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Au–Pd/C catalysts for glyoxal and glucose selective oxidations

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ABSTRACT

A series of Au–Pd/C catalysts were prepared on an activated carbon named SX PLUS (SX+) by fixing the pH of impregnation in aqueous phase at an optimal value for maximizing the interactions between metals and surface. This bimetallic association leads to highly active catalysts in the oxidation of glyoxal into glyoxalic acid and of glucose into gluconic acid, with the activity correlated to high surface Pd/C ratios measured by XPS and the presence of small metallic Pd particles, even if gold was present as big crystallites. A cooperative effect between the two metals was evidenced on the yield in carboxylic acids in both reactions, which is believed to arise from an interface between the two metals even if they are mostly present as separated phases. The incorporation of Au on Pd rather than the opposite and the concomitant activation of both metals influence positively the catalytic performance. The use of $NaBH_4$ as activating agent allowed the most active Au–Pd/C catalyst to be obtained, with similar performances to the best bimetallic Bi–Pd/C catalyst so far but without any metal leaching.

1. Introduction

The recent surge of interest in catalysis by gold [1–4] has led researchers to investigate the effects of adding other metals to gold within supported catalysts. As a result, there are many reactions with potential industrial application where combinations of gold with a platinum group metal have shown some advantage [5–12]. The group of Prati mainly has demonstrated that bimetallic Pd–Au catalysts supported on carbon can be applied to oxidation reactions in liquid phase [13–21]. Although it is known that the activity of dispersed metal catalysts depends strongly on both the preparation method and the characteristics of the support [22], the synthetic techniques for bimetallic materials supported on carbon are not yet well developed. In particular, stabilizing gold in nanoparticulate form on carbon has proven to be more difficult than on other supports. Prati et al. have managed to obtain carbon-supported bimetallic nanoparticles containing both gold and palladium using colloidal procedures. Here we would like to extend a procedure applied for the successful preparation of Pd/C catalysts [23] to the synthesis of bimetallic Pd–Au/C systems. This procedure implies prior determination in aqueous solution of the optimal pH for adsorption of the metallic precursor on the carbon support before preparing the catalyst by fixing the pH at this optimal value. Very small Pd nanoparticles supported on carbon were obtained, which displayed high activity in selective oxidation [23]. Here, the preparation of Au(5 wt.%)–Pd(5 wt.%)/C catalysts is carried out by investigating first the adsorption of Au and Pd species in aqueous phase on activated carbon SX PLUS, followed by reduction to obtain active bimetallic Au–Pd/C catalysts. The optimal pH for adsorption of Au and Pd on SX+ active carbon has been determined via a detailed study reported elsewhere [24]. The present paper focuses on the investigation of the catalytic properties of the materials obtained by in situ chemical reduction of the samples prepared by this adsorption method.

Two catalytic transformations in the aqueous phase were investigated: the selective oxidation of glyoxal into glyoxalic acid and of glucose into gluconic acid. The two acids produced play an important role as starting chemicals in the preparation of foodstuffs [25,26], pharmaceuticals [25–27] or agro-chemicals [28]. Gluconic acid is industrially prepared by enzymatic oxidation of glucose [25]. Numerous research groups have extensively studied glucose oxidation using Pd- or Pt-based catalysts [29–32], and in particular, our group has addressed specific aspects of the catalytic process using M–Pd/C formulations (M = Bi, Ru) [33–36]. Recently, some investigations have been focused on the preparation of gold catalysts to oxidize glucose [37–41] and these materials have displayed good performance. Various processes are also known for the preparation of glyoxalic acid. However, each of these methods presents some serious disadvantages, causing glyoxalic acid to be an expensive fine chemical. It is prepared in the industry by stoichiometric oxidation of glyoxal with nitric acid, but in spite of a high yield, large amounts of NO_x are generated in this process. Other methods exist but are not commercial [42–46] and are limited by the complexity in separating glyoxalic acid from the reaction mixture. Gallezot et al. have shown that heterogeneous Pt and Pd carbon-supported catalysts can be used in aqueous solution to overcome these draw-

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Table 1
Bimetallic M_2–M_1/C catalysts prepared.

Catalyst	Name	Mass percentage (%)		Synthetic pH values[a]	
		M_1	M_2	n°1	n°2
1	$Pd(OAc)_2$-Au/C[b]	4.7	5	4	10
2	$Pd(OAc)_2$-Au/C[b]	4.7	5	5	10
3	$Pd(OAc)_2$-$HAuCl_4$/C	5	5	10	10
4	$HAuCl_4$-$Pd(OAc)_2$/C	5	5	9	9
5	$HAuCl_4$-$Pd(OAc)_2$/C	5	5	10	10
6	$HAuCl_4$-$Pd(OAc)_2$/C[c]	5	5	10	10
7	$HAuCl_4$-Pd/C[b]	4.7	5	5	10
8	$HAuCl_4$-Pd/C[b]	4.7	5	10	10

[a] See Section 2 for definition of pH n°1 and 2.
[b] Preliminary reduction of M_1.
[c] Catalyst activated with $NaBH_4$, all others with formalin.

backs [47]. Since then, promoted M–Pd/C catalysts (M = Bi, Pb, Ru, Au) have been developed in our laboratory and were shown to be more active and more selective than monometallic formulations for this reaction [48–53]. As far as we know, Pd–Au/C catalysts have not yet been applied to the oxidation of glyoxal into glyoxalic acid outside our group [53].

2. Experimental

2.1. Starting materials

An activated carbon, named SX PLUS (SX+) supplied by NORIT (abbreviated as C in this paper, $S_{BET} \approx 900\,m^2\,g^{-1}$, particle size = 50–100 μm, total acidity = 32.0 mmol/100 g) was used as support. The palladium and gold precursors were palladium (II) acetate ($Pd(OAc)_2$, Aldrich, 98%) and hydrogen tetrachloroaurate (III) ($HAuCl_4 \cdot 3H_2O$, Aldrich, 99.9 + %).

2.2. Catalysts synthesis

Au(5 wt.%)–Pd(5 wt.%)/C catalysts were synthesized by impregnation in aqueous solution using the pH values where maximum adsorption occurs as determined previously [24], and maintaining it throughout all synthetic steps. Two procedures were used: a one-pot procedure and a two-steps procedure with prior reduction of the first metal introduced before impregnating the second one. Table 1 gives the characteristics of the bimetallic catalysts envisaged. In the one-pot procedure, an aqueous solution of the first metal precursor (0.1 g of $HAuCl_4 \cdot 3H_2O$ or 0.106 g of $Pd(OAc)_2$ solubilized with nitric acid) at fixed pH (pH n°1) was added to an aqueous suspension of 0.9 g carbon pre-conditioned at the same pH value (pH n°1) in order to get a final volume of 100 mL, and the suspension was agitated for 24 h. Then, 50 mL of a solution containing the second metal precursor pre-conditioned at the same pH value (pH n°1) was added and stirred for an additional 24 h. Depending on the incorporation order, these bimetallic catalysts will be noted $Pd(OAc)_2$-$HAuCl_4$/C or $HAuCl_4$-$Pd(OAc)_2$/C. In the two-steps procedure, the second metal precursor (0.1 g of $HAuCl_4 \cdot 3H_2O$ or 0.1055 g of $Pd(OAc)_2$) was solubilized in 50 mL water before being stabilized at a given pH (pH n°1) and transferred to an aqueous suspension of 0.95 g monometallic sample (pre-reduced Pd(5 wt.%)/C or Au(5 wt.%)/C sample pre-conditioned at the same pH value (pH n°1) and stirred during 24 h). Again, depending on the incorporation order, these bimetallic catalysts will be noted as $Pd(OAc)_2$-Au/C or $HAuCl_4$-Pd/C. The adsorption filtrates containing potentially non-adsorbed Pd and/or Au were analyzed by atomic absorption spectrometry, but no metal losses were found. All catalysts were activated in situ at 80 °C, after addition of a base (NaOH) to reach a higher pH value (pH n°2), by chemical reduction with either 1 mL of formalin (formaldehyde 37 wt.% aqueous solution) or $NaBH_4$. The activated catalysts were recovered by filtration and dried. Corresponding monometallic catalysts were also prepared by the same synthetic method, for comparison.

2.3. Physico-chemical characterization techniques

The solid samples were characterized by X-ray photoelectron spectroscopy (XPS), CO chemisorption, Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM) and X-ray powder diffraction (XRD).

X-ray photoelectron spectroscopy (XPS) was performed on an SSI-X-probe (SSX-100/206) spectrometer from Fisons. The samples were stuck onto small troughs with double-sided adhesive tape, and then placed on an insulating home-made ceramic carousel with a nickel grid positioned 3 mm above the sample surface, to avoid differential charging effects: a floodgun set at 8 eV was used for charge stabilisation. The energy scale was calibrated by taking the Au $4f_{7/2}$ binding energy at 84 eV. The C_{1s} binding energy of carbon ($\underline{C}$–C,H) set at 284.8 eV was used as internal standard value. Data treatment was performed with the CasaXPS program (Casa Software Ltd). The analyses of palladium and gold were based on the Pd 3d and Au 4f photopeaks and the following constraints were used for decomposition: intensity ratios $I(\mathrm{Pd}\ 3d_{5/2})/I(\mathrm{Pd}\ 3d_{3/2}) = 1.5$ and $I(\mathrm{Au}\ 4f_{7/2})/I(\mathrm{Au}\ 4f_{5/2}) = 1.33$, FWHM ratios = 1, $\Delta(\mathrm{Pd}\ 3d_{5/2} - \mathrm{Pd}\ 3d_{3/2}) = 5.26$ eV and $\Delta(\mathrm{Au}\ 4f_{7/2} - \mathrm{Au}\ 4f_{5/2}) = 3.67$ eV.

CO chemisorption measurements were carried out on an ASAP 2000 apparatus from Micromeritics. The samples (~100 mg) were first submitted to a pretreatment at 100 °C under He for 30 min followed by 10 min at 100 °C under hydrogen. The catalyst was then reduced during 2 h at 350 °C under H_2. The Pd dispersion was calculated by considering a surface Pd:CO stoichiometry equal to 1, and by considering that gold does not interfere (i.e. does not chemisorb CO under the present conditions).

SEM analyses were performed on a field effect gun Digitan Scanning Electron Microscope (DSM 982 Gemini from LEO), equipped with an energy dispersive X-ray system (EDAX Phoenix equipped with a CDU LEAP detector). The powder samples were pressed onto conducting double-face adhesive tape fixed onto 0.5” aluminum specimen stubs from Agar Scientific.

TEM images were obtained with a LEO 922 OMEGA Energy Filter Transmission Electron Microscope at 200 kV. The samples were suspended in hexane under ultrasonic treatment, then allowed to settle to discard the biggest particles. A drop of the supernatant was deposited on a holey carbon film supported on a copper grid, which was dried overnight under vacuum at room temperature, before introduction in the microscope.

XRD analyses were performed with a D5000 SIEMENS diffractometer equipped with a copper source ($\lambda_{K\alpha} = 154.18$ pm). The samples were supported on quartz monocrystals. The crystalline phases detected were identified by reference to the JCPDS database.

The quantification of Pd and Au in solutions of synthesis filtrates and catalytic tests was performed by atomic absorption analysis, using a Perkin-Elmer 3110 spectrometer equipped with an air–acetylene flame atomizer. Calibration curves (from 1 to 10 mg/L for Pd and from 1 to 15 mg/L for Au) were realized with standard solutions obtained by dilution of commercial palladium (1006 μg/mL, Acros) and gold (1003 μg/mL, Aldrich) solutions.

2.4. Catalytic tests

All catalytic tests were performed in a thermostatized double-walled glass reactor equipped with an automatic titration device for pH control, as described previously [48,50,54]. The experimental conditions used for glyoxal and glucose oxidation are summarized in Table 2. All reaction filtrates were analyzed by atomic absorption

Table 2
Experimental conditions used for glyoxal and glucose oxidation.

Parameter	Glyoxal	Glucose
Starting substrate solution	400 mL glyoxal 0.1 mol L^{-1}	72 g in 400 mL
Temperature	38 °C	50 °C
Stirring rate	1000 rpm	1000 rpm
pH	7.2	9.25
Basic solution to fix the pH	Na_2CO_3 0.3 mol L^{-1}	NaOH 5 mol L^{-1}
Oxidant	0.4 L min^{-1} air flow	0.4 L min^{-1} O_2 flow
Mass of catalyst	100 mg	100 mg
Duration of catalytic test	20 h	20 h

spectrometry but no metal leaching was found.

Many products might be formed during glyoxal oxidation besides glyoxalic acid: glycolic acid by Cannizzaro dismutation and oxalic and formic acids by over-oxidation (Fig. 1), as described previously [49,51,53]. The reaction products from glyoxal oxidation were quantified by HPLC, and the results are expressed in terms of yield in each different product (Y, %), corrected conversion (X^*, %) and corrected selectivity (S^*, %) [49,51,53,54]:

$$Y_{\text{Product}} = \frac{C_{\text{Product}}}{C_{\text{GLY}}}$$

where C is the concentration and 'Product' is either AGLY, OX, GLYC, or FORM, see Fig. 1 for abbreviations.

$$X^*_{\text{GLY}} = Y_{\text{AGLY}} + Y_{\text{OX}} + \left(\frac{Y_{\text{FORM}}}{2}\right)$$

$$S^*_{\text{AGLY}} = \left(\frac{Y_{\text{AGLY}}}{X^*_{\text{GLY}}}\right) 100$$

The "corrected" parameters do not take into account the production of glycolic acid, which depends only on the pH. The catalysts were thus compared on the basis of the yield in glyoxalic acid and selectivity in glyoxalic acid.

The composition of the reaction mixture arising from glucose oxidation was determined by ^{13}C NMR analysis [34]. The results are expressed in terms of conversion (X, %), yields (Y, %) and selectivity (S, %). Although the formation of numerous secondary products is possible (Fig. 2), the only carboxylic acid detected in the reaction media was gluconic acid, together with small amounts of fructose produced by glucose isomerization. Hence, the catalysts were compared on the basis of the yield in gluconic acid directly calculated from NaOH consumption.

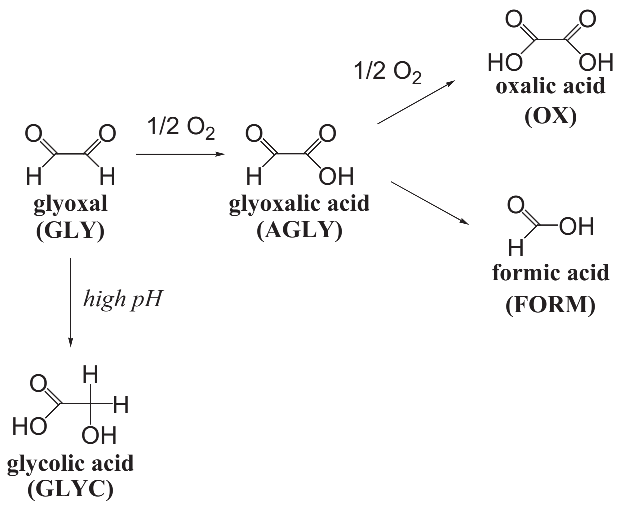

Fig. 1. Catalytic oxidation of glyoxal: possible by-products.

3. Results

Bimetallic Au(5 wt.%)–Pd(5 wt.%)/C catalysts were synthesized by controlling the pH of the solutions during all synthesis steps, in order to keep it within the maximum adsorption range, determined as previously described [24]. Briefly, adsorption curves (%metal adsorbed vs. pH) were established by bringing into contact samples of carbon pre-conditioned at fixed pH values with aqueous solutions of metal precursors at the same fixed pH. The amount of non-adsorbed metal in solution – after filtration – was determined after 24 h stirring. The solid samples collected were characterized by electron microscopy and X-ray photoelectron spectroscopy. The experimental pH values for adsorption of Au and Pd on C were selected to correspond to the pH range where the highest Pd/C and Au/C atomic intensity ratios were identified by XPS on the solid samples (see Supporting Information, Annex A). After adsorption, the AuPd/C samples were then reduced to give the actual bimetallic catalysts. Two reducing agents in aqueous phase were evaluated: formalin and $NaBH_4$.

3.1. Characterization of activated catalysts

In order to determine their microstructure, the catalysts were characterized after activation by XPS, CO chemisorption, SEM coupled with EDXS, TEM coupled with EDXS and XRD.

In the case of the monometallic Au/C catalysts, the Au/C surface atomic ratios determined by XPS (Table 3) were similar to the values calculated on the basis of the bulk composition (0.0032). The Au/C ratio was slightly higher when activating with formalin rather than $NaBH_4$. Only metallic gold was observed on the surface.

The experimental Pd/C atomic intensity ratios measured by XPS for the activated AuPd/C catalysts were superior to the values calculated on the basis of the bulk composition (Table 3), suggesting high concentration, probably in a well-dispersed form, of Pd on the surface. Only metallic palladium was detected. In opposite, the Au/C ratios were similar (if not lower) to the values calculated on the basis of the bulk composition, except for catalyst 6 activated with $NaBH_4$ which presents the highest Au/C surface ratio. Again, the oxidation state observed for gold on the surface was Au^0. These observations for the bimetallic catalysts are similar to the observations made with the corresponding monometallic samples taken separately.

The palladium dispersion at the surface of the catalysts was obtained by CO chemisorption (Table 3). It was moderate to high (up to 22%). No linear correlation between the Pd/C ratios determined by XPS and the percentage of accessible Pd atoms determined by CO chemisorption was observed. However, the measure of Pd dispersion carried out here by CO chemisorption is questionable for two reasons: (i) it includes a high temperature treatment under H_2 and might thus not be representative of the samples activated in aqueous solution, and (ii) we disregarded the presence of Au which might interfere.

AuPd/C catalysts were examined by SEM (Fig. 3). The SEM images obtained for catalyst 1 and catalyst 8 (Fig. 3(a) and (e)) show, on the one hand, a homogeneous distribution of small particles, which sizes were on average comprised between 10 and 50 nm, and on the other hand, big particles with sizes up to 150 nm. Fig. 3(b) and (c) shows electron micrographs for catalyst 3 and 5 respectively, which reveal small particles covering the carbon surface but not in a homogeneous manner. The pictures obtained by SEM for catalyst 6 (Fig. 3(d)) show a precipitate covering the surface. The EDXS analyses within the electron microscope revealed that the big particles were mainly gold while the smaller were most probably palladium. The precipitate, in the case of catalyst 6, was rich in palladium. The general trend that gold forms big particles is in line with the XPS results: the low surface Au/C ratios

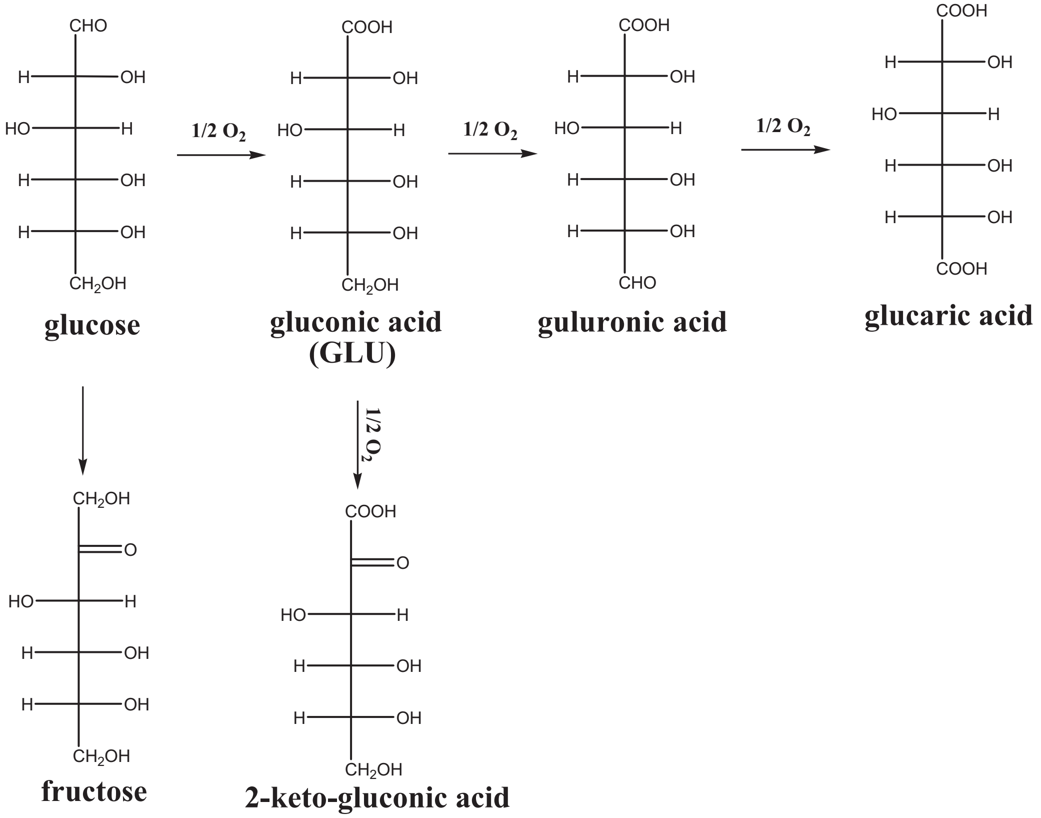

Fig. 2. Catalytic oxidation of glucose: possible by-products.

can be interpreted in terms of agglomerates, while the high Pd/C ratios are related to finer particles much better dispersed on the surface.

The same catalysts were also examined by TEM to determine the sizes of the smallest particles (Fig. 4). The images obtained for catalysts 1 ($Pd(OAc)_2$-Au/C, Fig. 4(a)) and 8 ($HAuCl_4$-Pd/C, Fig. 4(d)), which have been prepared in two steps, show a homogeneous distribution of very small particles of 4 nm and 2 nm in sizes, respectively. The images obtained for catalysts 3 ($Pd(OAc)_2$-$HAuCl_4$/C, Fig. 4(b)) and 5 ($HAuCl_4$-$Pd(OAc)_2$/C, Fig. 4(c)), prepared in one step, display bigger particles of variable sizes ranging from 4 nm to 15 nm. TEM images obtained for catalyst 6 ($HAuCl_4$-$Pd(OAc)_2$/C activated with $NaBH_4$, Fig. 4(e)–(f)) also reveal a distribution of sizes between 4 nm and 25 nm. The analysis by EDXS of the smallest particles showed that they are made of Pd, while the biggest are constituted of gold (see Supporting Information, Annex B).

The bimetallic catalysts have also been characterized by powder XRD before their use in catalytic tests. Gold metal phase was detected in all catalysts, while palladium could not be observed. Fig. 5 shows a typical diffractogram obtained in this study. This confirms the presence of big gold particles together with small Pd particles in the bimetallic materials prepared here.

3.2. Catalytic properties in glyoxal oxidation

The catalytic results in glyoxal oxidation obtained with the bimetallic Au–Pd/C catalysts studied in this work and the corresponding monometallic Au/C materials are displayed in Table 4. The first observation is that the monometallic Au/C catalysts are totally inactive while all bimetallic catalysts are efficient (X^*_{GLY} = 18.7–37.6%) in this oxidation reaction. Moreover, the activity is sensitive to the metals incorporation order and the synthetic

Table 3
CO chemisorption and XPS results before catalytic tests.

Catalyst	Name	Pd/C (X 100)		Au/C (X 100)		CO chemisorption
		Calc.	Exp.	Calc.	Exp.	Pd dispersion (%)
A[a]	Au/C	–	–	0.32	0.86	–
B[b]	Au/C	–	–	0.32	0.34	–
1	$Pd(OAc)_2$-Au/C	0.62	2.27	0.32	0.07	21.8
2	$Pd(OAc)_2$-Au/C	0.62	3.50	0.32	0.20	n.d.
3	$Pd(OAc)_2$-$HAuCl_4$/C	0.63	3.49	0.34	0.26	6.9
4	$HAuCl_4$-$Pd(OAc)_2$/C	0.63	4.10	0.34	0.39	14.6
5	$HAuCl_4$-$Pd(OAc)_2$/C	0.63	3.77	0.34	0.36	8.8
6[b]	$HAuCl_4$-$Pd(OAc)_2$/C	0.63	6.39	0.34	1.09	6.6
7	$HAuCl_4$-Pd/C	0.59	1.32	0.34	0.24	n.d.
8	$HAuCl_4$-Pd/C	0.59	1.71	0.34	0.72	18.4

[a] Sample described in Ref. [24].
[b] Catalyst activated with $NaBH_4$, all others with formalin.

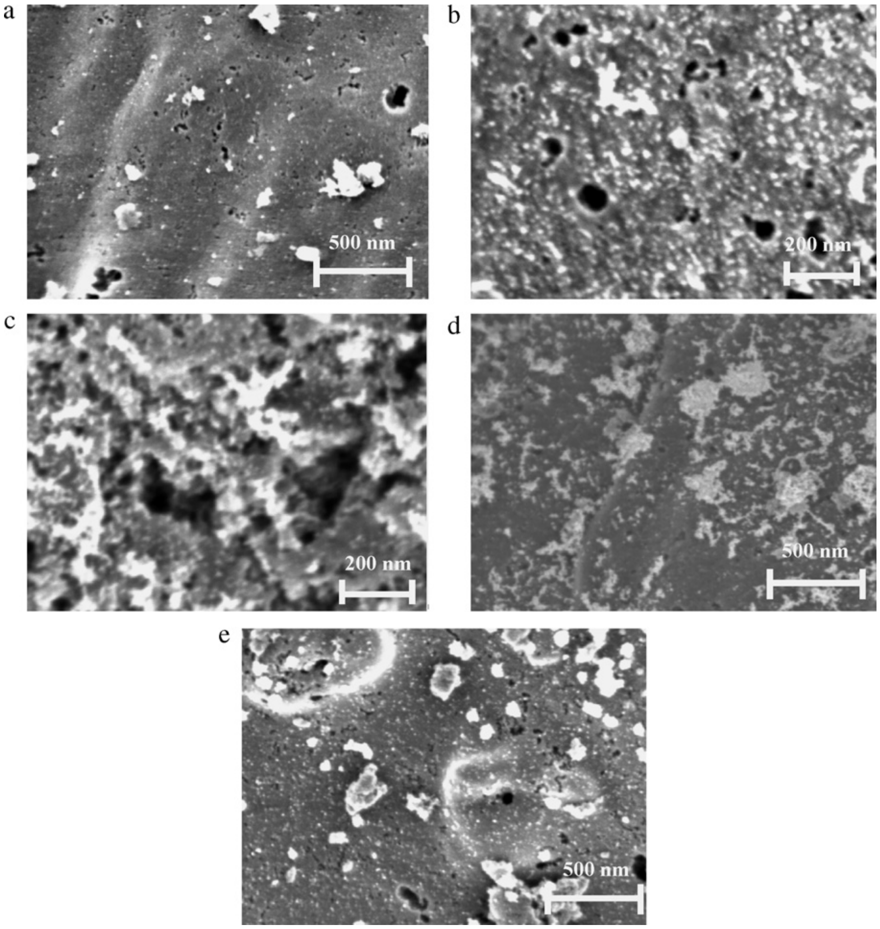

Fig. 3. SEM images obtained for Au–Pd/C catalysts: (a) catalyst 1 ($Pd(OAc)_2$-Au/C) (X 50 000), (b) catalyst 3 ($Pd(OAc)_2$-$HAuCl_4$/C) (X 100 000), (c) catalyst 5 ($HAuCl_4$-$Pd(OAc)_2$/C) (X 100 000), (d) catalyst 6 ($HAuCl_4$-$Pd(OAc)_2$/C activated with $NaBH_4$) (X 50 000), and (e) catalyst 8 ($HAuCl_4$-Pd/C) (X 50 000).

procedure. The materials giving the highest yields in glyoxalic acid are catalysts 4–6, prepared by adsorption of $Pd(OAc)_2$ in first position and by the one-pot procedure. If we compare catalysts 5 and 6 prepared in the same manner using the same pH values during all synthesis steps but activated with two different agents, we observe that the latter (activated with $NaBH_4$) is the most selective in glyoxalic acid ($S^*_{AGLY} = 94\%$) due to the low yields in oxalic and formic acids. The catalysts activated with formalin give selectivities of about 70%. In all cases, no Pd or Au leaching were found in the reaction medium.

Fig. 6 shows a comparison of the catalytic results obtained for the best Au–Pd/C materials obtained in this work (catalysts 5 and 6) and their corresponding monometallic Pd/C catalysts, which were the most efficient up to now [23,24]. It is obvious that the Au–Pd/C catalysts are more efficient than their monometallic counterparts, demonstrating that gold plays a promoter role for Pd in this reaction even in the form of big particles. Formalin as activating agent was giving a better selectivity in glyoxalic acid compared to $NaBH_4$ for Pd/C, but it is the opposite with the bimetallic Au–Pd/C materials.

3.3. Catalytic properties in glucose oxidation

Representative Au/C and Pd/C catalysts have been tested in glucose oxidation and the results are illustrated in Fig. 7. The two Au/C catalysts show no catalytic activity under the selected conditions, but the Pd/C materials present a yield of ~15% in gluconic acid

Table 4
Catalytic results in glyoxal oxidation.

Catalyst	Name	Y_{AGLY} (%)	Y_{OX} (%)	Y_{FORM} (%)	X^*_{GLY} (%)	S^*_{AGLY} (%)
A[a]	Au/C	0.0	0.0	0.0	0.0	–
B[b]	Au/C	0.0	0.0	0.0	0.0	–
1	$Pd(OAc)_2$-Au/C	17.0	2.6	4.0	21.6	79
2	$Pd(OAc)_2$-Au/C	13.9	1.8	5.9	18.7	74
3	$Pd(OAc)_2$-$HAuCl_4$/C	15.7	2.7	3.1	20.0	78
4	$HAuCl_4$-$Pd(OAc)_2$/C	24.6	4.5	6.3	32.2	76
5	$HAuCl_4$-$Pd(OAc)_2$/C	25.4	9.5	5.5	37.6	68
6[b]	$HAuCl_4$-$Pd(OAc)_2$/C	20.0	2.0	2.5	21.2	94
7	$HAuCl_4$-Pd/C	13.6	1.8	6.7	18.8	64
8	$HAuCl_4$-Pd/C	15.5	2.2	6.0	20.7	75

[a] Sample described in Ref. [24].
[b] Catalyst activated with $NaBH_4$, all others by formalin
Reaction conditions: 400 mL glyoxal 0.1 mol L^{-1}, 38 °C, pH 7.2, 0.4 L min^{-1} air flow, 100 mg catalyst, 20 h.

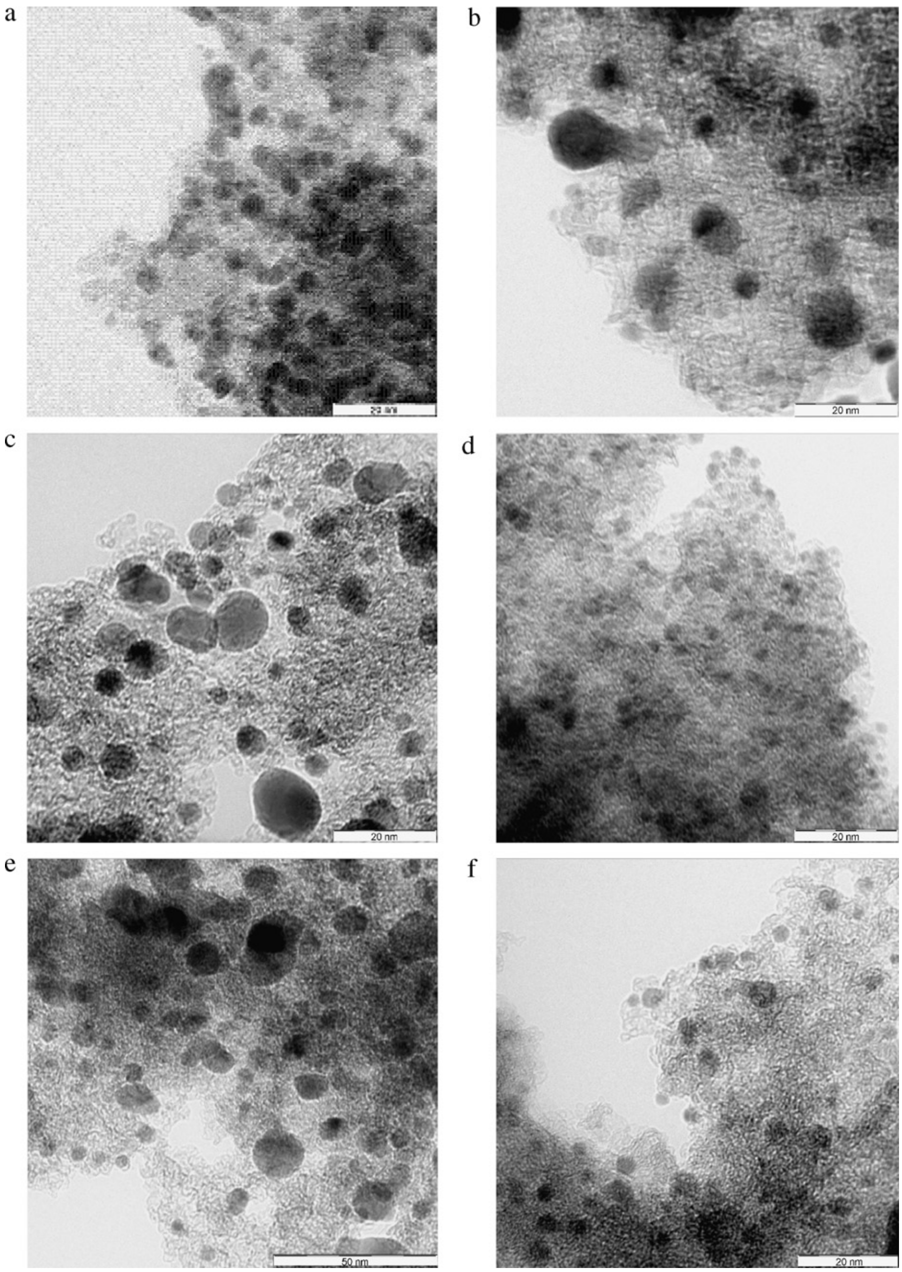

Fig. 4. TEM images of Au–Pd/C catalysts: (a) catalyst 1 ($Pd(OAc)_2$-Au/C), (b) catalyst 3 ($Pd(OAc)_2$-$HAuCl_4$/C), (c) catalyst 5 ($HAuCl_4$-$Pd(OAc)_2$/C), (d) catalyst 8 ($HAuCl_4$-Pd/C), and (e) and (f) catalyst 6 ($HAuCl_4$-$Pd(OAc)_2$/C activated with $NaBH_4$).

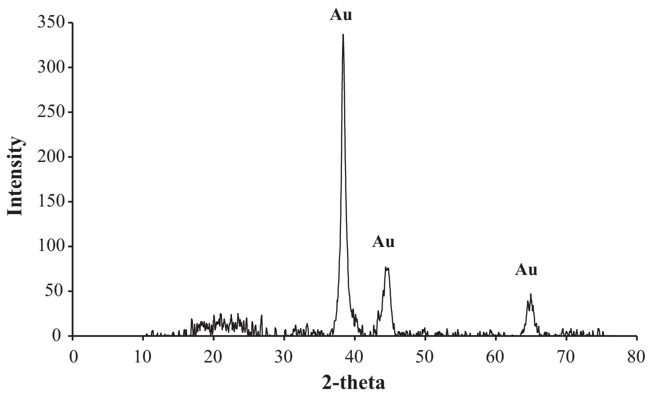

Fig. 5. A typical XRD diffractogram for AuPd/C catalysts (obtained for catalyst 8).

after 20 h, with a superior activity for the catalyst activated with formalin, as in glyoxal oxidation. Fig. 8 shows the catalytic performance obtained with some AuPd/C catalysts. It clearly appears that the bimetallic catalysts are very active in glucose oxidation. Again, the catalysts prepared by the one-pot procedure by adsorption of $Pd(OAc)_2$ followed by $HAuCl_4$ are more efficient (catalysts 5 and 6) than in the reverse order and much more efficient than when pre-reducing one of the metals before introducing the second. Like in glyoxal oxidation, $NaBH_4$ gives better results than formalin as reducing agent. The catalytic performances of catalysts 5 and 6 are compared with that of the corresponding Pd/C materials in Fig. 9. A synergetic effect between the two metals on the yield in gluconic acid is clearly observed. In order to better illustrate this bimetallic effect, a catalytic test was performed with a physical mixture of the two best monometallic Au/C and Pd/C catalysts in equal amounts. It gave a yield equivalent to 41% after 20 h, which is not as good

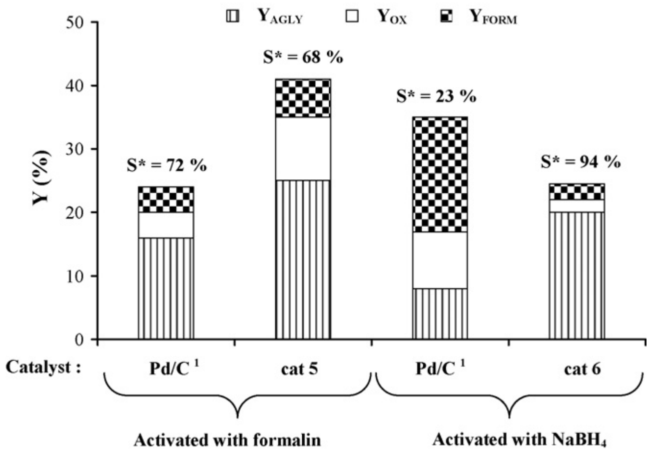

Fig. 6. Comparison of catalytic results in glyoxal oxidation for Pd(5 wt.%)/C and Au(5 wt.%)–Pd(5 wt.%)/C materials (see Section 2 for definition of *Y* and *S**). [1] Results taken from Ref. [23]. See Table 2 for experimental catalytic testing conditions.

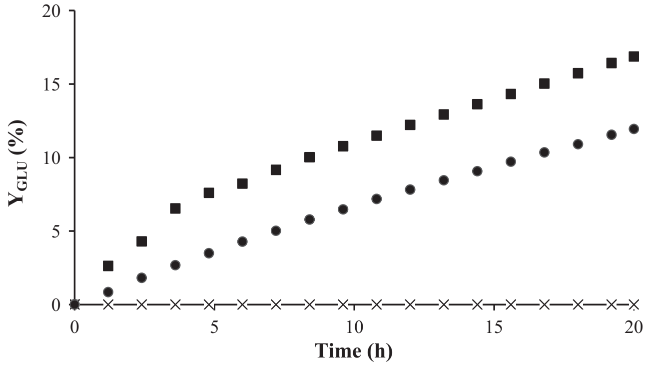

Fig. 7. Catalytic results obtained with monometallic Au/C and Pd/C catalysts in glucose oxidation: (■) Pd/C (Pd(OAc)$_2$/C activated with formalin), (●) Pd/C (Pd(OAc)$_2$/C activated with NaBH$_4$), and (×) Au/C (HAuCl$_4$/C activated with formalin [24] or with NaBH$_4$). See Table 2 for experimental catalytic testing conditions.

as with the bimetallic catalysts prepared in one step, but similar to the materials prepared in two steps.

Moreover, the ^{13}C NMR analyses of the catalytic filtrates showed that gluconic acid was the only carboxylic acid generated in the reaction. The only side-product detected was fructose (with a yield lower than 4%), demonstrating an excellent selectivity. In addition, no metal leaching was observed in the reaction filtrates.

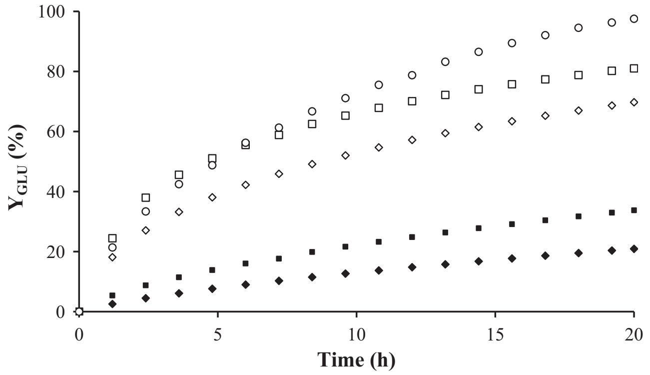

Fig. 8. Catalytic results obtained with bimetallic catalysts in glucose oxidation: (♦) catalyst 1 (Pd(OAc)$_2$-Au/C), (◊) catalyst 3 (Pd(OAc)$_2$-HAuCl$_4$/C), (□) catalyst 5 (HAuCl$_4$-Pd(OAc)$_2$/C), (○) catalyst 6 (HAuCl$_4$-Pd(OAc)$_2$/C activated with NaBH$_4$), and (■) catalyst 8 (HAuCl$_4$-Pd/C). See Table 2 for experimental catalytic testing conditions.

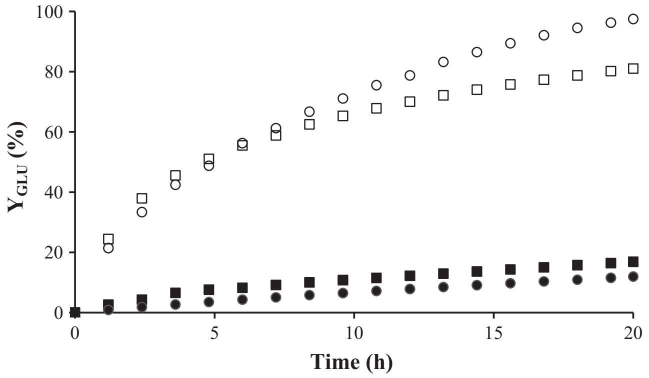

Fig. 9. Comparison of catalytic results for Pd(5 wt.%)/C and Au(5 wt.%)–Pd(5 wt.%)/C materials in glucose oxidation: (■) Pd/C (Pd(OAc)$_2$/C activated with formalin), (●) Pd/C (Pd(OAc)$_2$/C activated with NaBH$_4$), (□) catalyst 5 (HAuCl$_4$-Pd(OAc)$_2$/C activated with formalin), and (○) catalyst 6 (HAuCl$_4$-Pd(OAc)$_2$/C activated with NaBH$_4$). See Table 2 for experimental catalytic testing conditions.

The comparison between these catalytic results and the most performant Bi(5 wt.%)–Pd(5 wt.%)/C catalyst [34–36,54,55] (named Ac.PdBi/C$_{SX+}$ in Ref. [29] and prepared by deposition of carboxylate precursors on the same carbon SX+ support) shows that the bimetallic materials described here could constitute a good alternative to overcome the problem of dissolution of promoter element encountered with Bi-based systems.

4. Discussion

A first observation arises from the fact that all Au/C catalysts prepared here were totally inactive in glyoxal or glucose oxidation. This catalytic inactivity in glucose oxidation is surprising knowing the catalytic results of gold supported on titania [39], alumina [37,38] or carbon [40] prepared from gold colloids. This must be due to the small sizes of gold particles that are necessary to obtain an activity for this metal. Indeed, XPS characterization of the Au/C catalysts, showing low surface Au/C ratios, suggests Au agglomeration, and SEM images reveal big particles. This indicates that the adsorption method that had been successful for preparing Pd/C catalysts [23] is not appropriate to prepare Au/C catalysts.

In contrast, the Au–Pd/C catalysts prepared in this study give performances superior to their monometallic Pd/C analogues, and are obviously more active than the Au/C materials, demonstrating a cooperative effect between the two metals. However, the characterization data seem to indicate in the bimetallic catalysts a juxtaposition of characteristics arising independently from the two monometallic systems. Indeed, XPS reveals weak Au/C and very high Pd/C surface ratios, and metallic Pd on the surface. XRD characterizations showed only metallic gold in all catalysts, while SEM and TEM coupled with EDXS showed the presence of big Au particles and small Pd particles. The catalytic test carried out with a physical mixture of two monometallic catalysts gave results similar to the cases where the bimetallic catalysts were prepared from pre-reduced monometallic ones.

Another interesting observation is that the trends observed in glyoxal oxidation are also true in glucose oxidation. These two reactions must therefore have similar requirements in terms of active sites. The first straightforward conclusion is that these two reactions require an active metal (here Pd) in the form of small and highly dispersed particles in a reduced form at the surface. This has been shown before [58], and it demonstrated that liquid-phase oxidations such as those carried out here proceed through a dehydrogenation mechanism. Here, the catalysts displaying the highest experimental Pd/C atomic intensity ratios give the best catalytic activity in glyoxal and glucose oxidations. However, no quantitative correlation could be found between the Pd/C ratios determined by XPS, the Pd dispersion measured by CO chemisorption and the yields in glyoxalic or gluconic acids. These observations suggest that high activities are related, on the one hand, to an important degree of Pd reduction, and, on the other hand, to high Pd surface concentration. The reactions being carried out in water, which is highly demanding in terms of diffusion, especially with a hydrophobic support such as carbon (knowing in the present case that it is highly microporous), the trends observed are maybe not only linked to a dispersion effect, but also to the accessibility of the active metal that needs to be located on the external surface.

Regarding the bimetallic effect, SEM characterization coupled with EDXS indicated that the least active catalysts in the two reactions (catalysts 1 and 8 prepared as $Pd(OAc)_2$-Au/C and $HAuCl_4$-Pd/C respectively) displayed both small Pd particles and big Au particles, separated from each other. TEM showed that the Pd particles were homogeneous in terms of sizes and distribution and very small (<5 nm). The preparation procedure explains this microstructure as one metal has been reduced before incorporating the second one in both cases. The more active bimetallic materials display either a homogeneous distribution of smaller Pd and Au particles on the support (catalysts 3 and 5 prepared as $Pd(OAc)_2$-$HAuCl_4$/C and $HAuCl_4$-$Pd(OAc)_2$/C respectively), or a precipitate covering the carbon surface (catalyst 6 prepared as $HAuCl_4$-$Pd(OAc)_2$/C and activated with $NaBH_4$). TEM examination of the finest particles in these samples revealed a broader distribution of particles sizes centered on 10 nm. In these cases, both metals have been reduced concomitantly, and the occurrence of alloying/interfacing must be higher. It appears thus that the bimetallic materials are not just an addition of two independent monometallic systems but that the cooperative effect observed must be due to bimetallic active sites. Indeed, when carrying out a test with a physical mixture of two monometallic catalysts, these best results could not be attained. Alloying in the best bimetallic catalysts could not be unraveled by XRD or microscopy here, but the presence of Au in the form of big separated particles is probably a waste and only Au atoms in contact with Pd play a role. Prati et al. have shown that a Pd–Au/C catalyst containing exclusively bimetallic particles is more active that catalysts containing segregated metals [18]. Moreover, highly dispersed Pd sites in contact with Au are suggested to be the active sites [56]. Hutchings and co-workers argue that Au acts as an electronic promoter for Pd [57]. This has to be related to Pd–Bi/C systems, where Mallat and Baiker showed that Bi plays its promoter role when located on the Pd surface [58]. Here, the incorporation order of the two metals also plays a role, with incorporating Au in second position (thus giving it a chance to cover Pd) giving better results.

Finally, we must point out that the bimetallic material activated with $NaBH_4$ displayed the highest XPS Pd/C and Au/C ratios, a precipitate covering the carbon surface, and was the most selective catalyst in the transformation of glyoxal into glyoxalic acid, and the most active in the oxidation of glucose. So, although this activating agent decreased the selectivity in glyoxalic acid for monometallic Pd/C catalysts, it seems to improve the catalytic performance in the bimetallic formulations. TEM characterization showed that $NaBH_4$ allowed the formation of smaller Pd particles than formalin, related to higher Pd/C surface ratio, for monometallic Pd/C samples [23]. For Au also, the bimetallic AuPd/C sample activated with $NaBH_4$ displays the highest Au surface ratio. Traces of residues from $NaBH_4$, such as boron, could not be ruled out and might also play a role in improving the catalytic results obtained with this activation agent.

5. Conclusions

In this work, we have shown that Au–Pd/C catalysts prepared on SX+ activated carbon by an adsorption method based on maximizing the interactions between the metal precursors and the carbonaceous support in aqueous phase are very active in liquid phase glyoxal and glucose selective oxidations. The obtained catalysts give performances superior to the corresponding monometallic Pd/C and Au/C materials, and similar to the most performant bimetallic Bi–Pd/C catalyst so far, but without any metal leaching. The Au–Pd/C catalysts are characterized by high Pd/C surface ratios and by a total degree of Pd reduction. Moreover, the high activity is connected to the presence of small Pd particles. However, gold is present in the form of big particles, which makes the monometallic Au/C materials inactive. The bimetallic cooperative effect is explained by the presence of small amounts of gold in contact with palladium. Indeed, the synergetic effect seems to require an interface between the two metals to take place. In consequence, the incorporation of Au on Pd rather than the opposite and the concomitant activation of both metals influence positively the catalytic performance. The use of $NaBH_4$ as activating agent allowed the best Au–Pd/C catalyst both in glucose and in glyoxal oxidation to be obtained.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.apcata.2011.01.019.

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