Revealing the Role of Bromide in the H₂O₂ Direct Synthesis with the Catalyst Wet Pretreatment Method (CWPM)

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Abstract

A tailor-made Pd⁰/K2621 catalyst was subjected to post synthesis modification via a wet treatment procedure. The aim was the understanding of the role of promoters and how—if any—improvements could be qualitatively related to the catalyst performance for the H₂O₂ direct synthesis. The Catalyst Wet Pretreatment Method was applied in different methanolic solutions containing H₂O₂, NaBr, and H₃PO₄, either as single modifiers or as a mixture. The catalyst was characterized by Transmission Electron Microscopy and X-ray Photoelectron Spectroscopy. It was concluded that the modified catalysts give rise to higher selectivities compared to the pristine reference catalyst thus opening a possibility to exclude the addition of the undesirable selectivity enhancers in the reaction medium. This work provides original evidence on the role of promoters, especially bromide, allowing the formulation of a new reaction mechanism for one of the most challenging reactions recognized by the world.

Introduction

Hydrogen peroxide is a chemical commodity used in various applications ranging from the pulp and paper industry to chemical synthesis.¹ The anthraquinone auto-oxidation (or Riedl-Pfleiderer) process is the current industrial method of choice to produce hydrogen peroxide, notwithstanding that it suffers from numerous drawbacks such as large capital expenditures (CAPEX), the necessity of large scale plants and efficient post-process waste-water treatment facilities. Therefore, an alternative synthesis way circumventing the above mentioned issues should be developed. Indeed, nowadays the world is changing fast and the industries are looking for sustainable solutions to their processes. Most societies demand a more sustainable approach to industrial production and, therefore, catalytic direct synthesis (CDS) holds potential to greatly improve both the manufacture of H₂O₂ as well as a variety of oxidation processes which could make use of H₂O₂ as a clean and versatile oxidant. For the above mentioned reasons, the CDS of hydrogen peroxide is actively investigated as a potentially less expensive route to produce H₂O₂ in small scale plants.¹

Recently, four reviews have illuminated the fundamental challenges and key processes of this process,^{1–4} but many issues about the reaction remain still unresolved. The complexity of the CDS arises from the reaction network (Scheme 1) with several competitive routes to a thermodynamically very stable product, i.e., water. In addition, additional complexity arises from (a) operations taking place in three phases (transport and thermodynamics may be relevant),^{4,5} (b) interactions occurring on the catalyst materials (metal phase and support),^{6–8} (c) starting materials used as well as the nature of the products and their redox properties,^{3,6} (d) the solvent chosen,³ and (e) the influence of the selectivity enhancers (physical–chemical features).³ When targeting sustainable and feasible H₂O₂ direct synthesis, one should consider issues such as (1) improving the selectivity toward H₂O₂, (2) the safety of the reaction, obtained through tailored preparation of the catalysts and the study of reactor design, as well as (3) the demand on the level of concentration of H₂O₂ that should

be obtained (around 8 wt%⁴). Many aspects of the CDS process are today still foggy albeit the combination between chemistry and chemical engineering will likely boost the understanding and the interplay of the intrinsic material surface properties, mass transfer phenomena, and detailed reaction mechanism.

It is well known that palladium is considered as the most potent active metal for the CDS but, unfortunately, it also gives rise to by-product like the subsequent overhydrogenation (yielding water) or decomposition of the H₂O₂. So far, to solve the selectivity dilemma, different approaches have been tried to modify the catalytic properties of the palladium based catalysts: (1) addition of halides and mineral acids in the reaction mixture,³ (2) addition of a second metal to the palladium catalyst,^{6,9,10} (3) pretreatment of the support with nitric acid,^{11–13} (4) functionalization of different supports,¹⁴ (5) fine-tuning of the reaction conditions,^{15–19} and (6) reactor design.^{16,20–26} All these aspects are important but if applied simultaneously, will not lead to a real understanding of the process since each and every of these parameters are correlated and will influence each other (positively or negatively). As separated problems, if investigated deeply, these aspects may bring important insight to the true nature of the CDS. The common aim of the different approaches is to shut down or hamper the water formation by inhibiting the direct H₂O formation and/or the H₂O₂ hydrogenation and decomposition. Most of the research groups dealing with the CDS claim that the main issue to be solved is to block the active sites that are responsible for the cleavage of the OAO bond.^{1–3} Nevertheless, the exact nature of the active site is still unclear for the OAO cleavage, although most probably the formation of water and H₂O₂ hydrogenation (and decomposition) are promoted by the defects and highly unsaturated Pd centers (most active sites) of the catalysts.^{3,6} Halides/acids as well as the addition of a second metal (usually gold and platinum) apparently prevents the OAO bond cleavage.^{2,3}

In particular, the influence of the addition of the halides and acids was studied on a macroscopic level as recently reported.^{27,28} For instance, Choudhary et al.²⁷ studied the impregnation of bromide on a 5% Pd/Al₂O₃ catalyst and found an optimum, in terms of the catalyst activity/selectivity. More or less, it was found to be equal to 0.42 Br-to-Pd molar ratio. More recently, two studies were published that elucidated the influence of the bromide on the catalyst and that of acid pretreatments. In the first report, Ntainjua et al.²⁸ reported the results of bromide impregnation of the 2.5 wt % Au–2.5 wt % Pd catalyst in terms of CDS. The best results were obtained when the Br : Pd molar ratio was between 0.0002–0.02, thus obtaining a 30% increase on the H₂O₂ productivity and a substantial decrease of the hydrogenation rate (280% compared to 0.02 Br : Pd molar ratio). In the second report,²⁹ the same group demonstrated how the presence of bromide in the reaction medium influenced the catalytic performance of the catalyst in terms of H₂O₂ formation and H₂O₂ hydrogenation. Importantly, 2.5 wt % Au–2.5 wt % Pd/C catalyst with 0.1340.³³ Br:metal molar ratio gave rise to a strong retardation of the H₂O₂ hydrogenation rate although the H₂O₂ productivity remained almost unchanged. A new approach was adopted by Biasi et al.¹⁴ in a continuous reactor where the reactant medium composed of an aqueous solution of NaBr and H₃PO₄ was changed to pure water after reaching the steady state operations. After the removal of NaBr and H₃PO₄, the experiment was continued for another 12 h but still H₂O₂ was obtained at a constant concentration without added selectivity enhancers. After 12 h of operations without selectivity enhancers the H₂O₂ production suddenly decreased.

Until now, only one publication mention a procedure to wet pre-treat the catalyst with halides.³⁰ This approach may contribute with a new point of view in the approach to the direct synthesis of H₂O₂ and on the action of the selectivity enhancers (additives) in the reaction mechanism.

In light of this, the present work aims at better understanding of the behavior of selectivity enhancers on CDS. The use of a wet pretreatment method (Catalyst Wet Pretreatment Method—CWPM)³⁰ on the catalyst before activity tests aims at modifying the specific surface properties of the catalyst aiming at increased H₂O₂ production and higher selectivity. In fact, this approach might be a viable alternative way to Scheme 1. Scheme of hydrogen peroxide direct synthesis. eliminate the use of the halides in the working solution, thus overtaking the problems of plant corrosion, the product quality (without so many purifications steps) and the

catalyst reusability. For that reason, a wet pretreatment procedure in methanol is introduced here. The wet pretreatments were applied with all the possible combinations of NaBr, H₃PO₄, and H₂O₂, at fixed molar ratios of palladium-to-substrate. The activity of bromide alone, or in combination with H₃PO₄ and H₂O₂, should result in different surface structures and/or on the structure of the metal nanoparticles. To compare all the results obtained on various wet pretreatments, the contribution of the selectivity enhancers (in the reaction environment) was investigated. The results obtained brought new insights on the role of the bromide and the reaction mechanism of the H₂O₂ direct synthesis.

Experimental

Materials and apparatus

Unless otherwise stated, all the reagents and the materials were used as received from the supplier. A batch of Lewatit K2621, (Lanxess) in its acidic form (sulfonated polystyrenedivinylbenzene macroreticular ion-exchange resin (SPS); exchange capacity 51.92 mmol/g) was carefully washed with water and methanol and used as a catalyst support. Pd(NO₃)₂ was purchased from Alfa Aesar; sodium bromide (NaBr, 99.5%), methanol for Karl Fischer titration, Hydranal composite 2 and ammonium molybdate tetrahydrate (Fluka); phosphoric acid (H₃PO₄, 99%), sodium thiosulfate pentahydrate (99.5%), potassium iodide, starch, concentrated sulfuric acid, and tetrahydrofuran (THF, 99.99%, used freshly distilled) were all purchased from Sigma-Aldrich and hydrogen peroxide (H₂O₂, 30 wt % aqueous solution) from Merck. HPLC grade methanol (99.99%) was acquired from J. T. Baker; and H₂, O₂, and CO₂ (99.999% mol/mol purity) from AGA Oy (Linde group).

Inductively coupled plasma mass spectrometry (ICP-MS) measurements were carried out with a PerkinElmer Sciex, ICP Mass Spectrometer 6100 DRC Plus. The analysis was carried out at the quantitative standard mode. The elemental concentrations of the samples were determined with scanning electron microscopy and energy-dispersive X-ray spectroscopy (FESEM-EDX, Zeiss Ultra plus, Inca) from five different sample locations (analyzed area of 10 μm x 10 μm).

The Transmission Electron Microscopy (TEM) analyses were carried out with a JEOL JEM3010 operating at a 300 kV acceleration voltage and point-to-point resolution of 0.17 nm at Scherzer defocus and EFTEM, LEO 912 OMEGA, LaB6 filament, 120 kV. In short, the samples were prepared by suspending a few milligrams of the powdered materials in high purity isopropyl alcohol (or ethanol). After sonication (30 s), a small droplet (5 μL) of the suspension was transferred onto a holey-carbon film coated Cu grid which was eventually introduced into the microscope. The size distributions of the palladium nanoparticles in the catalysts were determined from TEM micrographs by measuring at least 250 particles for each sample. For all the samples, the nanoparticles demonstrated a spherical morphology and were well dispersed on the polymeric support. They generally showed a LogNormal size distribution, with a moderate statistical dispersion, estimated by skewness coefficient of LogNormal distribution.³¹

All X-ray Photoelectron Spectroscopy (XPS) spectra were recorded with a Kratos Axis Ultra electron spectrometer equipped with a delay line detector. A monochromated Al Kα source operated at 150 W, hybrid lens system with magnetic lens, providing an analysis area of 0.3 x 0.7 mm² and a charge neutralizer were used for the measurements. The binding energy (BE) scale was referenced to the C1s line of aliphatic carbon, set at 285.0 eV. Processing of the spectra was accomplished with the Kratos software.

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

Preparation of 1 wt % Pd/K2621 catalyst (denominated as 1PdK)

5.21 g of K2621 were suspended in 20 cm³ of distilled water for 2 h on the oscillating stirrer; an aqueous solution prepared with 137.5 mg of palladium nitrate was quantitatively added dropwise into the stirred

solution. As the next step, the suspension was let to react overnight under oscillating stirring and then recovered by filtration followed by a careful washing with distilled water (5 x 10 cm³) on the filter.

The light brown solid was suspended in 50 cm³ of THF and a flux of H₂ was bubbled in the suspension at room temperature and pressure for 5 h under gentle stirring. Subsequently, it was then filtered and washed carefully with THF. The solid (dark gray color) was dried in an oven at 110 °C overnight.

A small sample (ca. 30 mg) of the reduced material (starting catalyst) was digested and analyzed by ICP-MS to determine the amount of Pd (see the Supporting Information).

Pretreatment catalyst modifications

All the pretreatments on the catalyst materials were carried out similarly. Typically, 0.5 g of starting catalyst was suspended in 15 cm³ of methanol for 2 h and then let to react in the presence of one or more additive/s under ambient conditions for 1 h. The additives were introduced individually and in combination, adding aliquots of methanolic solutions, respectively: (a) 4 cm³ of 2.3 mM sodium bromide; the resulting catalyst was named p(B); (b) 3 cm³ of 3.4 mM of phosphoric acid, called p(A); (c) 6 cm³ of 0.05 M of hydrogen peroxide in methanol, called p(H). The final volume of the solutions was always adjusted to 30 cm³. These values were chosen to obtain 0.2 Br-to-Pd molar ratio, 0.02H₃PO₄-to-Pd molar ratio, and a H₂O₂ concentration of 0.05 M. The first two values were chosen as values used in literature to perform experiments on H₂O₂ direct synthesis and the last one as the molar concentration of H₂O₂ achieved during the experiments without selectivity enhancers.³² Previously, Ntainjua et al.^{28,29} reported that a Br : Pd mean molar ratio of 0.2 largely improved the performance of the pristine catalyst. In light of this, we chose to treat the pristine catalyst with a methanolic solution of NaBr with a Br : Pd molar ratio equal to 0.2. This molar ratio was also maintained when phosphoric acid was used, moreover the H : Br ratio was set to 1:1, considering H₃PO₄ as a monoprotic acid. This approximation is plausible in non-aqueous solvent, evaluating only the first acid dissociation as substantial. This molar ratio of acid and halide corresponds to 3.1 (NaBr) and 2.831024 mol/dm³ (H₃PO₄) for the wet pretreatments and 6.731026 mol/dm³ (NaBr and H₃PO₄) for the catalytic tests (refereing to the Br : Pd molar ratio of 0.2 and H : Br ratio of 0.9). However, the concentrations of these species were very low and, most importantly, the Br : Pd molar ratio was kept constant.

The solids were recovered by vacuum filtration and carefully washed on a filter with methanol (5310 cm³). The mother liquor of the pretreatments was analyzed by ICP-MS to check the amount of palladium and reported as percentage of the initial molar amount of Pd (Table 2). Finally, the solids were dried overnight in an oven, at 110 °C.

Activity measurements

Catalytic tests were carried out in a 600 cm³ stainless steel, tailor-made batch reactor with a maximum working pressure of 200 bar, equipped with a Heidolph RZR 2021 driver (200–1000 rpm) and a K-type thermocouple, for continuous temperature detection. A more detailed description of the reactor is given in previous work.^{9,10,32} Procedures are also detailed in the Supporting Material.

H₂O₂ and H₂O were determined by iodometric titration and Karl-Fischer titration, respectively. The product distribution was monitored along the 3 h reaction, always monitoring the H₂ mass balance

$$(H_2O_2 + H_2O)_{produced} = H_{2initial} - H_{2actual}$$

The H₂ conversion and the selectivity to H₂O₂, S_{H₂O₂} were calculated as:

$$X_{H_2}(\%) = \frac{(H_2O_2 + H_2O)_{produced}}{H_{2initial}} \times 100$$

$$S_{H_2O_2}(\%) = \frac{H_2O_2}{(H_2O_2 + H_2O)} \times 100$$

The initial rates toward the products and reported in Table 1 are estimated by the evolution of H₂O₂ and H₂O concentrations during the first 20 min. Consequently, these values were used to calculate the initial productivities of H₂O₂ and the initial cumulative productivities of H₂O₂ and H₂O. Further, in this manner one could obtain cumulative productivities, at H₂ conversion of 50%, to estimate the specific and overall catalyst activity in the CDS. The initial selectivity is the ratio between the H₂O₂ productivity and cumulative productivity. Naturally, the difference between the cumulative productivity and H₂O₂ productivity yields the H₂O productivity.

Results and Discussion

A synthetic summary of the results obtained during the batch experiments is reported numerically in Table 1 which is enough to develop the following discussion. The detailed evolution of H₂O, H₂O₂ concentration and derived performance indices, i.e., H₂ conversion and selectivity to H₂O₂ is reported in the Supporting Information Figures 1SM and 2SM. The nanoparticles morphology and catalyst leaching results are summarized in Table 2. Further details about the results can be found in the Supporting Information.

The reference catalyst (1PdK)

The 1PdK untreated catalyst was chosen as the benchmark to quantify the power of the pretreatment procedures. The activity of this catalyst, in terms of H₂ consumption, was among the best, resulting in the consumption of half of the initial hydrogen amount in the reactor in 10 min (see Table 1). However, the initial selectivity toward H₂O₂ was quite low, 23%, because the catalyst is very active toward H₂O production. This is precisely the actual limitation of most CDS catalysts that can be improved by promoters. The catalyst was used as benchmark for the CWPM.

Catalytic activity

The contribution of the different pretreatments on the activity of the catalysts is summarized in Figure 1, where catalysts are ordered by increasing initial selectivity toward H₂O₂. The ranking is based on the selectivity, this being the most critical limitation in CDS and the motivation for the introduction of promoters.

The catalysts that were in contact or were pretreated with bromide showed dramatically improved initial selectivities, by a factor of 2.5 and approaching 90% selectivity. The ranking and selectivity values remain comparable at 50% H₂ conversion. As frequently reported, higher selectivity implies lower productivity. Apparently, bromides contribute in poisoning of the sites responsible for the H₂O₂ production, in addition to those sites that support water formation, as also claimed,³ and resulted in a dramatic improvement in selectivity.

Acid addition, or purely acid-based pretreatments without bromide did not improve the catalyst activity and selectivity.

Still, the most important and unexpected conclusion is that the *a priori* bromide pretreatment of the catalysts resulted in comparable or near-comparable performance obtained when the bromide was present in the reaction medium.

Pd leaching

Leaching of the active metal(s) can be a relevant and undesired outcome of using promoters. However, the phenomenon of leaching could also influence the reaction mechanism, as suggested in the following. The

measurements to quantify the amount of Pd in methanol after the pretreatment and at the end of the 3 h reaction are reported in Table 2. A ranking of the catalysts is shown in Figure 2.

Compared to the pristine catalyst, leaching greatly increases on using of promoters. The apparent order is B > AB > A > no promoters. Bromine gives rise to a substantial amount of leaching already during the pretreatment. Once pretreated with bromine, the subsequent leaching is not as large as the one measured by using promoters directly in the reaction medium which further encourages one to choose this technique. During the reaction, bromide evidently was the strongest leaching promoter, especially when added directly in the reaction environment. Leaching is apparently correlated with the activity; it occurs mostly with catalysts that are more selective, but also less productive.

There are examples in the literature³³ where leaching is a temporary process, and in close reacting environments it varies with the reaction conditions, possibly reaching quite high levels but eventually being negligible toward the end of the reaction. That suggest the possibility that Pd nanoparticles may rearrange also through some Pd transfer across the solvent. Therefore, leaching and nanoparticle reconstruction could become correlated, and might depend on the specific pretreatment, with bromide, used. Such a possibility calls for an investigation of the evolution of the nanoparticle morphology.

The contribution of catalysts morphology

The size of the Pd nanoparticles were measured before and after the pretreatment procedures and also before and after the activity tests. Values are reported in Table 1. The correlation between leaching and nanoparticle size variation, due to the pretreatments and to the reaction, is shown in Figure 3. The catalysts that undergo a stronger leaching, also experience larger nanoparticles growth. The bromide appears the real key factor influencing the size of the metal nanoparticle.

The wet pretreatments with bromide alone, in a mixture with H₃PO₄ and/or H₂O₂, give rise to approximately the same increase in the nanoparticles size, leading to approx. doubling of the initial size. The standard deviation of the measurements in the set of catalysts pretreated with bromide was 0.17 nm, less than 3% of the average dimensions of the pretreated catalysts. The pretreatments carried out without bromide gave rise to much smaller increase on the nanoparticles size, compared to the pristine catalyst (approx. 30%). The standard deviation in this case was 0.05 nm, less than 1% of the average nanoparticles size. These data clearly show that three groups of pretreated catalysts can be identified, even though the pretreatments were several. The differences that are significant can be summarized as follows (in terms of dimension): pristine catalysts, no pretreatments ($\Delta \approx 0$) < pretreatments without bromide ($\Delta = 26\text{--}29\%$) < pretreatments with bromide ($\Delta = 70\text{--}79\%$).

It can be clearly concluded that bromide played the main role in inducing the size changes of the catalyst nanoparticles, while other agents (H₃PO₄ or H₂O₂) played a minor role. The skewness changed a little in the pretreatments with H₃PO₄ or H₂O₂ but when bromide was used the changes were larger, in comparison to the pristine catalyst (Table 2).

The analysis of the complete size distribution reported in the Supporting Information, Figure 3SM, shows that in case of pretreatments carried out in the absence of bromide, the population of the smaller nanoparticles (< 3 nm) drastically decreased compared to the pristine catalyst and the population of the bigger nanoparticles (> 10 nm, not even present in the pristine catalyst) slightly increased. This suggests that the H₃PO₄ and H₂O₂ (and their combination) may induce coalescence of the smaller nanoparticles, given that leaching is not significant to support the hypothesis of dissolution. The catalysts may also undergo a temporary leaching during the reaction, possibly larger compared to the one observed in the spent catalyst, similarly to other reported cases³³ where Pd is exposed to a dissolution due to an oxidative attack.

On the opposite side, in case of bromide, the reduction of the population of the smaller nanoparticles is associated with the formation of quite large nanoparticles (> 10 nm). This can suggest that the bromide enhances the dissolution of the small nanoparticles with a reconstruction of big nanoparticles also by a growth mechanism (i.e., deposition on the surface of mono- or oligonuclear species of palladium formed in the solution by leaching).

This hypothesis is further supported by the fact that leaching occurs during the pretreatments (shown in Figure 3: with bromide 1.7–3.6%). In fact, leaching was one order of magnitude stronger compared to the case when the pretreatments were carried out in the absence of bromide (0.1–0.2%). On pretreatment with Br^- , H_3PO_4 , and H_2O_2 , the two mechanisms (aggregation + growth) are present but aggregation dominates as illustrated by the observation that the mean dimension of the nanoparticles increased (Figure 3) while dispersion decreased (Figures 3SM, 4SM, 5SM, and 6SM).

In light of this, it is also evident that the leaching during the reaction is not depending on the nanoparticles size at the beginning of the reaction. Also, bromide during the reaction is not as correlated with a significant variation of nanoparticle size, unless directly added to the reaction medium. In other words, bromide used in the pretreatments already shaped the nanoparticles distribution that remained in essence stable during the reaction.

From the results reported in this work it is clear that the promoters have a dynamic role in continuously reconstructing the catalyst surface, arbitrated by the leaching. The reverse effect is that leaching is functional to nanoparticles restructuring.

The contribution of Pd oxidation state

The selectivity of CDS has been early suggested to be correlated with the metal oxidation state.^{8,34–37} We attempted to obtain clear evidence about it by measuring the influence of promoters and pretreatments on the Pd(0)/Pd(II) ratio. A full compilation of the XPS results is available in the Supporting Information. Figure 4 shows the correlation between the selectivity (initial and at t_{50}) and the Pd(0)/Pd(II) ratio measured on the surface of the fresh and spent catalysts, respectively.

After the catalytic runs, almost all the catalysts, independent on the pretreatment procedures, show a decrease in the Pd(II) content. Despite this, the Pd(0)/Pd(II) ratio does not seem to be moderately important. The pretreatments without bromide effectively increase the Pd(0)/Pd(II) ratio compared to the pristine catalyst, but the resulting selectivities and productivities are comparable with the reference catalyst (Table 1 and Figure 1).

It appears that the oxidation treatment with acids does not affect the sites related to the H_2O_2 direct synthesis and water formation. That means that there exists both Pd(II) and Pd(0) sites that are not active in the direct synthesis.

Based on the Pd(0)-to-Pd(II) ratio, the catalyst materials and the influence of the pretreatment procedures can be again divided in two categories of pretreatments: procedures relying on bromide and those without bromide. In case of bromide pretreatments, the Pd(0)-to-Pd(II) ratio changed significantly, leading to a decline in the concentration of Pd(II), while in case the pretreatments without bromide, the amount of Pd(II) increased compared to the pristine catalyst. Once again, the combined pretreatment with bromide, phosphoric acid, and hydrogen peroxide gives rise to performance on the border line between the two above cases (bromide present or not). Given that the XPS gives information on the surface state of the Pd nanoparticles, it can be concluded that the contribution of bromide was to reduce the Pd(II) fraction on the surface while the other pretreatments yielded the opposite effect. The influence of the reaction environment is quite clear (see Figure 4). All catalysts experienced a reduction in the amount of Pd(II), but the effect was larger in case of materials pretreated with bromide.

The models used in the theoretical calculations of the adsorption energies on the palladium surface are based on metallic clusters of Pd(0). However, it is well known that, at least, part of the palladium surface on CDS catalysts exists in oxide form. It is still unclear if the palladium is in the Pd-O form or in the PdO form. The role of the oxidation state was already described and studied in the literature,^{4,34–37} but is still debated and unclear which is the palladium form active in the. Although it is impossible to establish a relation between the catalytic performance and the oxidation state of the catalyst (since the characterizations of the catalysts are performed only before and after the reaction), some indications can be drawn comparing the catalytic data with the catalyst characterizations.

As depicted in Figure 3, the spent catalysts are less oxidized compared to the fresh ones, despite the reaction environment in a closed reactor becomes more oxidant as the H₂ is consumed. The most selective catalysts show a higher Pd(0)-to- Pd(II) ratio after the reaction (more than 1) and increased above an already low initial value in the fresh catalyst. This indicates that the catalyst is more selective when the fraction of Pd(II) is not so high or decreases during the reaction. Further, the pretreatments without bromide increase the amount of Pd(II) without significantly affecting the selectivity. The selectivity was enhanced by 20% only when H₃PO₄ was directly added in the reaction environment. Consequently, the possible explanation is that some of the oxidized surface does not participate actively to the useful reaction, i.e., H₂O₂ production. Consequently, Pd(0) catalytic centers appear as the more active metal form in CDS although a fraction of them (1) is reversibly poisoned by bromide bonded on the Pd surface (preventing the water production) and (2) some are not active in the direct synthesis.

The fact that highest ratios of Pd(0)-to-Pd(II) are associated with the pretreatments with bromide suggests that variations in the Pd oxidation state are likely also dependent on the reconstruction of the metal nanoparticles during the pretreatment and during the reaction by the bromide ion.

Therefore, evidently the catalytic active phase composition is dynamic and not static as supposed in the theoretical modelling used until now. Also, the activity of Pd sites in the direct synthesis is not only dependent on their oxidation state.

From the results reported above, we conclude that leaching, nanoparticle reconstruction and variations in the oxidation state are closely correlated. The analysis of the spent catalysts gave similar indications as seen by the Pd leaching, nanocluster size and Pd(0)-to-Pd(II) ratio variations. These results give important information on the role of the enhancers and especially on the Bromide role, summarized in a new model discussed in the following.

A MODEL concerning the role of the PROMoters-PROMOD

As shown in DFT calculations,³⁸ halogens can be grafted to the more reactive sites of Pd(0) surface where the direct oxidation of H₂ to H₂O prevails. Hereupon halides become selective poisons minimizing the water formation as already claimed.³⁸ The data collected in our work showed that bromide (a halide) affects not only the direct formation of water but also the H₂O₂ production, but to a less extent. Our data are consistent with the model proposed by Deguchi and Iwamoto³⁸ that assumes the existence of two types of sites, A and B, on the metallic surface of Pd that are characterized by different enthalpy of absorption of H₂, O₂, H₂O₂, and Br₂. The gap between a real catalyst and the ideal surface used for calculations cannot entirely describe the influence of the promoters. The leaching data demonstrated that the bromide ions can dissolve palladium in the reaction environment, in addition to grafting to the active metal surface. The dissolution is stronger if bromide is fed directly in the solution, compared to its use as pretreatment agent. This observation supports the hypothesis that the metal is more prone to be leached in the presence of O₂ because Br₂ preferentially attacks Pd(II) (in whatever form it is present). Accordingly, we can speculate that under reaction conditions some Pd(II) is continuously restored in the nanoparticles by O₂ and that this change favors further leaching. This is not possible during the pre-treatments because they are carried out without O₂, hence the leaching

action of Br_2 is not as prominent. The leaching reduced the population of the small nanoparticles where the more reactive and less selective sites (Sites A according to Deguchi and Iwamoto) were more abundant. Moreover, the reconstruction of the nanoparticles promoted by the bromide ions (alone or in combination with H_3PO_4 and H_2O_2), enlarge the population of the more selective sites for the CDS (Sites B, according to Deguchi and Iwamoto), thereby destroying or rearranging the less selective sites (smaller nanoparticles). This effect is coupled with the higher possibility of the sites A to adsorb the bromide ions and thus, results in a selective site blocking. A static particle model cannot describe these two dynamic effects together as reported by Deguchi et al.³⁸. Moreover, on studying the XPS and EDX data (Tables 1SM and 2SM), we could not identify any signal due to the bromide in the catalyst pretreated with bromide or when bromide was used as a promoter. This fact possibly means that the action of the metal reconstruction could be correlated to the site-blocking and that the amount of grafted Br_2 is below the detection limits. Nevertheless, the data reported in this work gives evidence that the catalysts were undergoing significant reconstruction during the pretreatment but did not reconstruct significantly during the reaction. Moreover, the catalytic tests over the pristine catalyst and in the presence of the promoters in the reaction environment resulted in good selectivity and a significant reconstruction, supported by the high levels of leaching and the large variation of nanoparticle dimensions. The catalyst pretreated with H_3PO_4 and $\text{H}_3\text{PO}_4 + \text{H}_2\text{O}_2$ experienced minor reconstruction and the selectivity remained low. A similar effect in terms of bromide was seen previously in experiments performed using in-situ Pd K-edge X-ray absorption fine structure spectroscopy.³⁹

After analyzing all the data, a plausible mechanism of the palladium reconstruction can be shaped and schematically described as depicted in Figure 5. Initially, bromide reacts with palladium and carries it in solution as bromocomplexes of palladium(II). These complexes can both equilibrate in solution with polynuclear (halides bond) and hydrolyzed (substitution of bromide with water or solvents molecules) species, or they can lead to a re-deposition of palladium(II) ions on the bigger metal nanoparticles, further increasing their dimensions. Moreover, the soluble bromoderivatives of palladium could also act as precursors of species of zerovalent Pd (reported as Pd^0 in Figure 5), which can directly contribute to the growth of the bigger metal nanoparticles or to the formation of Pd nanoparticles in solution (reported as Pd_n in Figure 5). These, in turn, can directly contribute to the growth of the bigger metal nanoparticles or to the formation of Pd nanoparticles in solution (reported as Pd_n in Figure 5). The Pd_n nanoparticles formed in the solution may redeposit on the bare support or on the already existing nanoparticles on the catalyst support by coalescence. The smallest nanoparticles on the support (both present from the synthesis and deposited from the solution, as described above) can also aggregate with bigger nanoparticles on the support, contributing to their size increase by coalescence. In the transformation process of nanoparticles, a small amount of bromide ions, grafted to the Pd surface, could be released from Pd nanoparticles and participate to a catalytic reconstruction mechanism of the nanoparticles. This would also explain why a low amount of the residual bromide present as a result of the pretreatments but analytically not detectable, could be really efficient during the reaction.

This mechanism aggregates all our experimental evidences and speculates on literature information since Pd species in the solution were not measured. Indeed, it is reported that heterogeneous catalysts undergo transformations during the crosscoupling reactions, especially during the Heck reactions.³³ The ability of bromide to dissolve the oxidized palladium is based on known facts. The halide ions are excellent ligands for the Pd(II) and the complexes $[\text{PdX}_4]^{2-}$ and other wellknown complexes, such as $[\text{Pd}(\mu\text{-X})_2\text{X}_4]^{2-}$, with $\text{X} = \text{Cl}, \text{Br}, \text{I}$. It is not known if halide-complexes of Pd(0) are stable, due to their soft features compared to the Pd(0) and due to the fact that the higher electronic density supports coordination of ligands with p-acid features, while the halides are p-basics. Based on these considerations, it is reasonable to hypothesize that not only the palladium species in solutions are bromocomplexes of Pd(II), but also that the bromide tends to react preferentially the oxidized palladium on the metal surface, compared to the reduced palladium. The sites of

palladium that are more oxidized are the ones where the superficial oxide is located (that can be considered as the product of the adsorption of the atomic oxygen), and the following mechanism can be expected:

The direct attack of the Br^{-} to the $Pd(0)$ cannot be neglected at the present, but it is the less probable, especially when an acid is not present.

If this mechanism is confirmed in the future, it will result that the bromide ions would play also a remediation role to the formation of superficial atomic oxygen by the dissolution of an oxide, an intermediate of the direct oxidation of hydrogen. It is clear that selective removal of the superficial oxide by the preferential attack of the bromide is expressed by an apparent reduction of the supported metal, also when the $Pd(0)/Pd(II)$ does not change due to a redox process. All these features of bromide render it a suitable candidate to tailor the selectivity of the H_2O_2 direct synthesis process.

Conclusions

We proposed new approaches and concepts to modify the metal phase in catalysts suitable for the CDS, aiming at improving their selectivity to H_2O_2 . The approach considers wet-pre-modification of the catalyst before use. The wetpretreatment can be considered an old approach but here is used with a modern thinking. The CWPM used as proposed above provides new insight and new interpretations of what happens during the CDS. It was successfully demonstrated that the CWPM is comparable to the addition of homogeneous, liquid-phase enhancers under the experimental conditions proposed.

The use of bromide clearly indicated that its use either as pretreatment agent or as a promoter (fed in the reaction environment) renders the catalyst less active but more selective toward H_2O_2 , and the use of bromide coupled with the H_3PO_4 and the H_2O_2 even boosts the selectivity. In general, bromide pretreatments or the use of bromide as an enhancer (also with H_3PO_4), reduces both the rates of direct formation of H_2O_2 and formation of water, but its effect was more pronounced in the case of H_2O .

Based on the original results, a reaction mechanism encompassing the role of bromide was formulated. In addition that the selective poisoning of the sites responsible for oxidation of H_2 to water already suggested, we collected evidence that Br^{-} contributes in reshaping the metal nanocluster. When Br^{-} was used, either on a pretreatment or in the reaction medium, the percentage of surface $Pd(0)$ centers increased as well as the H_2O_2 selectivity. Both species, surface $Pd(0)$ and PdO , play an important role in shaping the catalytic performance of the catalyst. In short, $Pd(0)$ appears the active metal for H_2O_2 formation whereas PdO appears to inhibit water formation. Also, acids stabilize the H_2O_2 formed and, in addition, the acid supports the oxidation of the metal nanoparticles to inhibit the sites responsible for water formation. The results provide new insights in terms of the optimal design of catalysts for selective

hydrogenations, particularly the direct synthesis of hydrogen peroxide. They can be summarized as follows:

1. Leaching helps to enhance the direct synthesis; the mechanism suggested here requires further validation.
2. $Pd(0)$ -to- $Pd(II)$ ratio is not to that crucial in the CDS.
3. Particle size is less important compared to the site blocking and the Pd leaching.

4. The final level of leaching is still insufficient to determine the mechanism of catalyst restructuring and, therefore, leaching should be monitored also during the reaction with a more detailed study of the metal nanoclusters features.

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Tables and Figures

Table 1. Activity of the Pristine (1PdK) and Pretreated Palladium Catalysts Supported on K2621

Sample	Pd mol	H2O2 rate H2O rate mmol/dm3 h		t50 min	H2O2 productivity mol/molPd h		Cum. productivity molH2O2+H2O/molPd h		H2 selectivity %	
		Initial	Initial		Initial	@ t50	Initial	@ t50	Initial	@ t50
1PdK	14.3	31.3	104.2	10	919	877	3980	3792	23	23
1PdK p(A)	14.1	39.5	127.1	8	1177	1052	4963	3896	24	27
1PdK p(B)	14.1	15.3	6.6	50	456	527	652	916	70	68
1PdK p(H)	14.1	30.1	99.5	10	855	798	3680	3070	23	26
1PdK p(AB)	14.2	7.5	2.6	105	222	265	299	357	74	75
1PdK p(AH)	14.1	35.7	100.3	9	1013	949	3859	3796	26	25
1PdK p(BH)	14.4	23.8	5.5	36	694	745	855	1070	81	70
1PdK p(ABH)	14.1	16.0	3.3	66	477	530	575	841	83	63
1PdK + A	14.1	17.7	22.6	42	527	373	1200	1381	44	23
1PdK + B	14.2	10.5	1.4	80	311	383	352	511	88	75
1PdK + AB	14.2	12.0	4.6	70	355	292	491	436	72	67

Table 2. Measured Mean Diameter, d, of Pd Nanoparticles, Skewness Coefficient, SC of Distribution (from LogNormal Fit) and Leaching of Pd in Fresh, Pre-Treated, and Spent Catalyst

Sample	After pre-treatment			Spent		
	d nm	SC	Leaching Pd % mol	D nm	SC	Leaching Pd % mol
1PdK	3.68	0.825	–	4.03	1.190	0.04
1PdK p(A)	4.73	0.715	0.1	4.89	0.752	0.03
1PdK p(B)	6.58	1.597	1.7	6.72	0.964	0.6
1PdK p(H)	4.70	0.936	0.1	5.74	0.943	0.15
1PdK p(AB)	6.24	1.545	3.6	6.76	2.060	2.1
1PdK p(AH)	4.62	0.880	0.2	4.80	1.057	0.07
1PdK p(BH)	6.28	1.283	2.4	6.80	1.248	0.6
1PdK p(ABH)	6.40	0.495	1.8	6.20	0.689	0.2
1PdK + A	–	–	–	n.d.	n.d.	2.8
1PdK + B	–	–	–	6.59	0.939	5.7
1PdK + AB	–	–	–	6.31	1.267	4.2

Scheme 1. Scheme of hydrogen peroxide direct synthesis.

Figure 1. Synthetic “activity” indices for different catalyst treatments, ordered by increasing selectivity to H₂O₂ (●). Also reported the H₂O₂ initial production rate (▲), in mmol/dm³ h, and the cumulative (initial) productivity of both H₂O₂ and H₂O (■), in mmolH₂O₂+H₂O/molPd h. Initial selectivity, above (Figure 1a), and selectivity at t₅₀, below (Figure 1b).

Figure 2. Ranking of different catalyst treatments, ordered by increasing leaching. Amount of Pd (% mol) in the methanol after pretreatment (■), and at the end of the 3 h of testing (▲). Also reported the initial selectivity to H₂O₂ (●).

Figure 3. Correlation between leaching and relative variation of Pd nanoparticle size. Leaching during pretreatments, above (Figure 3a), and during reaction, below (Figure 3b). $\otimes d = (d_{\text{after}} - d_{\text{before}})/d_{\text{before}} \times 100$.

Figure 4. Correlation between selectivity (initial, left (Figures 4a, c), at t_{50} , right (Figures 4b, d)) and the catalyst oxidation state $\text{Pd}^0/\text{Pd}^{\text{II}}$ as fresh, above (Figures 4a, b), and spent, below (Figures 4c, d).

Figure 5. Schematic representation of the bromide role on Pd-catalysts. Pd^0 : mono- or oligonuclear Pd species, zerovalent in solution; Pd_n : palladium nanocluster formed in solution; (S) and (L): small and large

Pd nanoparticle, pre-existing in the catalyst; (C): palladium nanoparticle pre-existing in the catalyst; thick arrows: sintering of nanoparticles (solid = growth; dotted = coalescence); thin arrows: reactions in solution.