in palladium. This ratio decreased in the used catalysts, while the Ru/C ratio remained approximately constant. This suggests that Ru leaching is unsignificant, as expected from data already available in the literature [33] and that the change in Ru/Pd ratio reveals surface restructuration (further Pd enrichment), in line with the fact that the surface energy of Pd is lower than that of Ru [34].

Trimetallic Ru-Pd-Bi/C catalysts were also prepared and tested for the same reaction. The activity was drastically increased, and only 54 mg of catalyst were used (rather than 0.5 g in all previous cases) in order to avoid mass transfer limitations. All the trimetallic catalysts were more active and selective towards gluconic acid than any of their mono- or bimetallic analogues (catalysts #10–12 in Table 2). The ratio of metals was varied, and the best results were obtained with a catalyst containing ruthenium, palladium and bismuth in a 2:2:1 molar ratio, which was prepared by successive depositions from suspensions in heptane (Fig. 5). It should be noted that the trimetallic catalyst prepared from the commercial Ru/C catalyst was better at short reaction times, but deactivates more rapidly. However, when the normalized activities are taken into account (Table 3), it appears that Ru has a slight inhibitory effect on the production of gluconic acid by Pd-Bi/C catalysts. This has probably to be related to the fact that completely different promotion mechanisms are involved, as suggested by the observation of other reaction products, like glucuronic acid, when Ru-Bi associations are used. A “poison effect”, as far as we know, has nearly never been associated with ruthenium in the literature.

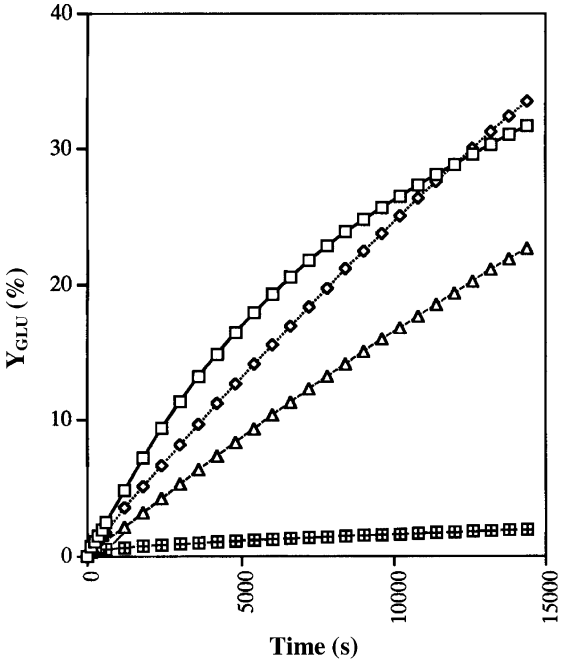


Fig. 5. Catalytic performances of trimetallic Ru-Pd-Bi/C catalysts (m_{cat} = 54 mg) at 50 °C: yield in gluconic acid vs. reaction time. (□) Ru[com]-Pd-Bi (2:2:1)/C (4.5 wt.% in each metal), (◇) Ru[$RuCl_3$, dep]-Pd-Bi (2:2:1)/C (4.5 wt.% in each metal), (△) Ru[$RuCl_3$, dep]-Pd-Bi (1:1:1)/C (2.6 wt.% Ru and Pd, 5 wt.% Bi), (⊞) Ru[$RuCl_3$, imp]-Pd/C (5 wt.% in each metal).

All the catalysts mentioned in this study were characterized by powder XRD, as well as XPS. The combination of these tools helped in identifying the nature of the active phase, and e.g. the Pd-Ru/C catalysts were found to contain ruthenium metal in association with palladium metal. Some information about the microstructure of the materials could also be gained, and the metal introduced in second position was found to be present in greater concentration at the surface (covering the first one). Atomic absorption was used to study the composition of the reaction media, in order to detect the presence of metal in solution after test (Table 5). In line with many previous investigations on Pd-Bi/C systems [6–10], bismuth was found to leach from the Ru-Bi/C and Ru-Pd-Bi/C catalysts

Table 4
XPS results: atomic intensity ratios

Catalyst[a]	Ru/C (×100)		Pd/C (×100)		Bi/C (×100)		Ru/Pd		Ru/Bi	
	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental	Theoretical	Experimental
Ru[RuCl$_3$, dep]-Bi/C	0.66	0.43	–	–	0.32	0.25	–	–	2.07	1.72
Ru[RuCl$_3$, co-imp]-Bi/C	0.66	2.45	–	–	0.32	1.75	–	–	2.07	1.40
Ru[Ru$_3$(CO)$_{12}$, dep]-Bi/C	0.66	0.96	–	–	0.32	1.05	–	–	2.07	0.91
Pd-Ru[RuCl$_3$, dep]/C 5 wt.% Pd, 0–10 wt.% Ru										
5 wt.% Ru	0.66	0.70	0.63	0.90	–	–	1.05	0.77	–	–
10 wt.% Ru	1.40	0.78	0.66	0.84	–	–	2.10	0.93	–	–
1.7 wt.% Ru	0.21	0.36	0.60	1.22	–	–	0.35	0.29	–	–
2.5 wt.% Ru	0.32	0.25	0.61	0.95	–	–	0.53	0.27	–	–
Ru[RuCl$_3$, dep]-Pd/C	0.66	0.71	0.63	0.76	–	–	1.05	0.93	–	–
Pd-Ru[com]/C	0.62	0.57	0.59	0.65	–	–	1.05	0.88	–	–
Pd-Ru[RuCl$_3$, dep]/C 10 wt.% (Pd + Ru)										
Pd:Ru (w/w) 1:2	0.88	0.34	0.42	0.16	–	–	2.10	2.31	–	–
(after catalysis)		(0.44)		(0.52)				(0.85)		
Pd:Ru (w/w) 1:1	0.66	0.70	0.63	0.76	–	–	1.05	0.77	–	–
Pd:Ru (w/w) 2:1	0.44	0.52	0.84	1.00	–	–	0.53	0.52	–	–
(after catalysis)		(0.45)		(1.30)				(0.34)		
Pd:Ru (w/w) 1:3	0.99	1.11	0.31	0.54	–	–	3.16	2.04	–	–
(after catalysis)		(0.96)		(0.59)				(1.64)		
Pd/C	–	–	0.63	0.93	–	–	–	–	–	–
Ru[com]/C	0.62	0.69	–	–	–	–	–	–	–	–
Ru[RuCl$_3$, dep]/C	0.62	0.33	–	–	–	–	–	–	–	–

[a] Within each subsection, the catalysts have been listed in the order corresponding to their catalytic performance (most active first).

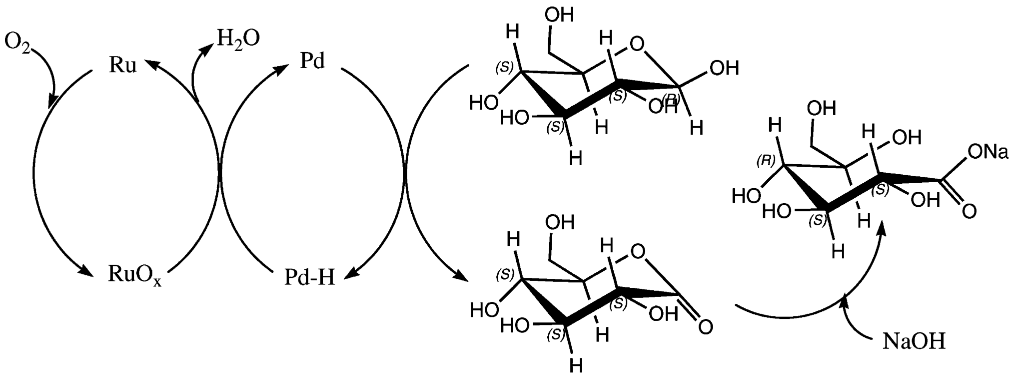
Table 5
Bi and Ru losses from Ru-based catalysts in the reaction media (from atomic absorption spectroscopy measurements)

Catalyst	Catalytic reaction temperature (°C)	Bi losses (%)	Ru losses (%)
Ru[com]/C	50	–	0.7
Ru[com]-Bi/C	50	2.7	<0.2
Ru[$RuCl_3$, dep]-Pd/C (1:1)	50	–	<0.2
Bi-Ru[$RuCl_3$, co-imp]/C	50	0.4	<0.2
	60	2	0.3
	70	11	0.7
Ru[$Ru_3(CO)_{12}$, dep]-Bi/C	50	8	0.5
	70	13	1.3
Ru[$RuCl_3$, dep]-Bi/C	50	16	<0.2
	60	63	1.3
Ru[$RuCl_3$, dep]-Pd-Bi (2:2:1)/C (4.5 wt.% in each metal)	50	16	<0.2
Ru[$RuCl_3$, dep]-Pd-Bi (1:1:1)/C (2.6 wt.% Ru and Pd, 5 wt.% Bi)	50	32	<0.2

during the reaction. The amount of Bi losses detected fluctuated in function of the preparation method or metallic precursor(s) used and increased with the temperature of the catalytic tests. On the other hand, ruthenium leaching was observed to be negligible in most cases and slightly in excess of 1% only at 60 °C or above (Table 5).

4. Conclusion

Monometallic Ru/C catalysts were found to be inactive for the oxidation of glucose. Bimetallic Ru-Bi/C catalysts also display a poor activity below 60 °C. They are able to oxidize glucose at higher temperature, but with low selectivity towards a single product and increased bismuth leaching. It is interesting to note, however, that the main product formed was glucuronic rather than gluconic acid, indicating that ruthenium could be used in order to direct the selectivity in a different direction than with palladium. The Pd-Ru/C catalysts, on the other hand, were active and selective for the transformation of glucose to gluconic acid (even at temperatures as low as 50 °C), and especially when the two metals were present in a one-to-one ratio. This points towards a role for ruthenium as a "promoter" rather than an active metal per se. The catalytic cycle shown in Scheme 2 can be suggested for the reaction. Various trimetallic Ru-Pd-Bi/C catalysts were also tested, and the best overall performance was



Scheme 2. Suggested catalytic cycle for the oxidation of glucose into gluconic acid with the Ru-Pd/C catalysts.

obtained with a catalyst containing the three metals in a 2:2:1 molar ratio. The results reported here are far from ideal in terms of conversion, especially given that yields over 99% have been reported previously for the same reaction. However, the identification of ruthenium as a new "promoter" for Pd(-Bi)/C catalysts should open new perspectives to modulate the activity/selectivity of catalytic selective oxidations involving alcohols, aldehydes or carboxylic acid transformations. This is especially true given the occurrence of bismuth losses in the reaction media when using a Pd-Bi/C formulation, suggesting that an alternative promoter such as ruthenium, which was demonstrably stable under the reaction conditions, would be advantageous.

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References

[1] (a) F. Giffhorn, Appl. Microbiol. Biotechnol. 54 (2000) 727;
(b) D.K. Allen, B.Y. Tao, J. Surfactants Detergents 2 (1999) 383;
(c) H. Guzmanmaldonado, O. Paredeslopez, Crit. Rev. Food Sci. Nutr. 35 (1995) 373.
[2] T. Mallat, A. Baiker, Catal. Today 19 (1994) 247.
[3] H. van Bekkum, Stud. Surf. Sci. Catal. 121 (1999) 117.
[4] M. Besson, P. Gallezot, Catal. Today 57 (2000) 127.
[5] M. Besson, P. Gallezot, in: R.A. Sheldon, H. van Bekkum (Eds.), Fine Chemicals through Heterogeneous Catalysis, Wiley, New York, 2001, p. 491, 507.
[6] M. Wenkin, R. Touillaux, P. Ruiz, B. Delmon, M. Devillers, Appl. Catal. A: Gen. 148 (1996) 181.
[7] M. Wenkin, C. Renard, P. Ruiz, B. Delmon, M. Devillers, Stud. Surf. Sci. Catal. 108 (1997) 391.
[8] M. Wenkin, C. Renard, P. Ruiz, B. Delmon, M. Devillers, Stud. Surf. Sci. Catal. 110 (1997) 517.
[9] M. Wenkin, P. Ruiz, B. Delmon, M. Devillers, J. Mol. Catal. A: Chem. 180 (2002) 141.
[10] M. Wenkin, M. Devillers, P. Ruiz, B. Delmon, Stud. Surf. Sci. Catal. 139 (2001) 295.
[11] (a) H. Hustede, H.J. Haberstroh, E. Schinzing, in: Ullmann's Encyclopedia of Industrial Chemistry, Vol. A12, VCH, Weinheim, 1989, p. 449;
(b) K. Buckholz, B. Godelmann, Biotechnol. Bioeng. 23 (1978) 1201.
[12] M. Besson, F. Lahmer, P. Gallezot, P. Fuertes, G. Flèche, J. Catal. 152 (1995) 116.
[13] S. Hermans, M. Wenkin, M. Devillers, J. Mol. Catal. A: Chem. 136 (1998) 59.
[14] C.K. Ryu, M.W. Ryoo, I.S. Ryu, S.K. Kang, Catal. Today 47 (1999) 141.
[15] M. Koussathana, D. Vamvouka, H. Economou, X. Verykios, Appl. Catal. 77 (1991) 283.
[16] G. Cordoba, J.L.G. Fierro, A. Lopezgaona, N. Martin, M. Viniegra, J. Mol. Catal. A: Chem. 96 (1995) 155.
[17] M. Viniegra, V. Arroyo, R. Gomez, Appl. Catal. 44 (1988) 1.
[18] M. Koussathana, N. Vamvouka, X. Verykios, Int. J. Energ. Res. 18 (1994) 243.
[19] R. Raja, G. Sankar, S. Hermans, D. S. Shephard, S. Bromley, J.M. Thomas, B.F.G. Johnson, T. Maschmeyer, Chem. Commun. (1999) 1571.
[20] F. Pinna, M. Signoretto, G. Strukul, A. Benedetti, M. Malentacchi, N. Pernicone, J. Catal. 155 (1995) 166.
[21] R. Pattabiraman, Bull. Electrochem. 15 (1999) 394.
[22] N. Furuya, T. Yamazaki, M. Shibata, J. Electroanal. Chem. 431 (1997) 39.
[23] C.Z. He, H.R. Kunz, J.M. Fenton, J. Electrochem. Soc. 144 (1997) 970.
[24] M.H. Liu, W.Y. Yu, H.F. Liu, J.M. Zheng, J. Colloid Interface Sci. 214 (1999) 231.
[25] J. Gao, F.D. Wang, S.J. Liao, D.R. Yu, React. Kinet. Catal. Lett. 64 (1998) 351.
[26] Z.K. Yu, S.J. Liao, Y. Xu, B. Yang, D.R. Yu, J. Mol. Catal. A: Chem. 120 (1997) 247.
[27] Z.K. Yu, S.J. Liao, Y. Xu, B. Yang, D.R. Yu, J. Chem. Soc., Chem. Commun. (1995) 1155.
[28] J. Storm, R.M. Lambert, N. Memmel, J. Onsgaard, E. Taglauer, Surf. Sci. 436 (1999) 259.
[29] T.S. Farris, J.N. Armor, Appl. Catal. A: Gen. 96 (1993) 25.
[30] H. Saïto, S. Ohnaka, S. Fukuda, European Patent EP 0142725 B1 (1987).
[31] (a) B. Bachiller-Baeza, A. Guerrero-Ruiz, I. Rodríguez-Ramos, Appl. Catal. A: Gen. 192 (2000) 289;
(b) S.M. Aboul-Fotouh, A.K. Aboul-Gheit, Appl. Catal. A: Gen. 208 (2001) 55;
(c) P.A. Gravil, H. Toulhoat, Surf. Sci. 430 (1999) 192;
(d) R. Burch, S. Chalker, P. Loader, J.M. Thomas, W. Ueda, Appl. Catal. A: Gen. 82 (1992) 77.
[32] (a) R. Oukaci, A.H. Singleton, J.G. Goodwin, Appl. Catal. A: Gen. 186 (1999) 129;
(b) R. Navarro, B. Pawelec, J.L.G. Fierro, P.T. Vasudevan, Appl. Catal. A: Gen. 148 (1996) 23;
(c) S. Bischoff, A. Weigt, K. Fujimoto, B. Lucke, J. Mol. Catal. A: Chem. 95 (1995) 259;
(d) R. Ianniello, V.M. Schmidt, U. Stimming, J. Stumper, A. Wallau, Electrochim. Acta 39 (1994) 1863.

[33] (a) A. Pintar, M. Besson, P. Gallezot, Appl. Catal. B: Environ. 31 (2001) 275;
(b) A. Pintar, M. Besson, P. Gallezot, Appl. Catal. B: Environ. 30 (2001) 123;
(c) K. van Gorp, E. Boerman, C.V. Cavenaghi, P.H. Berben, Catal. Today 52 (1999) 349;
(d)P. Gallezot, N. Nicolaus, G. Fleche, P. Fuertes, A. Perrard, J. Catal. 180 (1998) 51;
(e) P. Gallezot, S. Chaumet, A. Perrard, P. Isnard, J. Catal. 168 (1997) 104.

[34] A.R. Miedema, Z. Metallk. 69 (1978) 287.