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(Article begins on next page)
Application of the Catalyst Wet Pretreatment Method (CWPM) for Catalytic Direct Synthesis of H$_2$O$_2$

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Abstract

This work concerns a new technique to post-modify the catalytic material intended for use in H$_2$O$_2$ direct synthesis. The catalyst chosen was a commercially available 1 wt.% Pd/C. The catalyst was modified with the so-called Catalyst Wet Pretreatment Method (CWPM) that is used to post-modify prepared catalysts with aqueous solutions of NaBr, in different concentrations. The performance of pristine and the pretreated materials were then compared in the H$_2$O$_2$ direct synthesis and characterized before and after the catalytic tests in order to understand the role of the different concentrations of bromide in the CWPM procedure. The surface features of the different catalysts were analyzed with CO chemisorption (metal dispersion and mean particle size), Transmission Electron Microscopy (TEM, for Pd morphology and Pd particle size distributions), Inductive Coupled Plasma (ICP, for Pd content) and Ion Chromatography (IC, for bromide content). Various features of the materials prepared with the CWPM were correlated with the catalytic performance.
It was found that the bromide has an active role in the reconstruction of metal phase and it does not only act as a poison for the most active catalytic sites as often reported in literature. By using this new protocol, the production H₂O₂ was almost doubled compared to the non-modified material when no direct promoters were added to the reaction environment.

Keywords: nanoparticles reconstruction, direct synthesis, catalyst wet pretreatment, palladium

1. Introduction

Catalytic direct synthesis of hydrogen peroxide (CDS) is a challenging reaction aiming at partially substituting the well-established auto-oxidation process [1-3]. Nowadays, the CDS is attracting both academia and industry hoping to enable in-situ production of peroxide and thus answer to the growing market for new important green and niche applications of hydrogen peroxide [4, 5]. The typical niche applications can be fine chemicals synthesis as well as cleaning of surfaces or semiconductors whereupon small amounts of ultrapure and diluted H₂O₂ is required [6]. The main problem of the direct synthesis is the parallel formation of water and the consecutive reactions that consume the just-formed H₂O₂ to produce water. These reactions impair the selectivity and thus the possibility of the CDS process commercialization. To successfully achieve the dream of CDS process to yield ultrapure H₂O₂, one has to pay attention to both on the reaction engineering aspects as well as the catalyst design [3]. In a recent work, the focus on catalyst design was coupled to the study of the different reactor types to achieve both high performance and high selectivity [1, 2]. However, the mainstream research on the H₂O₂ CDS process is still focused on the catalyst design [7-11] and on the understanding of the still unclear, real mechanisms behind this reaction [12, 13]. Palladium has been recognized as the most active metal for this process and is used as monometallic or bimetallic catalysts [14]. Bimetallic catalysts are usually based on Pd/Au and Pd/Pt materials. It has been proposed that the effect observed upon addition of the second metal (Au and
Pt) is not really catalytic and the role seems to be as an electronic modifier acting to diminish the activity of overly active sites that are responsible for the water formation [8, 14]. Palladium based mono- and bimetallic catalysts have been studied on different supports [7-11, 13, 15]. It is not completely clear how the interaction between the metal phase and the support affects the catalytic properties but our hypothesis is that the formation of water is minimized with precise combinations of Pd content and the nature of the support [14, 16]. Moreover, it is well known that the use of acids or halides as co-fed promoters in the reaction environment enhance the system performance in terms of $\text{H}_2\text{O}_2$ selectivity [17-23]. Anyway, the use of these promoters brings along series of drawbacks (e.g. corrosion) and they have to be removed in order to obtain a solution that can be used [3]. Nevertheless, despite numerous published papers concerning the use of these two promoters in CDS reaction, the real role of them is still unclear. Some hypotheses have been recently formulated also taking advantage of DFT calculations [16], but the experimental evidence is still missing.

The aim of this work was to try to understand the influence of the most active halide (bromide) on a commercial catalyst using a post-synthesis approach. The catalyst used for this new procedure was a commercially available 1 wt.% Pd/C catalyst. This procedure was not only aiming at improving the catalyst performance but also to shed light into the ‘halide-effect’ from the mechanistic point of view. For this reasons, modified catalysts with six different bromide-to-palladium molar ratios were prepared. The aqueous solutions from the treatment were analyzed to estimate the possible leaching of palladium or the sorption of bromide on the material whereas Transmission Electron Microscopy (TEM) analysis and CO chemisorption measurements were applied to investigate the modified morphological features of the metal phase, i.e. fresh, pre-treated and spent catalysts. It was found that the action of bromide during the so-called Catalyst Wet Pretreatment Method (CWPM) was not only connected to a reversible poisoning of the active sites (responsible for the water formation) as reported very often in literature, but it can participate for the modification of metal nanostructured phase too. Further on, we are discussing the possible suggestions and the hypothetical mechanisms
involved hopefully giving new insights on the H₂O₂ direct synthesis.

2. Experimental

2.1 Materials, methods and apparatus

A batch of 1 wt.% Pd/C (coded 1PdC) purchased by Sigma Aldrich was used as starting material. Sodium bromide was purchased from Fluka. 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; H₂, O₂ and CO₂ (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, H₂O ultrapure water (18.2 Mohm cm).

The ICP-OES measurements were carried out with a PerkinElmer, Optima 5300 DV according to the quantitative standard mode. Also, Karl Fisher titrations were carried out with a Titrino GP 736 from Metrohm.

The spent catalyst was recovered by filtration of the reaction mixture and dried at 383K overnight whereas the determination of the metal dispersion (D) in the present work was carried out by using the Autochem 2910 apparatus (Micrometrics). The metallic accessibility was determined by CO chemisorption using a pulsed technique. The catalyst (ca. 0.1 g) was heated in He (50 cm³/min) at 383 or 573K (10K/min) for 30 min, then was reduced by H₂ (50 cm³/min) for 1 h, flushed by He flow (50 cm³/min) at same temperature for 1 h and finally cooled to 298K before CO pulses. The stoichiometric ratio between Pd and CO was assumed to be unity. The mean particle size d₀ was calculated from metal surface area (MSA, m²/g metal) according to Hugues et al. [24], the nanoparticles were assimilated to cubes with one face in contact with the support. Consequently, the equation assumes the following form: \( d₀ (\text{nm}) = 5 \times 10^5 / (\text{MSA} \times \rho) \) where \( \rho \) is metal density (g cm⁻³). A reduction procedure at 573K led to high level of sintering on the spent catalysts. Since the aim of the work was to estimate the differences on the catalyst features of fresh, pre-treated and spent materials, 383K was chosen as good compromise to avoid sintering effects during the cleaning
stage. After the reduction step, some oxide surface can still be present on the catalyst (due to the low reduction temperature); notwithstanding, since the reduction steps were conducted at the same temperature to all the materials analyzed the effect of the oxide surface is assumed constant.

Electron micrographs were obtained by a Jeol 3010-UHR high resolution transmission electron microscope (HRTEM) operating at 300 kV equipped with a LaB₆ filament and with an Oxford Inca Energy TEM 300 EDS X-rays analyzer by Oxford Link. Digital micrographs were acquired by an Ultrascan 1000 camera and processed by Gatan digital micrograph. Before the experiments, the samples, in the form of powders, were milled in an agate mortar and deposited on a copper grid covered with a lacey carbon film. Moreover, a statistical evaluation of the size of the Pd particles was carried out for each material. Histograms of the particle size distribution were obtained by considering at least 1650 particles on the TEM images, and the mean particle diameter ($d_m$) was calculated as $d_m = \Sigma d_i n_i / \Sigma n_i$, where $n_i$ was the number of particles of diameter $d_i$. The counting was carried out on electron micrographs acquired starting from 40,000 magnification, where Pd particles well contrasted with respect to the carbon support were clearly detected.

The bromide content in mother liquors of the pre-treatments and reaction mixtures were analyzed by ionic chromatography (IC). The instrument used was a Metrohm Ion Chromatography System composed by detector mod. 732 IC, separation center mod. 820 IC, interface mod. 830 IC, pump mod. 818 IC.

2.2 Wet pretreatment on 1 wt.% Pd/C catalyst

The wet pre-treatment of the catalyst was performed with aqueous solutions of sodium bromide on a 1%Pd/C catalyst sample (1PdC). Two diluted solutions (1.22 and 12.5 mM) were prepared to obtain the following Br-to-Pd molar ratios: 0.01, 0.06, 0.15, 0.25, 0.80 and 1.40, respectively. The catalysts pretreated with this procedure were then coded as pB001, pB006, pB015, pB025, pB080 and pB140 (where p denotes ‘pretreatment’, B ‘bromide’ and the numbers 001, 006, 015 etc… the Br-to-Pd molar ratio). Typically, 1.0 g of the pristine catalyst 1PdC was suspended in 15 cm³ of
water. The modifier was then introduced adding precise aliquot of one of the two starting aqueous solutions (1.22 or 12.5 mM) and the mixture let in stirring for 2 hours. The final volume of pretreatment was always adjusted to 30 cm$^3$. The solids were recovered by vacuum filtration and carefully washed on a buchner filter with water (5 x 5 cm$^3$). The mother liquors of the pretreatments were concentrated and analyzed by IC to estimate the amount of bromide. Consequently, the solids were dried in an oven at 383K overnight. About 50 mg of all the catalysts obtained with the above mentioned procedures were mineralized and the palladium content analyzed by ICP-OES.

2.5 Catalytic tests

Catalytic tests were carried out in a 600 cm$^3$ 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.

In order to test each catalyst, the autoclave was charged with the catalyst (0.15 g) and flushed four times with 3 bars of carbon dioxide. Then CO$_2$ (20.2 bar) and O$_2$ (6 bar) were fed directly from the cylinders at 298K, followed by introduction of 420 cm$^3$ ($V_L$) of methanol by means of an HPLC pump, at room temperature. The temperature was allowed to decrease to 275K, followed by stirring and recirculation (1000 rpm and 20 cm$^3$/min, respectively). After the stabilization of the pressure and the temperature (i.e. 275K), both the stirrer and the pump were switched off and H$_2$ was fed up to the desired amount. Hydrogen was always the limiting reagent and its partial pressure was always kept low enough to reside below the lower explosion and flammability limit of the system containing CO$_2$, O$_2$, H$_2$ and MeOH. The hydrogen amount introduced into the reactor ($n_{H_2,0}$) was calculated from the difference of hydrogen pressure in the pre-cylinder. Thus, the molar composition of the gases was 3.5 % H$_2$, 21.5 % O$_2$ and 75 % CO$_2$, respectively. Small samples of
reaction mixture for the analysis of the products were regularly taken and the concentration of H₂O₂ and H₂O were determined by iodometric and Karl Fischer titrations, respectively. The initial concentration of water, [H₂O]₀, 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, [H₂O]:

\[ [H_2O] = [H_2O]^' - [H_2O]_0 \]

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 at time \( t \) (\( C (\%)_{H_2,i} \)):

\[ C (\%)_{H_2,i} = 100 \cdot \{ [H_2O_2]_i + [H_2O]_i \} \cdot V_L / n_{H_2,0} \]

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

\[ S (\%)_{H_2O_2,i} = 100 \cdot [H_2O_2]_i / \{ [H_2O_2]_i + [H_2O]_i \} \]

The solids (spent catalysts) were recovered by vacuum filtration, carefully washed on a filter with methanol (5 x 5 cm³) and dried at 383K overnight. The dried materials were mineralized and the palladium content was analyzed by ICP-OES. The methanol was removed from the mother liquors of the reaction mixtures by evaporation and the aqueous solutions obtained were analyzed by IC to estimate the amount of bromide leached. \( \Delta \% \) is the defined as: \((V_f - V_i)/V_i \times 100\) where \( V_f \) is the inal value and \( V_i \) the initial value of the features measured.

3. Results and discussion

3.1 Catalyst Characterization
3.1.1 Features of metal nanostructured phase

ICP analysis on the fresh catalyst (pristine one) showed that the pretreatments using the so-called Catalyst Wet Pretreatment Method (CWPM) did not lead to a relevant leaching of palladium (Table 1).

Table 1: ICP results: relative differences reported as Δ mol.% Pd, calculated between experimental value of Pd content in fresh material and values of Pd leaching after pretreatment (1st column) and between the Pd leaching after pretreatment and the spent catalyst. Key: 1PdC is the 1 wt.% Pd/C, pB001, pB006, pB015, pB025, pB080 and pB140 (where p=pretreatment, B=bromide and 001, 006, 015 etc…= Br/Pd molar ratio).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Δ mol.% Pd fresh/pretreated</th>
<th>BR/AR*</th>
</tr>
</thead>
<tbody>
<tr>
<td>1PdC</td>
<td>//</td>
<td>-30</td>
</tr>
<tr>
<td>1PdC pB001</td>
<td>-2</td>
<td>-36</td>
</tr>
<tr>
<td>1PdC pB006</td>
<td>-8</td>
<td>-31</td>
</tr>
<tr>
<td>1PdC pB015</td>
<td>-26</td>
<td>0</td>
</tr>
<tr>
<td>1PdC pB025</td>
<td>-9</td>
<td>-32</td>
</tr>
<tr>
<td>1PdC pB080</td>
<td>-1</td>
<td>-34</td>
</tr>
<tr>
<td>1PdC pB140</td>
<td>-3</td>
<td>-23</td>
</tr>
</tbody>
</table>

*BR= before reaction, AR= after reaction

Indeed, it was found that the Pd leaching after the pretreatment was mainly between 2 and 10 mol.%. Only in the case of the catalyst pretreated with a Br-to-Pd molar ratio of 0.15 (pB015 sample), a more pronounced leaching could be observed (26 mol.%). The loss of palladium content in the catalysts before and after catalytic test was pretty much constant. In almost all the cases the loss in palladium after the CDS was around 30 mol.%. Only in the case of the catalyst treated with a Br-to-Pd ratio of 0.15 (pB015), the palladium content remained unaltered before and after the CDS reaction. Interestingly, the palladium leaching seemed not to be dependent on the bromide content. These results were coupled with the TEM analysis as well as the CO chemisorption to understand if there was a relation between the quantity of bromide used and the change of the nanoparticles features.
Firstly, in order to evaluate the effect of bromide content on the Pd dispersion, TEM measurements have been carried out on 1PdC (Figure S1), 1PdC pB001 (Figure S2), 1PdC pB006 (Figure S3) and 1PdC pB080 fresh catalysts. Due to the large contrast phase between the carbon and the metal, palladium is easily recognizable on this support as can be seen in Figure 1, sections a-c, where some representative images taken on 1PdC pB080 are shown. In all cases, very small roundish nanoparticles with size around 2 nm (section a), globular nanoparticles with diameter ranging between 5 and 20 nm (section b), big particles with size 60-90 nm and some particles agglomerates (section c) have been observed, pointing out a quite heterogeneous Pd dispersion.

However, looking at the Pd particles size distributions obtained on all examined samples (see Figure 2), the presence of different relative amounts of these Pd species on each sample can be deduced. This feature is an indication that an effect of the CWPM, depending on the Pd/Br ratio, on the morphology of the initial population of Pd particles is occurring. Indeed, small, roundish particles with diameter ranging from 2.5 to 15 nm as well as particles agglomerates and big particles of 30-100 nm were detected when analyzing the 1PdC commercial catalyst (data not shown here for the sake of brevity, see Figure S1). The CWPM induced a strong modification on the Pd particles in terms of size distribution when the Pd-to-Br ratio is 001: a large fraction of particles has a diameter of 2.5 nm (more than 40 n.p.%), being the majority with size below 10 nm. Pd particles with size ranging from this value up to 30 nm have been observed. In this case, the pretreatment with Br provoked a general decrease in the size of Pd particles (see Figure S2) as also put in evidence by the particle size distribution obtained for the 1PdC pB001 sample reported in section b of Figure 2.
Figure 1: TEM images taken on 1PdC pB080: small roundish nanoparticles (section a), globular nanoparticles (section b), big particles and particles agglomerates (section c). Instrumental magnification: 150000X, 100000X and 50000X, respectively.
This effect has been observed, but in minor extent, on both 1PdC pB006 (see Figure S3) and 1PdC pB080 catalysts, and in these cases the population of Pd particles with size around 2.5 nm reaches 15 and about 10 n.p. %, respectively, being the majority of the particles with diameter of about 5 nm, as shown in section c and d of Figure 2.

Figure 2: Pd particle size distributions obtained for 1PdC (section a), 1PdC pB001 (section b), 1PdC pB006 (section c) and 1PdC pB080 (section d) fresh catalysts.

Moreover, by assuming that all Pd particles have spherical shape, the ‘theoretical’ metal specific surface areas (SSA) were calculated, by applying the formula SSA = 3 \( \Sigma n_i r_i^2 / (\rho_{Pd} \Sigma n_i r_i^3) \) m\(^2\)/g, where \( r_i \) was the mean radius of the size class containing \( n_i \) particles, and \( \rho_{Pd} \) the volumetric mass of
Pd (12.02 g/cm³). The obtained Pd SSA are reported in Table 2 together with the average sizes. Due to the high heterogeneity observed in Pd dispersion, the reported values have to be taken as indicative ones.

Table 2: Pd Specific Surface Area (SSA) obtained from TEM analysis on the fresh catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(Indicative) average particle diameter (nm)</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fresh*</td>
<td>Fresh</td>
</tr>
<tr>
<td>1PdC</td>
<td>171.9</td>
<td>9.7</td>
</tr>
<tr>
<td>1PdC pB001</td>
<td>43.0</td>
<td>8.1</td>
</tr>
<tr>
<td>1PdC pB006</td>
<td>83.4</td>
<td>8.7</td>
</tr>
<tr>
<td>1PdC pB080</td>
<td>125</td>
<td>6.8</td>
</tr>
</tbody>
</table>

*not pretreated samples

The data further confirm that the pretreatment with bromide a restructuring of the Pd nanoparticles occurs. A sintering is observed in all treated materials and a correlation between the Pd-to-Br ratio and and the decrease of SSA is observed. In addition, CO chemisorption measurement were not used to estimate the metal nanoparticle size but to estimate the Pd(0) centres present on the catalysts surface with the aim to show, if any, change in surface features. A cleaning (reducing) procedure at low temperature (383K) was applied to remove the surface oxide avoiding any rearrangement of metal nanostructures. This procedure is surely unable to completely reduce the oxidized Pd centres, leaving a small portion of residual surface oxide. Indeed in literature it is reported that the complete reduction of Pd catalysts happens with temperature over the 523K [25]. A test at 573K was performed for comparison with the measurement at 383K and the results were reported in the Table 3.

Table 3: Data from CO chemisorption obtained on 1PdC with low and high temperature of reduction (cleaning).

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Dispersion (%)</th>
<th>Metal surface area (m²/g)</th>
<th>Diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>573</td>
<td>57.2</td>
<td>254.8</td>
<td>1.6</td>
</tr>
<tr>
<td>383</td>
<td>39.2</td>
<td>174.8</td>
<td>2.4</td>
</tr>
</tbody>
</table>
Using as model a Pd$_{561}$ nanoparticle with cuboctahedric geometry, a shape commonly diffused for palladium in literature[26, 27], a mean diameter of 2.5 nm was obtained, that corresponds to 51% of the dispersion at 383K, quite similar to the results reported for the material cleaned by H$_2$ at 573K (Table 3). Most probably the two temperatures used produced a different surface cleaning. The lowest temperature is not able to reduce all the Pd centers resulting in a decreasing of dispersion that avoids the sintering noticed in the procedure at 573 K. Although the milder cleaning procedure leaves a small amount of un-reduced Pd(II) centers on the catalyst surface, the aim of CO chemisorption in this work was the assessment of the difference in Metallic Surface Area (MSA) between all the materials (pristine, pretreated and spent catalysts) to point out the modifications of the (reduced) catalyst surface. Thus the CO chemisorption was chosen as a probe for estimating the reduced surface of metal nanostructured phase. In agreement with the TEM findings, the CO chemisorption results clearly show that the pretreatment with bromide is able to change the features of metal phase like the metallic surface area (MSA) of the metal nanoparticles. The values of the MSA variation between the fresh and pretreated (4th column - Table 4) varied between 50 and 70 %, clearly indicating that the concentration of bromide did not significantly influenced this parameter.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Metallic Surface Area (m$^2$/g metal)</th>
<th>Δ MSA (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Pretreated</td>
<td>Spent</td>
</tr>
<tr>
<td>1PdC</td>
<td>174.8*</td>
<td>56.3</td>
</tr>
<tr>
<td>1PdC pB001</td>
<td>75.1</td>
<td>38.9</td>
</tr>
<tr>
<td>1PdC pB006</td>
<td>51.2</td>
<td>29.3</td>
</tr>
<tr>
<td>1PdC pB015</td>
<td>60.9</td>
<td>30.3</td>
</tr>
<tr>
<td>1PdC pB025</td>
<td>59.6</td>
<td>37.4</td>
</tr>
<tr>
<td>1PdC pB080</td>
<td>89.4</td>
<td>50.6</td>
</tr>
<tr>
<td>1PdC pB140</td>
<td>91.2</td>
<td>42.1</td>
</tr>
</tbody>
</table>

Table 4: Results of metallic surface area (MSA) by CO chemisorption on fresh, pretreated and spent catalysts and their variation compared to the value of fresh material. Key: 1PdC is the 1%PdC, pB001, pB006, pB015, pB025, pB080 and pB140 (where p=pretreatment, B=bromide and 001, 006, 015 etc…= Br/Pd molar ratio)
Anyway, all the variations are negative, showing that during the pretreatment, the bromide clearly contributed to the restructuring of the Pd nanoparticles. Moreover, the Pd SSA obtained from TEM analyses (2nd column - Table 2) display the same trend observed for the MSA calculated from CO chemisorption results (see Table 4, 2nd column): a decrease in the metal surface area is observed in both case upon bromide pretreatment. The differences observed in the Pd surface area obtained by TEM and CO chemisorption can be explained by taking into account on one hand, the presence of very highly dispersed Pd particles escaping from the microscope detection, and on the other hand, the presence of Pd sites not completely reduced.

It is not an objective of this work to understand which mechanism works, but the reduction of metallic surface area deduced by TEM and CO chemisorption findings lead to hypothesize that the sintering can mainly be present during the restructuring process. The values of the MSA variation between spent pretreated catalysts and the spent non-pretreated one (last column – Table 4) were in the range of 10 to 50 %. The results indicated that the modified catalysts were more stable during the catalytic tests and, consequently did not undergo to structural changes as the non-modified 1PdC catalyst. This can be clearly observed comparing MSA variation between the couples Fresh-Spent and Pretreated-Spent (last two columns – Table 4). The interpretation of these results can explain how the CDS reaction plays a role in the restructuring of the nanoparticles when the catalysts were not subject to a priori modification (CWPM). These results support the hypothesis that one of the possible role of the bromide during the pretreatment (and also when added in the reaction environment) was to participate to the restructuring of the metal phase, thus giving rise to higher selectivity and \( \text{H}_2\text{O}_2 \) productivity during the CDS. The difference between the fresh and the spent catalysts are reported in Table 4 and Figure 3, respectively.

Upon, an increased bromide/palladium molar ratio the MSA variations on the palladium nanoparticles followed a well--plot (Figure 3). Thus, this indicates that the amount of bromide during the pretreatment influenced actively the restructuring of the metal phase (i.e. the MSA) in a non-linear way. It is interesting to note that the average MSA for the spent modified catalysts were
always lower compared to the pristine/pretreated catalysts (fresh and spent, Figure 3) and that the trend was similar to the one of the fresh/pretreated modified catalysts. Consequently, this indicates that the direct synthesis of H$_2$O$_2$ has an important role in the change of the morphological aspects of the metal phase as well. Evidently, bromide in wet condition works in the structural reorganization of the metal nanoparticles when used as an additive.

![Figure 3: Metallic surface area by CO chemisorption vs. the bromide-to-palladium molar ratio used in the pretreatment.](image)

- fresh/pretreated catalysts and Δ spent catalyst (after the reaction).

The observations that need particular attention are as follows: 1) the total Pd leaching was generally high and corresponded to about 30 mol.%; 2) the mean difference in terms of MSA between the fresh and spent catalysts was around 60 % and; 3) the amount of bromide is an important parameter influencing the variation of the nanoparticle size. Further, the amount of bromide absorbed by the catalyst during the wet treatment and the bromide released during the reaction has to be quantified in order to understand its possible role during the CDS (see Figure 4 in the next section).

### 3.1.2 Bromide content analysis
The bromide content measured with Ion Chromatography. The analyses pointed out that the bromide amount adsorbed by the catalyst increased almost linearly with the amount of bromide used in the pretreatments, as can be seen in Figure 4. Interestingly, the bromide released during the direct synthesis reaction was pretty constant during all experiments corresponding to $1 \times 10^{-6}$ moles. This indicates that the release of the bromide was independent from the quantity of Br absorbed during the pretreatments. However, since the bromide content was very low, quantification of it on the catalyst surface was not possible. EDS analysis performed on both fresh and spent 1PdC pB001 and 1PdC B080 catalysts did not reveal any peak related to the presence of Br in the composition, with the exception of 1PdC pB080 fresh sample, where the bromide amount is the highest. However, the intensity of the peak is very low and it was not possible to do any quantification. Consequently, it was impossible to clearly determine whether bromide was adsorbed on the metal nanoparticles or on the support and how large fraction of bromide was shared by the support and the metal nanoparticles.

**Figure 4:** Amount of adsorbed bromide by the catalyst during pretreatments and released by the same catalyst during the reaction vs. the bromide-to-palladium molar ratio used in the pretreatment. ▲ amount of bromide used in the pretreatments; ♦ amount of bromide absorbed by the catalyst during the pretreatments; X amount of bromide released by the catalyst during the CDS reaction.
What was clearly seen was that the palladium leaching and the bromide release detected were pretty much constant during the CDS reaction (i.e. palladium leaching around 30 mol.% \((4\times 10^{-6})\) moles and bromide release \(1\times 10^{-6}\) moles). Probably the release of the bromide and the palladium leaching were regulated by the same phenomena since they did not depend on the amount of bromide used upon modifications. An interpretation can be that the bromide works as ligand on the palladium(II) surface sites and, consequently, during the reaction a palladium-bromide complex is released. The bromide held on the catalyst is the one absorbed most probably by the support. This interpretation takes into account the possible role of support which can absorb the additive and the carbon support regulates the release of the bromide during the catalytic test. Thus the release of low amount of halide and CDS can work together on the in situ restructuring of metal phase. This hypothesis is plausible since the amount of halide in the reaction medium remained constant for all the experiments (Figure 4). Unfortunately, the mechanisms for the palladium leaching, the bromide release and their possible synergic effect are still unclear. In conclusion, the pretreatment with bromide produce a modification of the metal phase through its restructuring, showed by the change of surface proprieties. The bromide/Pd molar is an important parameter which played an effective role on the modification mechanism of Pd nanoparticles. The palladium leaching and the mild release of the bromide during the reaction are tangible individual phenomena that may probably cooperate in the restructuring of Pd nanoparticles.

### 3.2 CDS activity results

The results for the H\(_2\)O\(_2\) direct synthesis are reported in Figures 5, 6, 7 and 8. Figures 5 and 6 report the concentration of H\(_2\)O\(_2\) and H\(_2\)O produced during the first 180 minutes of reaction, respectively. Figure 7 depicts the selectivity towards H\(_2\)O\(_2\) during the same reaction time while the Figure 8 reports the H\(_2\) conversion in order to estimate the catalytic activity. The catalysts monitored were
pristine 1PdC and modified materials with different molar ratios of Br-to-Pd coded as before. In terms of H₂O₂ concentration, the catalyst with the Br-to-Pd molar ratio of 0.01 (i.e. the catalyst pretreated with the lowest amount of bromide) showed the lowest activity, even outperformed by the pristine 1PdC catalyst. When increasing the Br-to-Pd ratio to higher values (0.06 to 0.15), the activity of the H₂O₂ production seems to be similar to the pristine catalyst. The highest Br-to-Pd molar ratios to (0.25, 0.80 and 1.40) almost doubled the H₂O₂ concentration. The H₂O formation followed an opposite behavior as the lowest Br-to-Pd molar ratios gave rise to the highest concentrations of H₂O. The H₂ conversion followed the same trend as the production of water. The catalysts with the higher activity (i.e. highest rate of H₂ conversion) were the catalysts with the Br-to-Pd ratio of 0.01 and 0.06, respectively, while the other catalysts demonstrate rather similar trends (including the 1PdC). The selectivity is one of the most important parameter for the CDS and when observing the Figure 6 one can obviously conclude the following: the selectivity increased when the Br-to-Pd molar ratio increased. Further, the selectivity behavior followed the order, pB001 < pB006 < pB015 ≈ 1PdC < pB025 < pB080 ≈ pB140. It is interesting to observe that the pristine 1PdC catalyst showed similar activity and behavior concerning the H₂O₂ and H₂O production, selectivity and H₂ conversion as the sample with the Br-to-Pd molar ratio of 0.15 (i.e. pB015).

![Figure 5: H₂O₂ production during the batch experiments at 20 bar and 275K: * 1PdC, ○ 1PdC pB001, ■ 1PdC pB006, ▲ 1PdC pB006, ▲ 1PdC pB015, ▲ 1PdC pB025, ▲ 1PdC pB080, ▲ 1PdC pB140.](image-url)
X 1PdC pB015, ▲ 1PdC pB025, + 1PdC pB080 and ♦ 1PdC pB140. Key: 1PdC is the 1 wt.% Pd/C, pB001, pB006, pB015, pB025, pB080 and pB140 (where p=pretreatment, B=bromide and 001, 006, 015 etc. denotes the Br-to-Pd molar ratio).

**Figure 6:** \( \text{H}_2\text{O} \) production during the batch experiments at 20 bar and 275K: * 1PdC, ● 1PdC pB001, ■ 1PdC pB006, X 1PdC pB015, ▲ 1PdC pB025, + 1PdC pB080 and ♦ 1PdC pB140. Key as in figure 4.

**Figure 7:** \( \text{H}_2\text{O}_2 \) selectivity during the batch experiments at 20 bar and 275K: * 1PdC, ● 1PdC pB001, ■ 1PdC pB006, X 1PdC pB015, ▲ 1PdC pB025, + 1PdC pB080 and ♦ 1PdC pB140. Key as in figure 4.
Figure 8: H₂ conversion during the batch experiments at 20 bar and 275K: * 1PdC, ● 1PdC pB001, ■ 1PdC pB006, ▲ 1PdC pB015, ▲ 1PdC pB025, + 1PdC pB080 and ● 1PdC pB140. Key as in figure 4.

3.3 Interpretation of the catalysts features coupled to the catalytic activity data

The modifications due to the Br-to-Pd molar ratios of 0.01 or 0.06 pretreatment gave rise to a decrease in metallic surface area of the metal nanoparticles and was obtained the lowest selectivity and H₂O₂ production compared to the pristine 1PdC. However, these pretreatments enhanced the activity as can be observed from the H₂ conversion results. Looking at the Pd particle size distributions reported in Figure 2, sections b and c, the samples with Br-to-Pd molar ratios of 0.01 and 0.06 are those containing the higher amounts of particles with size well below 5 nm if compared to the other systems. It can be proposed [28] that the very small Pd particles expose at their surface more energetic sites that are able to chemisorb and dissociate both hydrogen peroxide and oxygen. The presence of chemisorbed hydrogen will lead to the formation of water either directly by reaction with oxygen atoms or by reaction with OH fragments coming from H₂O₂. Therefore, the selectivity on these catalysts is low. On the contrary, the presence of less energetic Pd sites exposed at the surface of the particles with larger average diameter (> 5 nm) can chemisorb molecular oxygen without dissociating it, giving the H₂O₂ product. This can occur on the 1PdC
B006 and 1PdC B080 catalysts, where a greater number of Pd particles with diameter > 5 nm has been observed (Figure 2, sections c and d, respectively).

The Br\textsuperscript{−} content in the solution during the Catalyst Wet Pretreatment Method (CWPM) was very low. First of all, the small amount of bromide does not act as a poison on the catalyst surface since the H\textsubscript{2} conversion was faster in the samples pretreated with a Br-to-Pd molar ratios of 0.01 and 0.06 compared to the other samples. Moreover, the TEM and CO chemisorption results clearly showed that the bromide participates in the restructuring of the palladium nanoparticles. Since H\textsubscript{2}O production under these conditions was favored compared to H\textsubscript{2}O\textsubscript{2} production, it is possible to state that the bromide in very small Br-to-Pd molar ratios works more as modifier of metal-nanoparticle structure than a poison of the most active sites thus rendering the nanoparticle surface more favorable towards the combustion of H\textsubscript{2} to produce water. Probably, since the consumption of hydrogen in these cases was faster compared to the 1PdC sample, it is possible to state that the bromide was not absorbed on the catalyst surface to block the active sites responsible for the H\textsubscript{2} combustion or for the H\textsubscript{2}O\textsubscript{2} production.

The catalyst with the Br-to-Pd molar ratio of 0.15 (CWPM) gave similar results in terms of H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O production compared to the ones obtained by the pristine 1PdC catalyst. H\textsubscript{2} conversion and selectivity were pretty much equal for these catalysts (i.e. 1PdC and the sample with the Br-to-Pd molar ratio of 0.15). Nevertheless, it is more difficult to deduce what happened since the MSA of the nanoparticles were different for the modified catalyst (i.e. pB015) and the pristine 1PdC. Different effects can be hypothesized upon this CWPM approach: 1) bromide can assist in the restructuring of the metal phase as shown by TEM and CO chemisorption results; 2) bromide can work as a remover of surface oxidized palladium sites – a sort of “scrubber” that produces the Pd leaching; and 3) bromide can be a reversible poison for the most active sites on the palladium nanoparticles (H\textsubscript{2} conversion), especially those responsible for H\textsubscript{2} combustion. Anyhow, probably all the above effects co-exist thus resulting in H\textsubscript{2}O\textsubscript{2} and H\textsubscript{2}O production profiles similar to that of the modified material and pristine 1PdC. The last analysis of the data concerns the catalysts with the
Br-to-Pd molar ratio of 0.25, 0.80 and 1.40, respectively. The results can be coupled together for the characterization since the catalyst activity, selectivity and \( \text{H}_2\text{O}_2 \) or \( \text{H}_2\text{O} \) production were of the same magnitude of order and higher compared to the earlier cases. The MSA measured by CO chemisorption showed to be between 59 and 92 \( \text{m}^2/\text{g} \) for the freshly pretreated materials while for the spent catalysts they were between 37 and 51 \( \text{m}^2/\text{g} \). These modification due to CWPM approach with different Br-to-Pd molar ratios showed overall activities similar to the pristine catalyst but the reaction route shifted from \( \text{H}_2 \) combustion (to produce water) to \( \text{H}_2\text{O}_2 \) production due to the restructuring of the metal phase. Moreover, the release of bromide from the materials during the catalytic runs was comparable to the previously cited cases, indicating that most probably this release was due to adsorbed bromide inside the porous support (unfortunately this hypothesis is not verifiable because the carbon support used for this catalyst is not commercially available). Also the palladium leaching was similar to the previous cases and thus all observations indicate that the CWPM method produced the different modifications on the metal nanoparticle leading to different catalytic effects on the direct synthesis.

The pristine 1PdC catalyst demonstrated unfavorable metal phase reconstruction during the CDS, while the reconstruction of the metal phase on the modified catalysts was uniform (i.e. the MSA). It is clear that the reaction itself promotes a very high reconstruction tendency, particularly in the case of the pristine material, while the reconstruction was less pronounced when the catalysts were modified with the CWPM approach. It seems that one of the roles of the bromide is to minimize the variations occurring in the palladium nanoparticles size during the course of the reaction, as shown by the comparison among the Pd particle size distributions of the fresh and spent 1PdC B001 and 1PdC B006 80 catalysts (Figure S4).

Thus, we have shown that upon pretreatments with the Br-to-Pd molar ratio of 0.25, 0.80 and 1.40, respectively, the activity of the catalysts was comparable to the pristine material, but the selectivity and the \( \text{H}_2\text{O}_2 \) production were enhanced.

In general, the following conclusions can be drawn from the results of the bromide modification: 1)
bromide works surely as metal surface modifier, probably a sort of “scrubber” of surface Pd(II) centers; 2) restructuring agent of metal nanoparticles involving a reduction of metallic surface area. 3) In principle it is not possible completely to discard the effect as poisoner on the catalyst surface, as largely reported in literature [22, 23, 29], but this work rises that the site-blocking effect is very less important than the other two aspects reported. All these findings obtained by CWPM approach are fundamental to develop new potential catalysts for CDS and other hydrogenation reaction as well. Consequently, it is clear that the role of the bromide is more than acting as a simple poison of the catalyst surface. In previous works [20, 22, 23] the effect of the bromide was analyzed only adding the halide directly to the reaction environment and assuming that the bromide was working as a poison only for the most active sites responsible for water production [22]. Moreover, the authors tried to analyze the effect of the adsorption of the bromide during the CDS reaction indicating that the bromide was absorbed by the catalyst [22]. Some attempts were made pretreating only the support with halides before the preparation of catalyst by impregnation and the conclusion was that the bromide acted a selective poison for the sites responsible for H2O2 hydrogenation [30, 31]. Here we demonstrated with a combinatorial use of different techniques that the real role of the bromide is more complex than acting as a poison for H2 combustion sites only. Despite this, the mechanism is still unclear, new insights for discovering the real role of the bromide, in the complex reaction environment prevailing during CDS, were achieved. Moreover, it was demonstrated that the CWPM approach can be a useful and a successful technique to modify the catalyst properties, also tackling the important problems connected to the use of halides in the reaction environment (i.e. the quality of product and corrosions in plants).

4. Conclusions

The main achievements of this work are related to a new procedure called Catalyst Wet Pretreatment Method (CWPM) used to modify catalysts properties under wet conditions. This new
procedure is handy upon fine-tuning and tailoring the catalysts for various changeling hydrogenations reactions as in the case of H₂O₂ direct synthesis. Further, in this work new ideas concerning the real role of the bromide in the CDS were proposed. Indeed, it was shown that the bromide does not mainly act as a poison for the most active sites on the palladium based catalysts but also works actively in the morphological restructuring of the metal phase. In particular, it was seen that the Br-to-Pd molar ratio is an important parameter involving important modifications on the structure of the metal phase. The morphological and catalytic features of the different pretreated materials on basis of CWPM method can be summarized as: 1) treatment with the Br-to-Pd molar ratios of 0.01 and 0.06 promoted a remarkable reduction of metallic surface area (MSA) and minimal Pd leaching involving an enhance of overall catalytic activity but detrimental for selectivity; 2) treatment with Br-to-Pd ratio of 0.15 promoted a deeper restructuring of the metal nanoparticles with same reduction of MSA but slightly higher Pd leaching involving an overall catalytic activity similar to the pristine catalyst (also H₂O₂ production and selectivity) and; 3) treatment corresponding to Br-to-Pd molar ratios of 0.25, 0.80 and 1.40, respectively, promoted a different restructuring of the metal phase with less reduction of MSA thus producing a better H₂O₂ formation over H₂O while still maintaining the overall catalytic activity at similar levels as observed for pristine 1PdC.

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**References**


Application of the Catalyst Wet Pretreatment Method (CWPM) for Catalytic Direct Synthesis of H$_2$O$_2$

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Supporting Information
**Figure S1:** TEM representative images taken on 1PdC pristine: globular nanoparticles (section a), small nanoparticles (section b) and big particles (section c). Instrumental magnification: 40000X, 50000X and 50000X, respectively.

**Figure S2:** TEM representative images taken on 1PdC pB001: small roundish nanoparticles (section a), globular nanoparticles (section b), very small nanoparticles (section c). Instrumental magnification: 100000X, 150000X and 250000X, respectively.
Figure S3: TEM representative images taken on 1PdC pB006: small roundish nanoparticles (section a), globular nanoparticles (section b), very small nanoparticles (section c). Instrumental magnification: 50000X, 150000X and 250000X, respectively.

Figure S4: Comparison of the Pd particle size distributions obtained for fresh and spent 1PdC pB001 and 1PdC pB080 catalysts.