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Promotional effects of Au in Pd–Au bimetallic catalysts supported on activated carbon cloth (ACC) for direct synthesis of H_2O_2 from H_2 and O_2

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ABSTRACT

In this study, the promotional effects of gold in Pd–Au bimetallic catalysts supported on activated carbon cloth for direct synthesis of H_2O_2 has been investigated. The bimetallic catalysts were prepared by simultaneous co-impregnation approach. Direct synthesis was performed batch-wise in a stainless steel autoclave under high pressure (38 bar) at 0 °C and methanol (220 ml) was used as the reaction medium. A series of experiments were conducted to assess the effects of: (i) the surface chemistry of the support and (ii) the amount and ratio of palladium and gold on the surface morphology of the bimetallic catalysts and on their catalytic performances, and (iii) the oxidation state of the metallic components on the activity of the catalysts. Moreover, (iv) the effects of heat treatment of the catalysts in H_2 at 185 °C and in air at 185–275 °C on the surface chemistry of the support, surface morphology of the metallic catalysts were more selective than the corresponding Pd monometallic catalysts. The results showed that the surface morphology of the Pd–Au bimetallic catalysts and their catalysts of the support and the amount and the ratio of Pd and Au in the catalyst. The presence of palladium oxide made the catalysts more selective than the corresponding zero-valent palladium (Pd⁰) catalysts.

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1. Introduction

Hydrogen peroxide (H2O2) is recognized as an important selective green oxidant since it contains a high fraction of active oxygen and the only by-product from oxidation is water. It has a wide range of applications in many large scale processes such as pulp bleaching, waste water treatment, cosmetic and pharmaceutical industries. In pulp and paper industry, hydrogen peroxide has partially replaced chlorine containing bleaching agents to address environmental issues. Industrially, H2O2 is produced by the cyclic sequential hydrogenation and oxidation of alkyl anthraquinones. This process is only economical at large scale and at high product concentrations [1]. However, H_2O_2 is often required in smaller scales and at lower concentrations. Direct synthesis would allow small scale

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http://dx.doi.org/10.1016/j.cattod.2014.04.011 0920-5861/© 2014 Elsevier B.V. All rights reserved. on-site production of dilute H_2O_2 solutions in a green and economical manner. Moreover, the direct process may eliminate the need of transportation with substantial safety risks involved [2].

A process for the direct synthesis of hydrogen peroxide from hydrogen and oxygen represents considerable challenges in catalysis and process design. Firstly, mixtures of hydrogen and oxygen are explosive over a wide range of concentrations $(4-94\% H_2 \text{ in } O_2)$ [3]. Secondly, the catalytic reaction of hydrogen and oxygen involves several reaction pathways, most of them result in the production of water [6] decreasing the selectivity.

Pd is the most common catalyst for this process. However, it suffers from low selectivity, as it catalyzes the decomposition/hydrogenation of H_2O_2 ($H_2O_2 \rightarrow H_2O + (1/2)O_2$; $H_2O_2 + H_2 \rightarrow 2H_2O$) and the non-selective water synthesis ($H_2 + (1/2)O_2 \rightarrow H_2O$). The performance of Pd catalysts is highly affected by the support material. Acidic support like SiO₂ results in more active and selective catalysts than basic ones (e.g. Al₂O₃) [4,5]. It has been shown that the existence of the oxidized state of

Pd (PdO) makes Pd catalysts more selective and more active than the corresponding zero-valent state of Pd (Pd⁰) [6–9]. Using of halide ions (especially Cl⁻ and Br⁻) and protons (H⁺) as promoters improve the selectivity of Pd catalysts in direct H_2O_2 synthesis [7–23].

Bimetallic catalysts have attracted considerable attention because their properties often differ remarkably from the corresponding monometallic ones. Among bimetallic catalysts, Pd–Au has received a great deal of attention because of its superior activity in a number of reactions, e.g. low-temperature CO oxidation, synthesis of vinyl acetate monomer, hydrogenation of hydrocarbons, cyclotrimerization of acetylene, and many others. Pure Au catalysts are not so active in direct H_2O_2 synthesis [2,24]. The addition of a second metal (e.g. Pt, Au, Ru, Rh) to Pd catalysts has been reported to affect catalytic activity and selectivity in direct H_2O_2 synthesis [5,25–34]. Addition of Au or Pt, at their optimum concentrations, to a Pd catalyst was reported to improve the catalyst selectivity, while the presence Rh or Ru exhibited an adverse effect [26].

The promotional effects of Au in Pd-Au bimetallic catalysts on direct H₂O₂ synthesis were firstly reported by G. J. Hutchings et al. [5,30,35,36]. It has also been found out that, unlike in the case of Pd monometallic catalysts, the addition of promoters, such as Br- ions and H₃PO₄, were deleterious for the Au-Pd catalysts in this reaction [31]. Supported Pd–Au catalysts can be prepared using traditional impregnation or deposition-precipitation of Pd and Au salts, either concurrently or sequentially, followed by calcination and reduction. The major drawback is the lack of homogeneity of the formed catalysts in terms of particle size, composition and shape. For example, it is not uncommon to observe Au and Pd monometallic particles, and Pd-Au alloy particles with different sizes and compositions on the same support [5,30,35–37]. Au–Pd catalysts prepared by impregnation have been shown to be very active for the direct formation of hydrogen peroxide [33]. In contrast, the catalysts prepared by co-precipitation or deposition-precipitation gave a very low hydrogen peroxide production rate [33].

In our previous paper [6], we studied Pd catalysts supported on activated carbon cloth for direct synthesis of hydrogen peroxide. In this study, the promotional effects of gold in Pd–Au bimetallic catalysts supported on activated carbon cloth were investigated. The goal was to study the effects of the surface chemistry of the support, the amount and ratio of palladium and gold, and the heat treatment of the catalysts in either H₂ or air on the dispersion and morphology of metallic components, and on the performance of the Pd–Au bimetallic catalysts.

2. Experimental

2.1. Catalysts preparation

A commercial activated carbon cloth ACC-5092-20 (Kynol Europa GmbH), after cleaning and a chemical treatment, was employed as a support. Palladium (II) chloride (PdCl₂) and gold (III) chloride hydrate (HAuCl₄) were used for making metal precursors. Nitric acid was used for acid pretreatment of the support. The activated carbon cloth was first treated in an oven at 100 °C for about 12 h. Then it was cleaned with 50% solution of methanol at room temperature for 1 h, and finally washed with plenty of deionized water. For wet oxidation, the cleaned ACC was treated with 20% solution of nitric acid at room temperature for 40 h. After this oxidative treatment the samples were washed with deionized water until neutral conditions were reached, and then dried at 60 °C for 24 h. This sample is referred as oxidized ACC (OACC). Acid pre-treatment step was used to create oxygen-containing functional groups on the surface of activated carbon and to modify the surface as suggested by several authors [38–43].

The Pd catalysts were prepared using impregnation method as described previously [6]. The Pd-Au bimetallic catalysts on nonoxidized and oxidized activated carbon cloth were prepared by simultaneous co-impregnation of the supports with an aqueous acidic solution of PdCl₂ and HAuCl₄ at room temperature for 6–7 h. The impregnation was done in a glass reactor with stirring rate of 400-500 rpm. The rate of the stirring was adjusted to get uniform distribution of the metal particles in the catalysts. The ratio of the solution volume to catalyst mass was 500 ml/g. The amount of the precursor (Pd + Au) between 7.2 and 17.3 mg per 200 mg of the support in a 200 ml glass reactor gave metal loading (Pd + Au) in the range of 1-5 wt%. After impregnation, the catalysts were dried at room temperature for 3 h, and then at 60 °C for 12 h. The reduction process was done by treating the fresh dried catalysts with H₂ at 185 °C under 3.5 bar for about 12 h. A series of different calcined catalysts were prepared by oxidizing the fresh dried catalysts at temperatures 185, 235, and 275 °C in static air for 12 h. The calcination temperatures were selected based on the TGA/DTA results in order to be in the safe thermal treatment region of the supports and their surface functional groups (in the case of oxidized ACC) [6].

2.2. Catalysts characterization

The pore size distribution and specific surface area of the supports and the catalysts were measured via nitrogen adsorption/desorption isotherms at liquid nitrogen temperature $(-350 \,^{\circ}\text{C})$ using an Automated Gas Sorption System, (Sorptomatic 1900, Carlo Erba Instruments). All the samples were degassed at a temperature of 100 $^{\circ}$ C for about 3 h prior to the measurements.

Metal (Au and Pd) contents of the catalysts were determined using flame Atomic Absorption Spectroscopy (AAS). AAS tests were performed with a Thermo Scientific ICE 3000 series atomic absorption spectrometer using an air-acetylene flame. Samples for analysis were prepared by dissolving 200 mg of the dried catalyst in an aqua regia solution followed by the addition of 500 ml of deionized water to dilute the solution. AAS was employed to determine the weight % of the metal incorporated in the support after impregnation. Moreover, it was used to determine the amount of Au or Pd leached out into the reaction medium during the direct synthesis test. The leached amount was calculated by comparing the Au and Pd content of the used catalyst and fresh catalyst.

Temperature programmed desorption (TPD) was employed to study different oxygen-containing surface functional groups in the supports and catalysts. The TPD tests were run in a set-up made of a U-shaped tubular reactor, placed inside an electrical furnace coupled to a Blazers Omnistar mass spectrometer for gas analyses. 200 mg of each sample was heated up to 1000 °C with a constant heating rate of 50 °C/min. During the tests, He was passed through the reactor with the flow rate of 60 ml/min. The amounts of CO and CO₂ desorbed from the samples were recorded by the mass spectrometer.

Ultra-high resolution field emission scanning electron microscopy (UHRFESEM) and scanning transmission electron microscopy (STEM) were hired to assess particle size, shape, surface morphology, and to monitor the agglomeration tendency of metal particles. The UHRFESEM, STEM, and energy dispersive spectroscopy (EDS) analyses were done by a Hitachi S-4800 microscope with an X-ray detector for micro-analytical X-ray mapping and quantitative analysis. The active area of the X-ray detector for quantitative analysis was 10 mm².

The oxidation states of the active components (Pd and Au) were determined by X-ray photoelectron spectroscopy (XPS). The spectra were obtained with a Perkin Elmer 5400 spectrometer, by using the Mg Ka (1253.6 eV) radiation of twin anode in the constant analyzer energy mode with pass energy of 37.75 eV. The pressure of

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the analysis chamber was maintained at 2×10^{-7} Pa. The binding energy scale was calibrated by setting the Au 4f7/2 transition to 84.0 eV. The spectra were analyzed by using Unifit peak-fitting program.

2.3. Direct synthesis reaction

The synthesis was carried out in a stainless steel autoclave (Parr Instruments Ltd) with a nominal volume of 450 ml and a maximum working pressure of 140 bar. The autoclave was equipped with an overhead stirrer (0-2000 rpm) and facilities to measure the temperature and pressure. Hydrogen (18 mmol) was fed into the reactor through a gas-holder with a volume of 33 ml and through a flow controller. The gas-holder was used to measure the precise amount of hydrogen. A circulation line equipped with a multi-way valve was installed for sampling at different times (as shown in the previous paper [6]). The sampling line was designed to cause minimum pressure changes and gas losses during sampling. Typically, the reactor was charged with about 60 mg of catalyst and successively with carbon dioxide up to 15.2 bar at room temperature. The pressure was thereafter elevated to 20.2 bar with oxygen and further to 35.2 bar with carbon dioxide again at room temperature. Catalysts were fixed in the reactor by means of a metal stand as shown in the previous paper [6]. Methanol was employed as a reaction medium. 175 g of methanol was pumped in and the reactor was cooled down to about -1 °C. Stirring (1250 rpm) was begun after 2/3 of the methanol had been fed. When the desired temperature was reached, the partial pressure of hydrogen was raised up to 3.2 bar. The reaction time now began. The gas-liquid and liquid-solid mass transfer effects were eliminated by adjusting the stirring speed. This was done beforehand by carrying out a series of tests varying the stirring rate. It was found out that 1250 rpm was a sufficient stirring rate to eliminate the mass transfer limitations.

The concentration of H_2O_2 which was formed in the reaction was measured quantitatively by a volumetric iodometry titration using the following chemicals: KI (Merck), CH₃COOH (Purity 100%, Merck), K₂Cr₂O₇ (purity 99.99%, Aldrich) and Na₂S₂O₃·5H₂O (Merck). The produced water was determined by coulometric Karl–Fischer titration using a Mettler DL35 Karl–Fischer titrator and hydranal reagents (Fluka). The water content in the reaction medium before catalyst addition was determined prior to each experiment. Palladium (II) chloride (PdCl₂, purity 99.999%, Sigma–Aldrich) and gold (III) chloride hydrate (HAuCl₄, purity 99.999%, Aldrich) were used as metal precursors. Nitric acid 65% (Merck) was used for acid pretreatment of the support. Research grade oxygen, hydrogen and carbon dioxide were purchased from AGA. Methanol with a purity of 99.9% was used as a solvent (Merck).

3. Results and discussions

Catalytic performance was evaluated by the means of the following parameters: the final concentration of the produced hydrogen peroxide and water (wt%), selectivity (%), yield (%), and total H_2 conversion (%). The last three parameters are defined as follows:

Selectivity (%) =
$$\frac{\text{moles of produced } H_2O_2}{\text{moles of produced } H_2O_2 + \text{moles of produced } H_2O} \times 100$$
(1)

Yield (%) =
$$\frac{\text{moles of produced } H_2O_2}{\text{moles of } H_2 \text{ fed}} \times 100$$
 (2)

Conversion (%) =
$$\frac{\text{moles of produced } H_2O_2 + \text{moles of produced } H_2O}{\text{moles of } H_2 \text{ fed}} \times 100$$
(3)

Another parameter which can be used in order to take in to account the metal content of the catalysts in their activities is productivity:

$$Productivity = \frac{moles of produced H_2O_2 (mol)}{reaction time (h) \times the metal content of the catalyst (kg)}$$
(4)

3.1. The effects of Au/Pd ratio and metal content in the catalytic activity of Pd–Au bimetallic catalysts

3.1.1. Increasing the amount of gold with a constant amount of palladium

The catalytic performance of Pd–Au bimetallic catalysts with 1 wt% Pd and 1–5 wt% Au supported on the oxidized ACC are presented in Fig. 1. For comparison, also the results with 1 wt% Pd monometallic catalyst are shown. It can be observed that:

- All Pd-Au bimetallic catalysts are more selective than the Pd monometallic catalyst. Especially in the first 60 min of the reaction time, almost all of the Pd-Au bimetallic catalysts are considerably more selective than the Pd monometallic catalyst (Fig. 1).
- In the case of Pd-Au bimetallic catalysts, with increasing the amount of gold, the selectivity drops, especially during the first 60 min. However, at reaction times above 1.5 h, the differences between the selectivity of the different Pd-Au catalysts became smaller (see the exact values in Table 1).
- In the case of Pd–Au bimetallic catalysts, the activity (yield, productivity and H₂ conversion rates) was increased when increasing the amount of gold (Fig. 1, Table 1).
- The Pd-Au catalysts with less than 3 wt% Au are less active in water production than the 1 wt% Pd catalyst. Especially the catalysts with 1 and 2 wt% gold produced substantially lower amount of water (more than 50% less) when compared to the Pd monometallic catalyst (see the exact values in Table 1). However, increasing the Au content from 3 wt% to 4 wt% seemed to cause a sudden increase in water production (see the exact values in Table 1).
- Indeed the 1% Pd_4% Au catalyst was substantially more active than the other catalysts in both H₂O₂ and water production.
- Fig. 1 demonstrates that the selectivity of catalysts (at least in the case of Pd-Au bimetallic catalysts) could be changing with the reaction time. This is because of the direct synthesis of H₂O₂ has a complex mechanism and could be influenced by different parameters. Therefore, in comparison of the performance of different catalysts, it is needed to consider the results versus time.

In general and according to the results presented in Fig. 1 and Table 1, the Pd–Au catalysts are more selective but less active (have lower yield and productivity) than the Pd monometallic catalyst even with lower total metal content. The only exception is the catalyst with 4 wt% Au. This catalyst is substantially more active in H_2O_2 and water production than the other bimetallic and monometallic Pd catalysts. Its selectivity is almost constant and does not change with the reaction time. However, the selectivity of the other Pd–Au catalysts is strongly dependent on reaction time, especially up to 1 h.

3.1.2. Increasing the amount of palladium with a constant amount of gold

In order to study the effect(s) of increasing the amount of palladium in Pd–Au bimetallic catalysts, a series of Pd–Au catalysts with constant amount of gold (1 wt%) and maximum 4 wt% palladium

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Fig. 1. The effect(s) of increasing the amount of gold on the catalytic activity of Pd_Au bimetalic catalysts supported on oxidized ACC; mass of catalyst = 56 mg, T_{reaction} = 0 °C, and all catalysts calcined in air at 185 °C.

were prepared. The results of the performance of the catalysts are presented in Fig. 2. It can be observed that:

When increasing the amount of palladium from 1 wt% to 2,
 3, and 4 wt%, the selectivity of the Pd–Au bimetallic catalysts

dropped a lot, especially in the first hour of the reaction time.

It dropped more than 37% during the first 15 min. At the reaction

times above 1.5 h, the differences between the selectivity of the

different Pd–Au catalysts became smaller (less than 15% in the worst cases; see Table 1).

- The Pd-Au bimetallic catalysts with 1 wt% gold and more than 1 wt% Pd almost demonstrated constant selectivity versus time (Fig. 2), otherwise than the corresponding catalysts presented in Fig. 1.
- When increasing the amount of palladium in the Pd–Au catalysts, the rate of H₂O₂ production, yield, and H₂ conversion were increased almost with similar trends (Fig. 2, Table 1). When

Table 1

The catalytic activity of the Pd and Au mono metallic, and Pd_Au bimetallic catalysts supported on oxidized ACC after 3 h of the reaction time (in H₂O₂ direct synthesis). All catalysts were calcined in air at 185 °C.

Catalyst	H ₂ O ₂ (mmol/L)	H ₂ O (mmol/L)	Selectivity (%)	Yield (%)	Productivity $\left(\frac{mol_{H_2}o_2}{h_{reaction} kg_{cat}}\right)$	H ₂ conversion (%)
1% Pd	12.47	13.04	48.88	14.20	1467	29.05
3% Pd	24.45	28.13	46.49	27.63	985	59.42
5% Pd	19.72	24.75	44.34	24.87	520	56.09
1% Pd_1% Au	6.33	3.77	62.63	7.67	408	12.24
1% Pd_2% Au	11.96	7.02	63.00	12.66	514	20.10
1% Pd_3% Au	15.03	12.60	54.40	15.81	522	29.05
1% Pd_4% Au	32.56	24.49	57.08	37.51	846	65.71
2% Pd_1% Au	22.85	21.77	51.22	25.68	984	50.15
3% Pd_1% Au	35.28	27.08	56.58	44.62	1141	78.88
4% Pd_1% Au	39.51	43.32	47.70	45.34	1025	95.07
3% Pd_2% Au	26.88	26.03	50.81	28.52	693	56.13
2% Pd_3% Au	21.98	16.99	56.41	24.36	570	43.18
2.5% Pd_2.5% Au	30.41	23.57	56.34	32.45	791	57.59

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Fig. 2. The effect(s) of increasing the amount of palladium on the catalytic activity of Pd_Au bimetalic catalysts supported on oxidized ACC; mass of catalyst = 56 mg, $T_{\text{reaction}} = 0 \,^{\circ}\text{C}$, and all catalysts calcined in air at 185 $\,^{\circ}\text{C}$.

increasing palladium from 1 to 2 wt% and from 2 to 3 wt%, the rate of H_2O_2 production, yield, productivity, and H_2 conversion jumped a lot (see exact values in Table 1). However, when increasing palladium from 3 to 4 wt%, these quantities did not change considerably. Indeed, the catalyst with 3 and 4 wt%Pd produced almost the same yields (see exact values in Table 1).

- When increasing the amount of palladium, the production rate of H₂O with the Pd–Au catalyst was also increased. However, when increasing palladium from 2 to 3 wt%, the rate did not change so much.
- Based on the results presented in Figs. 1–2 and Table 1, it can be said that the bimetallic catalysts with 1 wt% Au and ≥ 2 wt% Pd are more active (have higher yield and productivity) than the corresponding bimetallic catalysts with 1 wt% Pd and ≥ 2 wt% Au and Pd monometallic catalysts with same metal content.

In general, it can be concluded that increasing the amount of palladium in the Pd–Au bimetallic catalysts resulted in better activity but worse selectivity. Moreover, it should be mentioned that gold monometallic catalysts did not show any noticeable activity in direct synthesis of H_2O_2 .

3.1.3. Changing Au/Pd ratio with a constant total metal content

The effects of the Au/Pd ratio on the final performance of the Pd–Au bimetallic catalysts with constant total metal content (Pd + Au = 5 wt%) are presented in Fig. 3. It can be observed that:

- All Pd-Au catalysts with Au/Pd \geq 1 were more selective when compared to the 5 wt% Pd monometallic catalyst and the other bimetallic catalysts with Au/Pd < 1 (see exact values in Table 1).
- All Pd-Au bimetallic catalysts were more selective than the 5 wt%
 Pd monometallic catalyst when the reaction time was above 1.5 h.
- The bimetallic catalysts with Au/Pd < 1 were less selective when compared to the 5 wt% Pd monometallic catalyst when the reaction time was less than 1.5 h.
- The most selective one is the 2% Pd_3% Au bimetallic catalyst. However, it is also the least active catalyst. The rate of water production and H₂ conversion with this catalyst was considerably low when compared to the others (see exact values in Table 1).
- In the case of bimetallic catalysts, the 4% Pd_1% Au was substantially more active than the others (see exact values in Table 1). The rate of H_2O_2 and water production and consequently yield and H_2 conversion rate with this catalyst were considerably higher than with the others. However, it was the least selective one, especially when the reaction time was below 1.5 h.
- The second active catalyst was the one with 1 wt% of Pd and 4 wt% of Au. It was also one of the most selective ones. However, its activity was considerably less than the most active catalyst (4% Pd_1% Au).
- The third active catalyst was the one with 2.5 wt% of Pd and 2.5 wt% of Au. It was also one the most selective ones. Indeed, its selectivity was a little smaller than with the most selective catalyst (2% Pd_3% Au).

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Fig. 3. The effect(s) of the Pd/Au ratio on the catalytic activity of Pd.Au bimetallic catalysts supported on oxidized ACC with constant amount of metal content (Pd + Au = 5 wt%); mass of catalyst = 56 mg, $T_{\text{reaction}} = 0^{\circ}$ C and all catalysts calcined in air at 185 °C.

– The rate of water production and $\rm H_2$ conversion of the all the catalysts were almost the same, except with catalysts 4% Pd_1% Au and 2% Pd_3% Au.

3.1.4. Discussion

All of the catalysts presented in Figs. 1–3 were supported on the same carrier (oxidized ACC). Therefore, surface chemistry of the support is the same for all of them. However, different amount of the loaded metal could slightly affect the free available surface area of the support in the final catalyst (Table 2). Therefore, it can be concluded that the surface chemistry of the support cannot be main reason for the observed differences in the performance of different catalysts in Figs. 1–3.

Oxidation state of palladium and gold in the catalysts were determined by X-ray photo electron microscopy (XPS). XPS spectra of the presented bimetallic catalysts revealed that almost all of the

Table 2

The effect of impregnation of oxidized ACC with different amount of gold and palladium, on the specific surface area of the final bimetallic catalysts.

Oxidized ACC (OACC) 1550 (1% Pd.1% Au)/OACC 1521 (1% Pd.2% Au)/OACC 1480 (1% Pd.3% Au)/OACC 1468 (3% Pd.1% Au)/OACC 1424	Sample	$S_{N_2} (m^2 g^{-1})$
(1% Pd.1% Au)/OACC 1521 (1% Pd.2% Au)/OACC 1480 (1% Pd.3% Au)/OACC 1468 (3% Pd.1% Au)/OACC 1424	Oxidized ACC (OACC)	1550
(1% Pd.2% Au)/OACC 1480 (1% Pd.3% Au)/OACC 1468 (3% Pd.1% Au)/OACC 1424	(1% Pd_1% Au)/OACC	1521
(1% Pd_3% Au)/OACC 1468 (3% Pd_1% Au)/OACC 1424	(1% Pd_2% Au)/OACC	1480
(3% Pd_1% Au)/OACC 1424	(1% Pd_3% Au)/OACC	1468
((3% Pd_1% Au)/OACC	1424
(2.5% Pd_2.5% Au)/OACC 1397	(2.5% Pd_2.5% Au)/OACC	1397

palladium and gold were in zero-valent state or in metallic form (Pd^{0}) . However, traces of palladium were in the ionic form (Pd^{+2}) .

Ultra-High Resolution Field Emission Scanning Electron Microscope (UHRFESEM) images of the bimetallic catalysts with 1 wt% Pd and 1 wt% Au are presented in Fig. 4 (supplementary UHRFE-SEM images of different bimetallic catalysts were presented in the Supporting information (Figs. 3–5)). Based on the UHRFESEM images, the bimetallic catalysts consist of mainly small metal particles (Fig. 4b) with the size mostly 5–15 nm and also relatively big ones with different sizes in the order of 100 nm (Fig. 4a and c). All of them (small and big particles) are well dispersed in the support. Concerning the small metal particles, it can be said that:

- In the case of catalyst with 1 wt% Pd and 1 wt% Au, the size of small particles was mainly around 5 nm (Fig. 3a of Supporting information).
- When the amount of Pd was increased to 3 wt%, the size of the small particles was also increased to 10–15 nm. However, some particles with size 20–50 nm can be found (Fig. 4c and d of Supporting information).
- The catalyst with 1 wt% Pd and 3 wt% Au consist of considerable number of gold particles with different shape and the size mainly 20–50 nm (Fig. 5c and d of Supporting information). However, similar to the catalyst with 3 wt% Pd and 1 wt% Au, the small Pd particles were mostly 10–15 nm (Fig. 5e of Supporting information).

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Fig. 4. The ultra-high resolution field emission scanning electron microscopy (UHRFESEM) images (with different magnifications) of 1 wt% Pd_1 wt% Au catalyst supported on oxidized ACC with different magnification.

- Based on EDS analysis of UHRFESEM images, small particles consist of monometallic palladium and gold along with Pd–Au alloy particles.
- In the case of catalyst with 3 wt% Pd and 1 wt% Au, small particles mostly consist of monometallic Pd particles. However, in the case of catalyst with 1 wt% Pd and 3 wt% Au, the number of Au monometallic particles was considerable.

Dispersion of the metal particles could be related to surface chemistry of the oxidized ACC and the electrostatic interaction between the surface of ACC fibers and ionic gold and palladium in the precursors. Ionic gold (Au³⁺) in chloroauric acid (HAuCl₄) solution is mainly in the form of $(AuCl_4^{-})$ [44]. Ionic palladium (Pd^{2+}) in acidic solution of palladium dichloride (PdCl₂) appears mainly as tetrachloropalladic ion complex (PdCl₄^{2–}) [45]. Wet oxidation of activated carbon cloth (ACC) with nitric acid leads to formation of oxygen-containing functional groups on the surface of ACC fibers (see Section 3.3 for more detailed discussion). These acidic groups charged negatively the surface of ACC fibers. The electrostatic interaction (repulsion) between the metal precursors ($AuCl_4^{-}$, $PdCl_4^{2-}$) and the negatively charged surface of the oxidized ACC could result in good dispersion of metal precursors on the support surface. However, largely aggregated metallic particles (specially Au) were obtained principally due to the redox properties of activated carbon [46,47] In fact, the higher variety of activated carbon functionalities than those present on oxides (like silica and alumina) can promote other electrostatic interactions [46]. Concerning the big metal particles, it can be observed that:

 In the case of the catalyst with 1 wt% Pd and 1 wt% Au, the images with higher magnification of a big metal particle (Figs. 4c and 3b of Supporting information) and the Energy Dispersive X-ray Spectroscopy (EDS) analysis of STEM image of a Pd–Au particle (Fig. 5) reveal that these relatively round and big particles consist of a gold-rich core which was surrounded by a lot of small palladium particles. As a result, the outer surface of activated carbon cloth in 1% Pd_1% Au catalyst was changed to dark gray which is slightly lighter than the black color of the ACC. This pale gray color could possibly be assigned to the natural color of palladium.

- When increasing the amount of palladium, like in 3 wt% Pd_1 wt% Au bimetallic catalyst, the small Pd particles seemed to form a thicker and denser layer around the golden core. Therefore the Pd-Au particles on the outer surface of ACC fibers grew bigger (Fig. 4a and b of Supporting information).
- When the amount of gold was increased, like in 1 wt% Pd_3 wt% Au bimetallic catalyst, the round core-shell morphological Pd-Au particles were formed over bigger thin spots of gold (Fig. 5a and b of Supporting information). The round Pd-Au particles had almost the same morphology as the particles in 1% Pd_1% Au catalyst. The new morphology of Pd-Au particles was supported by EDS analysis of UHRFESEM images (Fig. 6). However, the changes of the color of the surface of the activated carbon cloth to pale yellow in the bimetallic catalysts with higher amount of gold can be seen.
- The morphology of the Pd–Au particles on the outer surface of ACC fibers in the 2.5 wt% Pd_2.5 wt% Au bimetallic catalyst looked almost the same as in 1 wt% Pd_3 wt% Au catalyst.
- The big Pd-Au particles formed on the outer surface of ACC fibers mainly consist of gold-rich core covered by small Pd particles with the size mostly less than 10 nm (Figs. 4c and 3b of Supporting information). Therefore, they could not be inactive. Indeed, it is assumed that Au acts as an electronic promoter for the Pd-rich shell [5,30,31].



Fig. 5. STEM-EDS mapping and analysis of a separated Pd_Au particle in the 1 wt%-1 wt% Au bimetallic catalyst; (a) STEM image, (b) Au map, and (c) Pd map.

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Fig. 6. STEM-EDS mapping and analysis of the 1 wt%_3 wt% Au bimetallic catalyst; (a) STEM image, (b) Au map, and (c) Pd map.

Based on the discussion above, it can be concluded that the morphology and size of the metal particles in the bimetallic catalysts are determined by the amount of palladium and gold and their ratio. Consequently, the different selectivities and activities of the Pd–Au catalysts presented in Figs. 1–3 could mostly be related to the different morphology and size of the metal particles.

3.2. The effects of the oxidation state of the loaded metal

In order to investigate the effects of the oxidation state of the metal components (Pd and Au), the catalysts supported on non-oxidized ACC were selected. In the case of oxidized ACC, the presence of the oxygen-containing surface functional groups also affected the final catalytic performance. Therefore, the results would reflect combined effect of different factors (surface chemistry of the support, oxidation state of the metal part ...). In the case of the non-oxidized ACC, lack of the oxygen-containing surface functional groups makes it possible to investigate merely the effects of the oxidation state of the metallic part of the catalysts.

The results of the catalytic activities of the different 3% Pd_1% Au bimetallic catalysts supported on non-oxidized ACC are presented in Table 3. One of the catalysts was calcined in air at 185 °C and, the other one at 275 °C. It can be observed that:

- The yield and H_2O_2 production rates demonstrate that the catalyst calcined at 275 °C is more active in H_2O_2 production than the other.
- However, the H₂ conversion and water production rates reveal that the catalyst calcined at 185 °C is more active in water production than the other.
- Therefore, the catalyst calcined at 275 °C is more selective (about 50%) than the other.

The X-ray photo electron microscopy spectra of the calcined 3% Pd_1% Au catalysts (Fig. 7 of Supporting information) revealed that:

 Palladium in the catalyst calcined at 185 °C was almost in zerovalent or in metallic state (Pd⁰) and only traces of the palladium were in the form of Pd^{+2} originated from palladium dichloride $PdCl_2$.

- When increasing the calcination temperature to 235 °C almost 8 wt% of the total amount of the palladium was oxidized to palladium oxide (PdO).
- In the catalyst calcined at 275 °C, almost 63 wt% of the total amount of palladium is in the form of palladium oxide. Therefore, increasing the calcination temperature increases the amount of palladium oxide.
- In the case of 1% Pd-4% Au bimetallic catalyst, when increasing the calcination temperature, the amount of PdO was substantially low compare to the corresponding calcined catalysts with 3% Pd and 1% Au. Indeed, in the 1% Pd.4% Au catalyst calcined at 275 °C, only 8% of the total amount of palladium was in the form of palladium oxide.
- In general, in the case of Pd–Au bimetallic catalysts with Au/Pd > 1, calcination at 235–275 °C resulted in smaller amount of palladium oxide than with Au/Pd \leq 1.
- Gold in all calcined catalyst was still in metallic or zero-valent state.

Based on the results and discussions above, it could be concluded that the presence of palladium oxide (PdO) made the Pd–Au bimetallic catalysts more selective and more active than the corresponding catalysts with Pd⁰.

Low amount of PdO in 1% Pd_4% Au catalyst calcined at 275 °C resulted in smaller differences in catalytic performance of the two catalysts calcined at 185 °C and 275 °C when compared to the corresponding differences observed for the 3% Pd_1% Au catalysts (Table 3).

3.3. The effects of the surface chemistry of the ACC fibers on the final catalytic performance and surface morphology of the Pd–Au bimetallic catalysts

The results of the catalytic performance of two bimetallic catalysts with different amounts of palladium and gold supported on

Table 3

The catalytic activity of the Pd–Au bimetallic catalysts supported on non-oxidized ACC and ACC oxidized with nitric acid after 2 h of the reaction time (in H₂O₂ direct synthesis). The catalysts calcined in air at 185–275 °C.

Catalyst	H ₂ O ₂ (mmol/L)	H ₂ O (mmol/L)	Selectivity (%)	Yield (%)	H ₂ Conversion (%)		
Catalysts supported on non-oxidized ACC							
3% Pd_1% Au, T _{cal} = 185 °C	23.49	57.41	29.04	26.64	91.73		
3% Pd_1% Au, T _{cal} = 275 °C	30.77	40.69	43.06	36.82	85.52		
1% Pd_4% Au, <i>T</i> _{cal} = 185 °C	20.45	37.00	35.72	23.15	65.11		
1% Pd_4% Au, $T_{cal} = 275 ^{\circ}\text{C}$	20.49	32.87	38.40	23.13	60.24		
Catalysts supported on oxidized ACC							
3% Pd_1% Au, <i>T</i> _{cal} = 185 °C	29.09	19.31	60.10	36.79	61.22		
1% Pd_4% Au, T_{cal} = 185 °C	24.19	17.03	58.69	33.30	47.47		

Table 4

Total amount of CO and \mbox{CO}_2 desorbed according to temperature programmed desorption test.

Sample	CO (µmol/g)	CO ₂ (µmol/g)
Non-oxidized ACC	115.13	82.73
Oxidized ACC (OACC)	1147.52	1290.44
3%Pd_1% Au/OACC (T _{red} = 185 °C)	1015.26	445.81
3%Pd_1% Au/OACC (T _{cal} = 185 °C)	1390.23	935.57
$3\%Pd_1\%$ Au/OACC ($T_{cal} = 235 \circ C$)	1483.51	742.43
3% Pd_1% Au/OACC ($T_{cal} = 270 \circ C$)	1569.35	529.53

non-oxidized ACC and ACC oxidized with nitric acid are presented in Table 3. It can be observed that:

- The catalysts supported on oxidized ACC were substantially more selective than the corresponding ones supported on nonoxidized ACC. In the case of the catalyst with 3 wt% Pd and 1 wt% Au, the catalyst supported on oxidized ACC was almost 2 times more selective than the corresponding one on non-oxidized ACC.
- According to the results of yield and rate of H₂O₂ production, the catalysts supported on oxidized ACC were also more active than the corresponding catalysts on non-oxidized ACC.
- H₂ conversion results and the rate of water production demonstrated that the catalysts supported on non-oxidized ACC were considerably more active in water production than the corresponding ones on the oxidized ACC.
- Almost similar results were observed for the other bimetallic catalysts presented in this paper. The only difference is that in the case of bimetallic catalysts with Au/Pd \geq 1, the differences between performances of the catalysts supported on oxidized ACC and non-oxidized ACC is smaller than the catalysts with Au/Pd < 1. This can be explained as, in general, with increasing the amount of Au, bimetallic catalysts become more selective and less active.

In our previous work [6], it was demonstrated that the oxidation pretreatment of activated carbon cloth (ACC) with nitric acid introduce considerable amounts of oxygen-containing functional groups on the surface of ACC fibers. These functional groups can be classified as strong acidic oxygen-containing groups (like carboxylic and anhydride groups) and weak acid ones (like lactones, phenols and carbonyl groups) [38-43]. These acidic functional groups affect a lot the activity and physicochemical properties of final catalysts [6]. The oxygen-containing functional groups can be characterized by thermal programmed desorption (TPD) test [6,38–41]. Strong and weak acidic oxygen-containing groups are responsible for CO₂ and CO desorption in TPD, respectively (Table 4). Different surface chemistry of the supports (Table 4) leads to different morphology in Pd-Au bimetallic catalysts supported on non-oxidize and oxidized ACC. The morphology of Pd-Au particles in the catalysts supported on oxidized ACC has been discussed in Section 3.1.4 In the case of non-oxidized ACC, palladium and gold form really big and joined particles at the outer surface of ACC fibers (Fig. 6 of Supporting information). In most areas, the metal particles almost cover the outer surface of the ACC fibers. These completely different surface morphologies result in different catalytic performance. The considerable surface morphology changes in the non-oxidized could be explained as follow.

It was mention earlier (Section 3.1.4) that the ionic gold (Au³⁺) and palladium (Pd²⁺) in acidic solution of hydrogen tetrachloroaurate (HAuCl₄) and palladium dichloride (PdCl₂) appear mainly as ion complexes (AuCl₄⁻ and PdCl₄²⁻). The pH of the precursors during the impregnation of the ACC was in the range of 3.5-4. According to isoelectric point measurements [6], the pH_{IEP} of the oxidized and non-oxidized ACC were 3.5 and 5, respectively. At pH below the pH_{IEP} the surface is negatively charged while at pH over the pH_{IEP}, the surface is positively charged. During the impregnation of non-oxidized ACC with gold and palladium precursor, the pH of the precursor is considerably less than pH_{IEP} of the surface of the ACC fibers. Therefore, the electrostatic attraction between the positively charged surface (pH < pH_{IEP}) and the catalyst precursor anions (AuCl₄⁻ and PdCl₄²⁻) facilitate the adsorption of ionic gold and palladium species (AuCl₄⁻ and PdCl₄²⁻) on the surface of the ACC fibers. Moreover, carbon is essentially not hydrophilic in nature and it has a very low affinity for solvents of polar character such as water [40]. Therefore, the metal precursors will be mostly exposed to the outer surface of the ACC fibers when using water. This factor together with electrostatic attraction between the surface of non-oxidized ACC and the catalyst precursor anions (AuCl₄⁻ and PdCl₄²⁻) leads to a rapid massive deposition of Au and Pd on the outer surface of ACC fibers.

Moreover, in the case of oxidized ACC, oxygen-containing surface functional groups might also affect directly the final performance of the catalysts. These acidic groups negatively charge the surface of activated carbon cloth [6] and decrease the hydrophobicity of the surface [40]. Therefore, the concentration of water on the surface of ACC's fibers and pores is higher in the oxidized ACC than in non-oxidized one. The affinity of the surface of oxidized ACC holding water molecules might also affect the final rate of water production by H_2O_2 decomposition/hydrogenation $(H_2O_2 \rightarrow H_2O + (1/2)O_2; H_2O_2 + H_2 \rightarrow 2H_2O)$ and non-selective H_2O synthesis $(H_2 + (1/2)O_2 \rightarrow H_2O)$, according to the Le Chatelier's principle.

3.4. The effects of heat treatment of the catalysts in H_2 and air at different temperatures

The results of the catalytic performance of the different 3% Pd_1% Au catalysts supported on oxidized ACC are presented in Fig. 7. It can be observed that:

- The catalysts calcined in the air at 185–275 °C were almost 3 times more selective than the catalyst reduced by H_2 at 185 °C.
- According to the results of yield and H₂O₂ production rate, the calcined catalysts were substantially more active in H₂O₂ production than the corresponding reduced one.
- The catalyst reduced by H₂ was dramatically more active in water production than the calcined catalysts.
- The catalyst calcined at 235 $^\circ C$ was considerably more active in H_2O_2 and also in water production than the other calcined catalysts.
- In the case of calcined catalysts, the catalyst calcined at 185 °C had the highest selectivity and, the one calcined at 235 °C had the lowest selectivity. However, the selectivities of the different calcined catalysts were quite close to each other.
- In the case of calcined catalysts, the catalyst calcined at 275 $^\circ\text{C}$ showed lower activity in H_2O_2 and water production than the other ones.
- Almost similar results were observed for the other bimetallic catalysts supported on oxidized ACC.

The ultra-high resolution field emission scanning electron microscope (UHRFESEM) images and EDS analysis confirmed that the heat treatment in H₂ at 185 °C and the calcination in air up to 275 °C had no noticeable effects on the morphology of the Pd–Au particles in the catalyst. However, the heat treatment of the oxidized ACC damages the oxygen-containing surface functional groups (Table 4). In the case of calcined catalysts, increasing the calcination temperature increased the damage, especially to the stronger acidic surface functional groups. These groups are responsible for CO₂ releasing in temperature programmed desorption (TPD) test (Table 4). Heat treatment of Pd–Au catalysts supported

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Fig. 7. The catalytic activity of the different 3 wt% Pd_1 wt% Au bimetallic catalysts on oxidized ACC; mass of catalyst = 56 mg, T_{reaction} = 0 °C.

on oxidized ACC by H_2 at 185 °C causes maximum damage to the stronger acidic oxygen functional groups (Table 4).

From the other side, increasing the calcination temperature increases the amount of PdO in the final catalyst (see Section 3.2). Based on the results and discussions in Sections 3.2 and 3.3, higher amount of palladium oxide in the catalyst and fewer damages to the surface functional groups (in the case of ACC oxidized with nitric acid) are favored for direct catalytic synthesis of H_2O_2 . Therefore, increasing the calcination temperature has two opposite effects, namely the damage to the oxygen-containing surface functional groups (Table 4) and increasing the amount of palladium oxide, and the resultant of these two effects mainly determine the different activities observed in Fig. 7.

In the case of the catalyst reduced by H_2 at 185 °C, it seems that the lack of palladium oxide and maximum damages to the oxygencontaining surface functional groups (Table 4) caused the catalyst to be considerably less selective and less active in H_2O_2 production and substantially more active in water production than the calcined catalysts.

4. Conclusions

The results showed that the surface morphology of the Pd–Au bimetallic catalysts and their catalytic performance in direct synthesis of H_2O_2 were highly influenced by the surface chemistry of the support and the amount and the ratio of Pd and Au in the catalyst.

Wet oxidation of activated carbon cloth (ACC) resulted in formation of oxygen-containing functional groups on the surfaces of ACC's fibers. These functional groups mainly control surface morphology, and consequently the selectivity and activity of the bimetallic catalysts in direct synthesis of H_2O_2 . The bimetallic catalysts supported on the oxidized ACC were substantially more selective and also more active in H_2O_2 production than the corresponding ones supported on non-oxidized ACC. However, the catalysts supported on non-oxidized ACC had high H_2 conversion since they were considerably more active in water production than the corresponding catalysts on oxidized ACC.

Almost all of the Pd–Au bimetallic catalysts were more selective than Pd monometallic catalysts. In the case of bimetallic catalysts:

- Increasing the amount of Au resulted in more selective but less active catalysts.
- Increasing the amount of Pd resulted in more active but less selective catalysts.
- Moreover, morphology of Pd-Au particles was also affected with the amount and ratio of gold and palladium in the catalysts.

The presence of palladium oxide made the catalysts more selective and active in H_2O_2 production but less active in water production than the corresponding catalysts consisting of zero-valent palladium (Pd⁰).

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Appendix A. Supplementary data

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