Catalysis Today xxx (2014) xxx-xxx



Contents lists available at ScienceDirect

### Catalysis Today



journal homepage: www.elsevier.com/locate/cattod

# The effect of the metal precursor-reduction with hydrogen on a library of bimetallic Pd-Au and Pd-Pt catalysts for the direct synthesis of $H_2O_2$

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#### ARTICLE INFO

Article history: Received 27 November 2013 Received in revised form 30 January 2014 Accepted 13 February 2014 Available online xxx

*Keywords:* Bimetallic Pd-Pt catalysts Pd-Au catalysts H<sub>2</sub>O<sub>2</sub> Direct Synthesis

#### ABSTRACT

Two sets of bimetallic Pd-Pt (Pd: 1.0; Pt: 0.25-1.0%, w/w) and Pd-Au (Pd: 1.0; Au: 0.25-1.0%, w/w) catalysts have been used, with no added promoter, in the catalytic direct synthesis (CDS) of hydrogen peroxide from its elements at  $2 \degree C$  with a  $CO_2/O_2/H_2$  mixture (72/25.5/2.5%, respectively). The catalysts were supported on the commercial macroreticular ion-exchange resin Lewatit K2621 and were obtained from the reduction with H<sub>2</sub> of ion-exchanged cationic precursors at 5 bar and at 60 °C. The addition of Pt or Au to Pd produced an increase of the initial overall catalytic activity in comparison with monometallic Pd with both the second metals, but with Pt the increase was much higher than with Au. Moreover, the addition of 0.25% (w/w) Pt, or more, invariably made all the Pd-Pt catalysts less selective with respect to Pd alone. In the case of Au, by contrast, the addition of 0.25% w/w produced an increase, albeit small, of the selectivity. As the  $result, the most active and productive Pd-Pt catalyst was 1Pd025PtK2621 with 1891 mol_{(H_2)} mol_{(Pd+Pt)}^{-1} h^{-1} h^{-1}$ initially consumed, 1875  $mol_{(Pd+Pt)} mol_{(Pd+Pt)}^{-1} h^{-1}$  initially produced, a 45% selectivity towards  $H_2O_2$  at 50% conversion of  $H_2$ . In the case of the Pd-Au bimetallic catalysts, 1Pd025AuK2621 was the best one, with 1184  $mol_{(H_2)} mol_{(Pd+Pt)}^{-1} h^{-1}$  initially consumed, 739  $mol_{(H_2O_2)} mol_{(Pd+Pt)}^{-1} h^{-1}$  initially produced, a 55% selectivity towards H<sub>2</sub>O<sub>2</sub> at 50% conversion of H<sub>2</sub>. Although the characterization of the Pd-Pt and Pd-Au catalysts with TEM showed that the morphology of the nanostructured metal phases in the Pd-Pt and Pd-Au catalysts was very different from each family to the other, no clear correlation between the size of the nanoparticles and their distribution and the catalytic performance was apparent. These catalysts were also generally different, especially the Pd-Au ones, from previously reported related materials obtained from the same support and the same precursor, but with a different reducing agent (formaldehyde). © 2014 Elsevier B.V. All rights reserved.

#### 1. Introduction

 $H_2O_2$  is a desirable clean oxidant for many chemical applications, but its industrial use is limited due to its high cost. The

http://dx.doi.org/10.1016/j.cattod.2014.02.021 0920-5861/© 2014 Elsevier B.V. All rights reserved. catalytic direct synthesis (CDS) from  $H_2/O_2$  with catalysts based on Pd could potentially lower the cost to less than half its current value and make the use of  $H_2O_2$  feasible for processes such as primary and waste water treatments, cleaning of semiconductors and oxidations in industrial chemical synthesis [1]. The CDS is only seemingly a simple reaction, because several side-reactions (Scheme 1) yield water, the most stable molecule in the reaction network, and adversely affect the selectivity. The latter typically decreases with  $H_2$  conversion, limiting the final concentration of  $H_2O_2$ . Safety is also a critical issue in the CDS, because  $H_2/O_2$  mixtures are explosive in a wide composition range (4–96%, v/v). Due to its higher cost,  $H_2$  is usually the limiting reagent and for safety reasons it is generally very diluted in the reaction mixture [2]. This

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$\mathrm{H}_2 + \mathrm{O}_2 \longrightarrow \mathrm{H}_2\mathrm{O}_2$	$\Delta H^{\circ} = -187.8 \text{ KJ} \cdot \text{mol}^{-1}$	(eq. 1)
$\mathrm{H}_2 + \frac{1}{2} \mathrm{O}_2 \rightarrow \mathrm{H}_2\mathrm{O}$	$\Delta H^{\circ} = -285.8 \text{ KJ} \cdot \text{mol}^{-1}$	(eq. 2)
$H_2 + H_2O_2 \rightarrow 2 H_2O$	$\Delta H^{\circ} = -98.2 \text{ KJ} \cdot \text{mol}^{-1}$	(eq. 3)
$\mathrm{H_2O_2} \rightarrow \mathrm{H_2O} + \frac{1}{2} \mathrm{O_2}$	$\Delta H^{\circ} = -379.4 \text{ KJ} \cdot \text{mol}^{-1}$	(eq. 4)

Scheme 1. Reaction network of hydrogen peroxide direct synthesis (side reactions shadowed).

can severely limit the final concentration of H<sub>2</sub>O<sub>2</sub> and calls for very selective catalysts. As a matter of fact the design of the catalyst has apparently been so far the main tool to solve the dilemma opposing safety to performance, with many literature reports on this topic in the last decade

Particular attention has been paid to bimetallic palladiumplatinum and palladium-gold catalysts supported on inorganic oxides, such as SiO<sub>2</sub> [3], TiO<sub>2</sub> [4], ZrO<sub>2</sub> and CeO<sub>2</sub> [5,6], carbon [7] and ion-exchange resins (sulfonated polystyrene-divinylbenzene) [8,9].

For the bimetallic Pd-Pt catalysts, good performances have been reported in both the patent [10,11] and the open literature [5,9,12]. For instance, Pd-Pt/SiO<sub>2</sub> catalysts (Pd/Pt=95/5, mol/mol) showed excellent results, with a 2.5-fold increase in the production of H<sub>2</sub>O<sub>2</sub> and only a slight decrease in selectivity in comparison with monometallic Pd catalyst [12]. However, the addition of higher amounts of platinum resulted in a significant decrease in the selectivity. The addition of Au as promoter to Pd catalysts has also been thoroughly investigated and reported in many papers to have beneficial effects [7,9,13].

In this context we have already shown that reduced palladium catalysts (1%, w/w) and bimetallic Pd-Pt and Pd-Au supported Lewatit K2621 are interesting catalysts in CDS. In the absence of promoters (acids or halides) they perform better than e.g. the Pd/SiO<sub>2</sub> catalyst in terms of H<sub>2</sub>O<sub>2</sub> selectivity [1,9,14].

Lewatit K2621 is a the macroreticular sulfonated polystyrenedivinylbenzene resin (S-PS/DVB), which has been already used as the support for CDS [9,14,15]. S-PS/DVB resins show at least two interesting features. The metal precursors can be easily introduced into the support by simply exchanging the counter-ions of the sulfonic groups (H<sup>+</sup> or Na<sup>+</sup>, for instance) with metal containing cations. Moreover, the reduction of the metal precursors takes place inside porous system of the polymer, thus controlling the size and the size distribution of the metal nanoparticles [15-18].

In this paper we report on the preparation, characterization and testing in CDS of two sets of bimetallic Pd-Pt and Pd-Au supported on K2621, featured by a fixed palladium loading (1%, w/w) and different amounts of either platinum or gold (0, 0.25, 0.5, 1%, w/w, respectively). A new protocol for the synthesis of catalytic materials has been developed allowing to obtain metal nanoparticles upon the reduction of the metal precursors with hydrogen in an autoclave (5 bar) at 60 °C.

The use of the cationic complexes  $[Pd(NH_3)_4]^{2+}$ ,  $[Pt(NH_3)_4]^{2+}$ and [Au(en)<sub>2</sub>]<sup>3+</sup> allows their straightforward immobilization in K2621 by ion-exchange from aqueous solutions. In order to evaluate the intrinsic properties of the pristine catalysts, we decided to prepare and study these new catalysts with neither halide ions (Br<sup>-</sup>, Cl<sup>-</sup>) nor mineral acids added as selectivity enhancers [19] in the reaction mixture.

### 2. Experimental

### 2.1. Materials and apparatus

A batch of Lewatit K2621 (sulfonated polystyrenedivinylbenzene macroreticular ion-exchange resin; exchange capacity = 1.92 mmol/g) was used as a metal/catalyst support. First, the support was washed with deionized water (300 cm<sup>3</sup> for 10 g of material) and rinsed with methanol (100 cm<sup>3</sup> for 10 g material).

Unless otherwise stated, all the other reagents and materials were used as received from the supplier. [Au(en)<sub>2</sub>]Cl<sub>3</sub> (en = 1,2-diaminoethane) was synthesized according to ref. [20]; [Pd(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub> and [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> were purchased from Alfa Aesar; sodium thiosulfate pentahydrate (99.5%), potassium iodide, starch, concentrated sulphuric acid and methanol were purchased from Sigma-Aldrich; HPLC grade methanol (99.99%) from J.T. Baker; H<sub>2</sub>, O<sub>2</sub> and CO<sub>2</sub> (99.999% mol/mol purity) from AGA (Linde group). Methanol for Karl Fischer titration, Hydranal composite 2 and ammonium molybdate tetrahydrate were purchased from Fluka.

ICP-MS measurements were carried out with a PerkinElmer Sciex, ICP Mass Spectrometer 6100 DRC Plus according to the quantitative standard mode. Samples were prepared upon diluting the mother liquor from the metalation experiments (aqueous solutions of the unreacted metal precursor, see section 2.2) up to a known fixed volume.

Karl Fisher titrations were carried out with a Titrino GP 736 from Metrohm

The nanocluster size and the distribution thereof, as well as the structure of the support, were assessed by energy filtered transmission electron microscopy (EFTEM, LEO 912 OMEGA, LaB6 filament, 120 kV).Samples were prepared by suspending a few milligrams of the powdered materials in high purity isopropyl alcohol. After sonication (30 s), a small droplet (5 µl) of the suspension was transferred onto a holey-carbon film coated Cu grids and was eventually introduced into the microscope.

All XPS spectra were recorded with Kratos Axis Ultra electron spectrometer equipped with a delay line detector. A monochromated Al K $\alpha$  source operated at 150 W, hybrid lens system with magnetic lens, proving an analysis area of  $0.3 \times 0.7 \text{ mm}^2$  and a charge neutralizer were used for the measurements. The binding energy (BE) scale was referenced to the C1s line of aliphatic carbon, set at 285.0 eV. Processing of the spectra was accomplished with the Kratos software.

### 2.2. Ion exchange of Pd and Pt

In a typical experiment, K2621 (1.0 g) was suspended in 10 cm<sup>3</sup> of distilled water and let to stand for 2 h. Then aqueous solutions of [Pd(NH<sub>3</sub>)<sub>4</sub>]SO<sub>4</sub> and of [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> were added to the suspension. The total amount of the  $[Pd(NH_3)_4]SO_4$  was always the same (0.094 mmol) and corresponded to 1% (w/w) palladium in the final catalysts. The amount of [Pt(NH<sub>3</sub>)<sub>4</sub>](NO<sub>3</sub>)<sub>2</sub> changed from one experiment to another in order to achieve 0.25, 0.5 and 1% (w/w) nominal Pt loadings, respectively (Table 1). After adding the metal precursors, the suspension was let to react overnight under mechanical stirring (swirling plate). After filtration it was carefully washed on the filter with distilled water  $(3 \times 10 \text{ cm}^3)$  and eventually dried overnight at 110 °C. The mother liquor (filtrate and water from washing) was analyzed for the unreacted metal by ICP-MS, which was always found to be less than 0.1% of the initial amount for both metals. Accordingly, the experimental metal loading was equal to the nominal value in all the catalysts.

### 2.3. Ion exchange of Pd and Au

Before introducing the metals, K2621 was transformed into its neutral sodium form (K2621Na) by flowing a 0.1 M NaOH solution (ca. 200 cm<sup>3</sup> in 4 h) though a glass column where 20 g of the resin had been packed into. K2621Na was carefully washed with distilled water until neutral pH of the eluate and dried overnight in oven at 110°C. In a typical experiment K2621Na (1.0g) was suspended in 10 cm<sup>3</sup> of distilled water and let to stand for 2 h. Then

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Fable 1 Selected analytical on the bimetallic Pd-Pt and Pd-Au catalysts supported by K2621 (experimental loading: Pd 1%, w/w; Pt or Au, 0.25, 0.5, 1.0%, w/w).							
Final catalyst	K2621 (g)	[Pd(NH <sub>3</sub> ) <sub>4</sub> ]SO <sub>4</sub> (g)	[Pt(NH <sub>3</sub> ) <sub>4</sub> ](NO <sub>3</sub> ) <sub>2</sub> or [Au(en) <sub>2</sub> ]Cl <sub>3</sub> (g)	Pd loading <sup>a</sup> (%, w/w)	M' loading <sup>a,b</sup> (%, w/w)	$M'/(Pd + M')^b$ (mol/mol)	
1PdK2621	1.0120	0.0285	-	1.1	-	0	
1Pd025PtK2621	1.0243	0.0262	0.0052	1.0	0.25	0.12	
1Pd05PtK2621	1.0196	0.0274	0.0101	1.1	0.5	0.22	
1Pd1PtK2621	1.0173	0.0283	0.0205	1	1	0.36	
1Pd025AuK2621	1.0420	0.0292	0.0062	1.1	0.27	0.12	
1Pd05AuK2621	1.0359	0.0285	0.0120	1.1	0.5	0.21	
1Pd1AuK2621	1.0359	0.0275	0.0312	1.0	1.4	0.42	

a: Experimental amount; b: M' = Pt or Au.

aqueous solutions of  $[Pd(NH_3)_4]SO_4$  and of  $[Au(en)_2]Cl_3$  (en = 1,2diaminoethane) were added to the suspension. The total amount of the  $[Pd(NH_3)_4]SO_4$  was always the same (0.094 mmol) and corresponded to 1% (w/w) palladium in the final catalysts. The amount of [Au(en)<sub>2</sub>]Cl<sub>3</sub> changed from one experiment to another in order to achieve 0.25, 0.5 and 1% (w/w) nominal Pt loadings, respectively (Table 1). After adding the metal precursors, the suspension was let to react overnight under mechanical stirring (swirling plate). After filtration it was carefully washed on the filter with distilled water  $(3 \times 10 \text{ cm}^3)$  and eventually dried overnight at  $110 \,^\circ\text{C}$ . The mother liquor (filtrate and water from washing) was analyzed for the unreacted metal by ICP-MS, which was always found to be less than 0.1% of the initial amount for both metals. Accordingly, the experimental metal loading was equal to the nominal value in all the catalysts.

#### 2.4. Reduction of bimetallic materials in autoclave with 5 bars of hydrogen at 60°C

The beige solid recovered from the ion-exchange reaction was suspended with 50 cm<sup>3</sup> of THF in a glass vessel inserted into the autoclave. After flushing three times with H<sub>2</sub>, the autoclave was filled with hydrogen and the reduction was carried at 5 bar of hydrogen and 60 °C for 5 h. After cooling and venting the autoclave, the catalyst was recovered as a black material by vacuum filtration and carefully washed on the filter with THF ( $3 \times 10$  cm<sup>3</sup>). The solid was dried in oven at 110 °C overnight (Table 1) and then ground with pestle and mortar.

#### 2.5. Catalytic tests

 $H_2$  and  $O_2$  mixtures are explosive in the 4–96% range [21]; in the presence of methanol the mixtures can be flammable even outside of the  $H_2/O_2$  explosion range [22]. For safe operations the H<sub>2</sub>/O<sub>2</sub>/MeOH mixtures must be kept outside of the explosion and flammability range by dilution with an inert gas (CO<sub>2</sub> in this work). Not doing so, deliberately or accidentally, increases the fire and explosion hazards, with possible severe consequences.

Catalytic tests were carried out in a 600 cm<sup>3</sup> stainless steel, tailor made jacketed batch reactor with a maximum working pressure of 200 bar, thermostated at the desired temperature by a cryogenic unity and equipped with a Heidolph RZR 2021 rotor (200-1000 rpm), an HP-pump (High Pressure pump) for the recirculation of the liquid phase and a K-type thermocouple, for continuous temperature detection. Further details can be found in ref. [23].

In order to test each catalyst for CDS, the autoclave was charged with the catalyst (0.15 g) and flushed four times with 3 bars of carbon dioxide. Then CO<sub>2</sub> (18.4 bar) and O<sub>2</sub> (6 bar) were fed directly from the cylinders at 25 °C and 420 cm<sup>3</sup> ( $V_L$ ) of methanol were fed with an HPLC pump, at room temperature. The temperature was allowed to decrease to 2 °C, followed by stirring and recirculation (1000 rpm and  $4 \text{ cm}^3/\text{min}$ , respectively). After the stabilization of

the pressure and the temperature  $(2 \circ C)$ , both the stirrer and the pump were switched off and H<sub>2</sub> was fed up to the desired amount. It was always the limiting reagent and its partial pressure was always kept low enough to be below the lower explosion and flammability limit [21,22] of the CO<sub>2</sub>, O<sub>2</sub>, H<sub>2</sub> and MeOH mixture. The hydrogen amount introduced into the reactor  $(nH_2O)$  was calculated from the difference of hydrogen pressure in the pre-cylinder [23]. Thus, the composition of the gases was 2.5% H<sub>2</sub>, 25.5% O<sub>2</sub> and 72% CO<sub>2</sub>, respectively. These conditions have been previously shown to ensure operations under kinetic regime [23].

Samples for the analysis of the product were regularly taken and the concentration of H<sub>2</sub>O<sub>2</sub> and H<sub>2</sub>O were determined by iodometric and Karl Fischer titrations, respectively. The initial concentration of water, [H<sub>2</sub>O]<sub>0</sub>, was also estimated from the Karl Fischer titration of the neat solvent and was used to calculate the concentration of water actually produced by the reaction, [H<sub>2</sub>O]:

$$[H_2O] = [H_2O]' - [H_2O]_0$$

where  $[H_2O]'$  is the uncorrected value directly obtained from the titration. These data were used to monitor the progress of the reaction and the changes of the selectivity with time. The former was represented as the cumulative yield:

$$C(\%)_{\mathsf{H}_{2},t} = 100 \cdot \{[\mathsf{H}_{2}\mathsf{O}_{2}]_{t} + [\mathsf{H}_{2}\mathsf{O}]_{t}\} \cdot \frac{V_{L}}{n_{\mathsf{H}_{2},0}}$$

If not otherwise stated, the selectivity towards hydrogen peroxide at time  $t(S_{H_2O_2,t})$  was calculated as:

$$S(\%)_{H_2O_2,t} = 100 \cdot \frac{[H_2O_2]_t}{\{[H_2O_2]_t + [H_2O]_t\}}$$

The initial productivities (rates of H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> production per total mol of metal) were calculated in a similar way as in reference [9]. The points of the initial sections of the kinetic plots were interpolated with a linear fit and the slopes divided by the sum of Pd and M (Pt or Au) moles. The initial cumulative rates were obtained from the interpolation with the linear fit of the initial section of the hydrogen consumption plots. The initial selectivity towards H<sub>2</sub>O<sub>2</sub> was calculated as the initial slope from the interpolation of the plot of hydrogen peroxide concentration vs time divided by the slope of the plot of hydrogen consumption vs time. According to the mass balance of hydrogen, the latter curve was obtained simply as the plot of the sum of  $H_2O_2$  and  $H_2O$  concentrations as a function of time. This method will be hereafter referred to as RISLI (ratio of initial slopes from linear interpolation).

#### 3. Results and discussion

#### 3.1. Synthesis and characterization

The successful preparation of a number of Pd [8,14] and bimetallic Pd-Au and Pd-Pt catalysts [9] for the production of hydrogen peroxide from the gaseous elements has already been achieved in

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Table 2



**Fig. 1.** Low resolution TEM images of 1PdK2621 (A, 160 K), 1Pd025AuK2621 (B, 160 K), 1Pd05AuK2621 (C, 250 K), 1Pd1AuK2621 (D, 250 K) 1Pd025PtK2621 (E, 250 K), 1Pd1PtK2621 (F, 250 K) samples.

our laboratory. These catalysts were obtained by supporting the metal nanoparticles the commercial S-PS/DVB macroreticular ionexchange resin Lewatit K2621, which proved to be an efficient support for CDS [9,14,15]. Its ability to exchange cations is a very useful feature, which allows the straightforward incorporation of metals. Under the conditions required to prepare 1% (w/w) metal catalysts, with the metal precursors as the limiting reagents, the di-cationic complexes [Pd(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and [Pt(NH<sub>3</sub>)<sub>4</sub>]<sup>2+</sup> and the tricationic [Au(en)<sub>2</sub>]<sup>3+</sup> complexes were quantitatively taken up by the resin, as shown by the mass balance of the metals based on ICP analysis. The counter ions of the cationic precursors  $(SO_4^{2-}, NO_3^{-},$ Cl<sup>-</sup>), repelled by the fixed anion charges of the ion-exchanger, were removed from the polymeric framework by careful washing, together with any cation (H<sup>+</sup> or Na<sup>+</sup>) released in the ion exchange process. As the result the ion-exchanged stocks of K2621 contained 1% (w/w) of palladium and from 0.25 to 1% (w/w) of the second metal (Table 1).

Figs. 1 and 2, respectively, show the Transmission Electron Microscopy (TEM) images and the particle size distributions of the Pd, Pd-Pt and Pd-Au catalysts after the reduction with  $H_2$  at 5 bar of the precursors in the materials suspended in THF. The low resolution images of the monometallic sample 1PdK2621 (Fig. 1A) illustrate that the nanoparticles are well separated and their diameter ranges from 1.5 to 8.5 nm (Fig. 2, upper left panel). The particle size distribution, estimated by sampling more than 1000 nanoparticles, was relatively symmetric and the center estimated

Sample	Photoelectron line	BE (eV)	FWHM (eV)
1PdK2621	Pd 3d <sub>5/2</sub>	336.4 Pd(0) 337.9 Pd(II)	1.05 1.75
1Pd1PtK2621	Pd 3d <sub>5/2</sub>	335.8 Pd(0) 337.4 Pd(II)	1.3 1.45
	Pt 4f <sub>7/2</sub>	71.7 Pt(0) 73.0 Pt(II)	1.85 1.75
1Pd025PtK2621	Pd 3d <sub>5/2</sub>	336.0 Pd(0) 337.7 Pd(II)	1.05 1.8
	Pt 4f <sub>7/2</sub>	72.7 Pt(0) 74.0 Pt(II)	1.55 2.05
1Pd1AuK2621	Pd 3d <sub>5/2</sub>	335.2 Pd(0) 337.6 Pd(II)	1.05 1.8
	Au 4f <sub>7/2</sub>	84.0 Au(0)	1.05
1Pd05AuK2621	Pd 3d <sub>5/2</sub>	336.2 Pd(0) 338.0 Pd(II)	2.35 2
	Au 4f <sub>7/2</sub>	84.0 Au(0) 85.0 Au(I)	1.05 1.45
1Pd025AuK2621	Pd 3d <sub>5/2</sub>	335.4 Pd(0) 337.8 Pd(II)	1.05 1.75
	Au 4f <sub>7/2</sub>	84.0 Au(0)	1.0

by LogNormal fit is at 4.8 nm with a skewness coefficient (SC) of 0.91 [24]. The metal nanoparticles of 1PdK2621 are smaller than those of other 1% (w/w) Pd catalysts supported on K2621, which were obtained upon reduction of either the same immobilized precursor with formaldehyde [9] or immobilized palladium acetate with a refluxing mixture of methanol and water [14].

In the Pd-Pt catalysts (Fig. 1E and F) the metal nanoparticle size are significantly smaller than in 1PdK2621 (Fig. 2; distribution analyzed on a set of more than 540 nanoparticles). Moreover the increase of the Pt amount from 0.25 to 1% (w/w) made the nanoparticles smaller and narrowed their size distribution, as already reported in the literature [25,26].

In the Pd-Au catalysts the metal nanoparticles (Fig. 1B-D) are completely different in comparison with the Pd-Pt ones. Upon increasing the amount of gold from 0.25 to 1 wt.% their size and size distributions (estimated from the analysis of more than 250 nanoparticles) get larger and broader: whereas in 1Pd025AuK2621 the center of the size distribution (LogNormal fit) is at 8.2 nm (SC = 1.24), it is at 11.2 nm in 1Pd1AuK2621 (SC = 2.05). Moreover in 1Pd1AuK2621 very large aggregates of metal nanoparticles are also present (Fig. 1D).

Table 2 shows the results of XPS analysis on fresh catalysts. The oxidation states were assessed from peak fitting, but the metal loading was too low for the reliable quantitative determination of the metal surface concentration.

The deconvolution of the Pd  $3d_{5/2}$  signals provided two components. The first has a binding energy (BE) in the 335.2-336.4 eV range and can be assigned to zerovalent Pd; the second has a BE in the 337.4-338.0 eV range and can be attributed to Pd(II) species. Whereas the Pd(II) component is relatively little sensitive to the presence of the second metal, the BE observed for Pd(0) is generally lower in the bimetallic catalysts. This suggests that the second metal acts as an electron donor towards palladium. Gold seems more efficient than platinum in this respect. This could depend on the fact that whereas platinum is never completely reduced, gold is generally present only as Au(0), with the exception of 1Pd05AuK2621 in which the BE of Pd(0) is almost as high as in 1PdK2621. The Pt  $4f_{7/2}$  signals of all the Pd-Pt catalysts could be separated into two components. The first has a BE ranging from

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Fig. 2. Particle size distributions for 1PdK2621, 1Pd025PtK2621, 1Pd1PtK2621 (left), 1Pd025AuK2621, 1Pd05AuK2621, 1Pd1AuK2621 (right) samples (average diameter estimated from LogNormal fit of the size distribution; SC calculated from the LogNormal parameters of size distribution [24]).

71.7 to 72.7 eV, close to 71.1 of bulk platinum [27], and can be assigned to Pt(0). The second component has a BE of ca. 74.0 eV and can be attributed to Pt(II) species (Table 2). In the case of gold the signals from the  $4f_{5/2}$  can overlap with those of the Pd 4s ones and, accordingly, only the  $4f_{7/2}$  peak was analyzed for Au. In this case we found a single peak at BE equal to 84.0 eV, which can be attributed to Au(0). Only in the case of 1Pd05AuK2621 a component at 85.4 eV, which can be attributed to Au(1), was also observed.

The shift to lower values of the BE for Pd(0) 3d<sub>5/2</sub> in the bimetallic catalysts is suggestive of the increase of the electron density of palladium due to donation from the second metal. This implies the electronic communication between Pd and either Pt or Au and is consistent with the hypothesis of nanoalloying between the metals [28]. A negative shift of BE of the Pd 3d signals has already been reported for Pd-Au alloys with Pd:Au higher than 1:1 (ca. 0.5 by weight), as it is in this work. In any case, the nanostructured metal phase contained at least oxidized Pd. The data presently available do not allow to suggest the structure of the nanostructured metal phase(s), because we cannot even know the surface composition. For this purpose other techniques are required to investigate the composition of the metal surface, such as Low Energy Ion Scattering (LEIS) [29], or of the whole metal phase and could be the subject of further investigation.

#### 3.2. Catalytic tests

The behavior of the Pd-Pt and Pd-Au catalysts is illustrated in Figs. 3–6, which represent the concentrations of the products ( $H_2O_2$ ,  $H_2O$ ; Figs. 3 and 5) and the conversion f  $H_2$  and the selectivity towards  $H_2O_2$  (Figs. 4 and 6) as functions of the reaction time over the Pd-Pt (Figs. 3 and 4) and Pd-Au (Figs. 5 and 6) catalysts.

It is possible to separate all the catalytic runs into two stages, as already reported previously [9]. The first one is observed when the hydrogen concentration is still relatively high (2.5-1.25 mol%) in the gas phase. This initial stage is featured by a relatively high hydrogen consumption rate and in general a fairly linear change of H<sub>2</sub> conversion with time. It is also characterized by relatively fast H<sub>2</sub>O<sub>2</sub> formation and slow H<sub>2</sub>O<sub>2</sub> consumption (due

to  $H_2O_2$  hydrogenation and dismutation). It ends in approximately 20–40 min, i.e. when the  $H_2$  conversion exceeds 50%. In the second stage, hydrogen is almost completely consumed and the main active reaction, if any, is expected to be the dismutation of hydrogen peroxide (see Scheme 1). However, with these catalysts the conversion of  $H_2$  is always slightly lower than 100%, so that in the case of the Pd-Au catalysts some  $H_2O_2$  is likely still produced and the decrease of its concentration, if any, is little in comparison to the monometallic and the bimetallic Pd-Pt catalysts.

The initial activity of the catalysts was assessed as the cumulative amount of  $H_2O_2$  and  $H_2O$  per mole of either palladium or total metal (Pd+Pt) and (Pd+Au) and unit time (Table 3). This corresponds to rates of  $H_2$  consumption, which were provided by the ratios of the slopes obtained from the linear interpolation of



**Fig. 3.** Concentration of water and hydrogen peroxide produced over the Pd-Pt catalysts as a function of time.

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 Table 3

 Results of the catalytic runs with the Pd-Pt and Pd-Au bimetallic catalysts supported on K2621.

Cat.	Employ metal a	ed mount <sup>a</sup>	Initial cumul. rate <sup>b</sup>	Initial cumul. productivity <sup>c,f</sup>		Initial H <sub>2</sub> O <sub>2</sub> productivity <sup>d,f</sup>	Initial selectivity <sup>e</sup>	Selectivity at $t_{1/2}$ <sup>g</sup>
	Pd	Pd + M' <sup>f</sup>		vs Pd	vs Pd + M' <sup>f</sup>			
1PdK2621	1.45	-	29.3	nd <sup>h</sup>	-	nd <sup>h</sup>	nd <sup>h</sup>	50 (38)
1Pd025PtK2621	1.44	1.64	73.8	2151	1891	875	46	45 (25)
1Pd05PtK2621	1.44	1.84	77.7	2267	1774	783	44	45 (22)
1Pd1PtK2621	1.42	2.2	81.3	2406	1553	694	45	45 (21)
1Pd025AuK2621	1.43	1.63	45.9	1349	1184	739	62	55 (28)
1Pd05AuK2621	1.42	1.81	45.1	1334	1047	249	24	22 (31)
1Pd1AuK2621	1.42	2.19	55.4	1637	1062	588	55	52 (25)

a: mol·10<sup>5</sup>; b: mmol(H<sub>2</sub>O<sub>2</sub> + H<sub>2</sub>O)·dm<sup>-3</sup> h<sup>-1</sup>; c: mol<sub>(H<sub>2</sub>O<sub>2</sub>+H<sub>2</sub>O)</sub> mol<sup>-1</sup><sub>(Pd+M')</sub> h<sup>-1</sup>; d: mol<sub>(H<sub>2</sub>O<sub>2</sub>)</sub> mol<sup>-1</sup><sub>(Pd+M')</sub> h<sup>-1</sup>; e: %; f: M' = Pt or Au; g: selectivity at 50% of H<sub>2</sub> conversion ( $t_{1/2}$  min, in parentheses); h: not determined (see text).



Fig. 4.  $H_2$  conversion and  $H_2O_2$  selectivity over the Pd-Pt catalysts as a function of time.

the initial sections of the cumulative yield plots. Their comparison allows to analyze the influence of platinum and gold addition on the activity of the catalysts. In addition, the catalyst selectivity was compared both at the beginning of the reaction and at 50% H<sub>2</sub> conversion (Table 3, "Selectivity at  $t_{1/2}$ " column).

There is only a little difference in the  $H_2$  conversion curves over the Pd-Pt catalysts hence in the absolute initial rate of  $H_2$ 







Fig. 6.  $\rm H_2$  conversion and  $\rm H_2O_2$  selectivity over the Pd-Au catalysts as a function of time.

consumption. Accordingly the initial cumulative productivity (per unit amount of total metal) undergoes a slight decrease with the increase of the Pt content of the catalyst, because the relative change of the absolute initial cumulative rates is smaller than the relative change in the sum of Pd and Pt amounts. In comparison with 1PdK2621 the Pd-Pt bimetallic catalysts are initially more active, as shown in Fig. 3 (due to the presence of an induction time in the plot of the H<sub>2</sub> conversion as a function of time, the RISLI method was not applied to calculate the initial cumulative productivity).

The changes of the size and size distribution of the metal nanoclusters from 1Pd05PtK2621 (3.3 nm) to 1Pd1PtK2621 (3.0 nm and narrower distribution) seem to have only a little effect and, if any, not the expected one. The reduction of the size, for instance, is not associated to an increase of the activity. However, the productivity of the Pd-Pt catalysts is generally appreciably higher than that of the monometallic catalyst, as also indicated by the shorter  $t_{1/2}$ . The change of the Pt amount affects more or less equally the H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub> productivity, so that the selectivity of the Pd-Pt catalysts appears to be almost independent of the composition of the metal phase (Fig. 4). This holds in the comparison of both the initial selectivity calculated with the RISLI method (Table 3, "Initial selectivity" column) and of the values at 50% of H<sub>2</sub> conversion (Table 4, rightmost column). From the point of view of selectivity the addition of platinum has an adverse effect in this case. The initial selectivity of 1PdK2621 was not calculated with the RISLI method, because the concentrations of  $H_2O_2$  and  $H_2O$  did not increase linearly with time at the beginning of the reaction due to the presence of an induction time for both. However, bimetallic catalysts were always initially less selective than the monometallic one, as shown by Fig. 4 (upper panel), and at 50% conversion of H<sub>2</sub> as well (Table 3). Apparently the

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addition of 0.25% (w/w) platinum, or more, suppressed the induction times for the production of both H<sub>2</sub>O and H<sub>2</sub>O<sub>2</sub>. As the former was longer than the latter, this made the bimetallic Pd-Pt catalysts less selective. The related bimetallic Pd-Pt catalysts obtained from the reduction of the precursors with formaldehyde were initially somewhat more productive, but even less selective (<40%) [9] than their counterparts reduced with H<sub>2</sub> described herein. Also the monometallic catalyst reduced with formaldehyde was pretty less selective than 1PdK2621. From the point of view of the selectivity, H<sub>2</sub> seems therefore to be better than formaldehyde as the agent for the reduction of the precursors of Pd and Pt. Also in the case of the formaldehyde reduction route the bimetallic catalysts in general were never more selective than the related monometallic one, with the only exception of the material with 0.1% Pt [9]. This relatively low level of Pt was not used in the present work; nevertheless the selectivity data of the new catalysts obtained from the H<sub>2</sub> reduction route confirm that platinum is useful to improve the catalytic performance only in very little amount, in agreement with our own [9] and other previous literature findings [12].

In comparison with platinum, the addition of gold has a similar effect on the activity, which was higher than in the monometallic catalyst, as shown by the kinetic plots of Fig. 6 (lower panel). However the productivities are smaller than those of the bimetallic Pd-Pt. This is reflected also in the values of  $t_{1/2}$ , which are intermediate between those of the Pd-Pt catalysts and the one of the monometallic catalyst. In comparison with 1PdK2621, only 1Pd025AuK2621 was somewhat more selective. In fact its selectivity at 50% H<sub>2</sub> conversion was higher and inspection of Fig. 6 (upper panel) shows that it was likely just a bit more selective also in the first 10-15 min of the reaction. With higher Au amounts, the Pd-Au bimetallic catalysts described herein are never more selective than 1PdK2621, unless relatively long reaction time are considered. This is in line with the observation that relatively little amounts of gold are required to have an effective promotion of palladium, although positive effects have been observed up to a molar Pd:Au ratio of 2:1 (corresponding approximately to 1% (w/w) for both in the catalyst) [4,5,7,16]. As pointed out above, the conversion of H<sub>2</sub> over these Pd-Au catalysts is never quantitative and some production of H<sub>2</sub>O<sub>2</sub> in the final stage still balanced its dismutation, hence no final decrease of its concentration was observed. As the consequence, 1Pd025AuK2621 and 1Pd1AuK2621 were appreciably more selective than 1K2621 when t > 60 min. In this respect, the plots in the upper panel of Fig. 6 show that the selectivity of 1PdK2621 decreased faster than that of all the Pd-Au catalysts. The result is that by the time that H<sub>2</sub>O<sub>2</sub> reached its respective top concentrations over 1PdK2621, 1Pd025AuK2621 and 1Pd1AuK2621, the selectivity of the bimetallic catalysts had surpassed that of the monometallic one. With the Pd-Au catalysts too there is not a clear correlation between the size and size distribution of the metal nanoparticles and the catalytic performance. Also in the case of Pd-Au bimetallic catalysts obtained upon reduction of the metal precursors with formaldehyde [9] we did not find compelling evidence that the nanoparticle size was distinctly more important than other factors in directing the catalysts' performance, in spite of the fact that they had sizes and size distributions pretty much different from those of the H2-reduced catalysts investigated in the present work. However, we argued there that the presence of large aggregates could have beneficial effects on the selectivity [9].

This could help in explaining, at least in part, some differences in the behavior of the Pd-Au catalysts obtained with  $H_2$  (this work) and with formaldehyde [9] as the reducing agent. With the latter, we observed a steady decrease of the initial selectivity with the increase of the Au amount. In line with this, 1Pd05AuK2621 is also less selective than 1Pd025AuK2621. The difference in selectivity here is higher than in the case of the related catalysts from the formaldehyde reduction route. Although we do not have XPS data for the latter set of catalysts to compare with, it can be appreciated that 1Pd05AuK2621 is featured by the presence of some Au(I) in the nanostructured metal phase and this could be also connected to the selectivity decrease. On the other hand 1Pd1AuK2621 is practically as selective as 1Pd025AuK2621. The presence of larger nanoclusters in 1Pd1AuK2621, which has larger size and broader size distribution than 1Pd025AuK2621, could at least in part explain this recovery of selectivity upon increasing the gold content from 0.5 to 1% (w/w) [9].

To summarize, our data show that the addition of platinum to the polymer-supported Pd catalysts yielded more active, but less selective, materials when the platinum amount is 0.25% (w/w) or higher. It is not clear, however, why the changes in the metal composition of Pd-Pt catalyst, in the size and size distribution of the metal nanoparticles did not influence appreciably the selectivity. We also found some differences between the catalysts (both monometallic Pd and bimetallic Pd-Pt) obtained upon reduction of the metal precursors with H<sub>2</sub>, described in this work, and related materials which were obtained upon formaldehyde reduction of the same precursors [9]. Whereas the catalysts reduced with  $H_2$ are less active, but generally more selective, at the highest Pt contents, the bimetallic catalysts from the formaldehyde reduction route are practically as selective as the related monometallic material. Moreover, the differences in the catalytic performance of the Pd-Pt catalysts from the formaldehyde reduction route were comparatively larger and were tentatively explained by product poisoning (in particular by H<sub>2</sub>O<sub>2</sub>). In the case of the H<sub>2</sub>-reduced catalysts differences are too small to provide either further support or disputation of this hypothesis. These circumstances are in agreement with previous reports [6,12,30] that the overall catalytic performance seems to be much more dependent by the preparative method used for synthetize the metal nanoparticles compared to their size and size-distribution. This could be related to changes in the topology or other features of the surface, when different protocols of reduction are employed, possibly arising from different morphological properties of the nanostructured metal phase. To unravel these properties an in-depth investigation, which was beyond the scope of this work, is required and will be the subject of future work.

The bimetallic Pd-Au catalysts described herein are even more different from those obtained with formaldehyde as the reducing agent of the (same) metal precursors. In the latter case, the catalyst with 0.25% (w/w) Au added was appreciably less active than the related monometallic catalyst, but much more selective. By contrast 1Pd025AuK2621 is more active than 1PdK2621, but only slightly more selective. Moreover, in the formaldehyde reduced catalysts the activity and the selectivity underwent a steady increase and decrease, respectively, as the gold content was increased. As shown above this was not the case with the catalysts reduced with H<sub>2</sub> described in this work. It is not clear at the moment why different reducing agents give catalysts performing differently, starting from the same support and the same precursors. TEM characterization did not provide useful information and again the reasons could be connected to differences in the structures of the metal nanoparticles, which could arise, for instance, from different reduction rates of the precursors with different reducing agents with different ability to diffuse inside the support [31].

#### 4. Conclusion

Two sets of bimetallic Pd-Pt (Pd: 1.0; Pt: 0.25–1.0%, w/w) and Pd-Au (Pd: 1.0; Au: 0.25–1.0%, w/w) catalysts supported on the macroreticular ion-exchange resin Lewatit K2621 were prepared by means of a simple ion-exchange procedure in water from suitable precursors and reduction under hydrogen pressure (5 bar)

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at 60 °C. It was found that the addition of a small amount of gold (0.25%) makes the catalyst more active and slightly more selective than a 1%, w/w, palladium catalyst on K2621. 1Pd025AuK2621 was the best one, with  $1184 \text{ mol}_{(H_2)} \text{ mol}_{(Pd+Pt)}^{-1} h^{-1}$  initially consumed,  $739 \text{ mol}_{(H_2O_2)} \text{ mol}_{(Pd+Pt)}^{-1} \text{ h}^{-1}$  initially produced, a 55% selectivity towards  $H_2O_2$  at 50% conversion of  $H_2$ . This performance is lower than that obtained with a related catalyst obtained by using formaldehyde as the reducing agent, which was at the same time more active and selective. No obvious trend appeared when the amount of Au was increased to 0.5 and 1.0% (w/w). In fact 1Pd05AuK2621 (0.5% Au, w/w) was poorly selective, possibly because Au was not completely reduced. Accordingly, no clear connection between the nanocluster size and size distribution and the catalytic performance was found, although the presence of relatively high proportions of large nanoclusters in 1Pd1AuK2621 could help in explaining why it is almost as selective as 1Pd025AuK2621. On the other hand 1Pd025PtK2621, the best Pd-Pt catalyst, initially consumed  $1891 \text{ mol}_{(H_2)} \text{ mol}_{(Pd+Pt)}^{-1} h^{-1}$  and produced 875 mol<sub>(H<sub>2</sub>O<sub>2</sub>)</sub> mol<sub>(Pd+Pt)</sub><sup>-1</sup> h<sup>-1</sup>, but its selectivity towards H<sub>2</sub>O<sub>2</sub> at 50% conversion of H<sub>2</sub> was 45%. Further increase of the platinum amount changed the initial rates values to more or less the same extent, so that at 50% conversion of H<sub>2</sub> all the Pd-Pt catalysts turned out to be equally selective.

It can be finally recalled that reactions under batch-wise conditions imply non-steady-state kinetics. Therefore semi-continuous or continuous reactors could be best suited to better assess, under steady-state conditions, the effect of Pt or Au addition to Pd.

#### Acknowledgments

Lanxess is kindly acknowledged for providing the K2621 resin. S. Sterchele gratefully acknowledges the Johan Gadolin Scholarship for financial support. P. Biasi gratefully acknowledges the Kempe Foundations for financial support. In Sweden, also the Bio4Energy program is acknowledged. This work is also a part of the activities of the Process Chemistry Centre (PCC), a centre of excellence financed by Åbo Akademi University.

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Please cite this article in press as: S. Sterchele, et al., The effect of the metal precursor-reduction with hydrogen on a library of bimetallic Pd-Au and Pd-Pt catalysts for the direct synthesis of H<sub>2</sub>O<sub>2</sub>, Catal. Today (2014), http://dx.doi.org/10.1016/j.cattod.2014.02.021

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