

Article

Direct Synthesis of Hydrogen Peroxide under Semi-Batch Conditions over Un-Promoted Palladium Catalysts Supported by Ion-Exchange Sulfonated Resins: Effects of the Support Morphology

Francesco Frison¹, Chiara Dalla Valle¹, Claudio Evangelisti², Paolo Centomo^{1,*} and Marco Zecca¹

- ¹ Dipartimento di Scienze Chimiche, Università di Padova, via Marzolo 1, I-35131 Padua, Italy; frisonfrancesco1992@gmail.com (F.F.); chiaradallavalle.cdv@gmail.com (C.D.V.); marco.zecca@unipd.it (M.Z.)
- ² CNR Institute of Molecular Science & Technology, Via G Fantoli 16-15, I-20138 Milan, Italy; claudio.evangelisti@istm.cnr.it
- * Correspondence: paolo.centomo@unipd.it

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Abstract: Palladium catalysts supported by a mesoporous form of sulfonated poly-divinylbenzene, Pd/ μ S-pDVB10 (1%, w/w) and Pd/ μ S-pDVB35 (3.6% w/w), were applied to the direct synthesis of hydrogen peroxide from dihydrogen and dioxygen. The reaction was carried for 4 h out in a semibatch reactor with continuous feed of the gas mixture ($H_2/O_2 = 1/24$, v/v; total flow rate 25 mL·min⁻¹), at 25 °C and 101 kPa. The catalytic performances were compared with those of a commercial egg-shell Pd/C catalyst (1%, w/w) and of a palladium catalyst supported by a macroreticular sulfonated ion-exchange resin, Pd/mS-pSDVB10 (1%, w/w). Pd/ μ S-pDVB10 and Pd/C showed the highest specific activity (H₂ consumption rate of about 75–80 h^{-1}), but the resin supported catalyst was much more selective (ca 50% with no promoters). The nanoparticles (NP) size was somewhat larger in Pd/μ S-pDVB10, showing that either the reaction was structure insensitive or diffusion limited to some extent over Pd/C, in which the support is microporous. The open pore structure of Pd/ μ S-pDVB10, possibly ensuring the fast removal of H_2O_2 from the catalyst, could also be the cause of the relatively high selectivity of this catalyst. In summary, Pd/µS-pDVB10 was the most productive catalyst, forming ca 375 mol_{H₂O₂ \cdot kg_{Pd}⁻¹ \cdot h⁻¹, also because it retained a constant selectivity, while the other} ones underwent a more or less pronounced loss of selectivity after 80-90 min. Ageing experiments showed that for a palladium catalyst supported on sulfonated mesoporous poly-divinylbenzene storage under oxidative conditions implied some deactivation, but a lower drop in the selectivity; regeneration upon a reductive treatment or storage under strictly anaerobic conditions (dry-box) lead to an increase of the activity but to both a lower initial selectivity and a higher drop of selectivity with time.

Keywords: hydrogen peroxide; support morphology; mesoporous poly-divinylbenzene; palladium; ageing

1. Introduction

The direct synthesis of hydrogen peroxide (DS) has been under investigation as an alternative to the anthraquinone process [1] for more than 15 years [2–4]. The anthraquinone process is the most affordable for large-scale productions, which include also the H_2O_2 synthesis step of the integrated HPPO (Hydrogen peroxide-Propylene Oxide) process by BASF/Dow [5]. However, the use of H_2O_2 in



the large-scale chemical manufacturing is still limited and the most common down-stream applications of H_2O_2 generally require dilute solutions of H_2O_2 . In spite of this H_2O_2 from the anthraquinone process must be extracted in water and concentrated up to ca 70%, w/w in order to store and transport it. This makes hydrogen peroxide much more expensive than it would be otherwise and raises safety concerns about the handling of the concentrated solutions. For this reason, alternative processes for the on-demand, small-scale, on-site production of diluted solutions of H₂O₂ have been taken into account and the DS seems to be particularly promising. Many authors stress that most of the down-stream applications of H₂O₂ produced upon the on-site, on-demand DS would require small-scale plants, with a reduced risk of operation and a much lower CAPEX too. However, the handling of H_2/O_2 mixtures would be a major safety issue; moreover wide-spread diffusion of small scale DS plants would require an extended network for H₂ transportation, another safety issue, or local facilities for its production. Particularly interesting results have been obtained so far by Fierro and co-workers, who were able to implement a DS protocol leading to the production of H_2O_2 solutions in MeOH up to ca 9% (w/w) concentration [6]. For this purpose, they used catalytic supports bearing acidic groups (e.g., SO₃H) and covalently functionalized with Br. Among these supports ion-exchange resins like Lewatit K2641 play an important role [7–9]. However, Fierro's catalysts require relatively high pressure (up to 5 MPa) and the selectivity (calculated on H_2) is around 50%.

The problem of selectivity if of paramount importance in the DS, although its reaction scheme is relatively simple, with only two reagents (H_2, O_2) , two products (H_2O_2, H_2O) and four steps (Figure 1).



Figure 1. Reaction scheme for the DS of H_2O_2 from its elements with standard reaction enthalpy data (25 °C).

In fact, the activation of H_2 and O_2 over active metals (palladium or alloys thereof) generally leads to both H_2O_2 and H_2O , which is much more thermodynamically stable. In particular, it is very difficult to obtain a high selectivity and a relatively high concentration of H_2O_2 in the final mixture. A low selectivity is at the same time an economic and a safety issue. On the one hand, with a little selective catalyst a high proportion of H_2 is transformed into valueless water; on the other one, a relatively high H_2 partial pressure should be employed to form appreciable amounts of H_2O_2 . However, this is not recommended because H_2/O_2 mixtures have a very large explosion range [10]: for this reason, the DS is generally carried out with a H_2/O_2 ratio below its lower limit. Hutchings and coworkers were among the first to report a catalytic activity well exceeding 90%, with an AuPd catalyst supported on activated carbon pre-treated with an oxidizing acid [11]. In spite of these successes the commercial application of the DS is still an open challenge. At the same time, it is a fascinating scientific question, too, which was addressed by several research groups around the world [3,12–21].

Our research group gained over the years an appreciable experience in the use of cross-linked organic polymers [22–25] (hereafter referred to as resins) as supports for heterogeneous metal catalysts. Resins are much less popular catalytic supports in comparison with inorganic materials, in view of

their lower thermal and mechanical stability. However, when reaction conditions are mild, as it is the case of DS, resins can easily withstand them and be successfully employed. Resins are available in very different chemical structures and textures and can be conveniently tailor-made by a "molecular engineering" approach [26]. Moreover, catalytic reactions can occur in their interior and the micro-environment of the polymer framework can positively affect the outcome [27,28]. The use of an ion-exchange resin as support in the DS was first reported by Fierro and co-workers in 2004 [7]. They employed Lewatit K2641, a sulfonated co-poly-(styrene-divinylbenzene) (S-pSDVB), in which palladium was introduced as divalent cations and used without any reduction. Shortly after one of us co-authored a report [29] describing the DS promoted by palladium and palladium-gold catalysts supported by Lewatit K2621 (a S-pSDVB resin similar to K2641) [30] and an acrylic resins, either sulfonated or functionalized with alkylsulfide groups [29]. Since then our group contributed to a number of other papers illustrating the performance of palladium, palladium-platinum and palladium-gold catalysts in the DS with and without halide ions as promoters [31–37]. Among crosslinked resins "solvothermal" poly-divinylbenzene [38] recently emerged as the first representative of a new class of porous polymers, including also acrylic resins [39]. It has permanent mesopores with diameters up to several tens of nm, relatively high pore volumes (up to almost 2 cm³·g⁻¹) and practically no permanent micropores. In spite of this, its specific surface area can be as high as $400 \text{ m}^2 \cdot \text{g}^{-1}$. This is one order of magnitude higher than in macroreticular S-pSDVB conventional resins. In addition to this it absorbs a volume of liquids much higher than its pore volume, which further increase its specific surface area to almost 1000 $m^2 \cdot g^{-1}$ [40]. These features apparently arise from the high nominal cross-linking degree and the high dilution of the monomer in the polymerization mixture [41], which favors the chain growth with respect to cross-linking and the switch from macroto microsyneresis as the mechanism of phase separation [42]. As the result the pore system of this kind of pDVB, which will be hereafter referred to as mesoporous (μ -pDVB), can be described as interconnected cavities crossing a continuous polymer framework rather than void spaces between partially aggregated polymer lumps (Figure 2), as in conventional macroreticular resins [39,40,42].



Figure 2. Sketch of the chemical structure (top) and of the pore morphology (bottom) of a typical macroreticular pSDVB resin (\mathbf{a} ; x = 15, y = 85) and of μ -pDVB (\mathbf{b} ; x = 85, y = 15). Ethylstyrene from technical grade divinylbenzene usually employed in polymerization is the source of the ethylbenzene moieties, which can be also present in low amount in pSDVB (omitted for simplicity).

Interestingly, μ -pDVB can be sulfonated with retention of its morphology to give a very useful ion-exchange resin (μ S-pDVB) with pore features comparable to those of μ -pDVB [40,43].

Sulfonated ion-exchangers have been the kind of resins most commonly employed as supports for DS so far, which makes μ S-pDVB an interesting candidate as a catalytic support for this reaction. Its very open porous system should allow a fast diffusion of reagents, intermediate, and products, which could be particularly relevant to the control of the selectivity. In DS H₂O₂ must in fact be considered as a relatively little stable intermediate in the full reduction (4 e⁻) of dioxygen to water. Hence, the fast departure of H₂O₂ from the catalyst could enhance the selectivity towards this product. In this paper, we report for the first time on the use of μ S-pDVB as a support for unpromoted palladium catalysts in the DS and on the effect of the morphology of ion-exchange resins as supports on the catalytic performance. For this purpose, the behavior of of μ S-pDVB supported catalysts will be compared with those of catalysts supported on a commercial mS-pSDVB macroreticular ion-exchange resin and on activated carbon.

2. Results and Discussion

2.1. Catalyst Preparation

The palladium catalysts supported on the resins can be readily prepared upon ion-exchange of $[Pd(NH_3)_4]SO_4$ with the sulfonated resins. To prevent the adventitious presence of halide ions no chloro- or bromo-metal precursors were used in the preparation of the catalysts. The ion-exchanged resins were then suspended in THF and treated with H₂ at 506 KPa and 60 °C fo 5 h to reduce Pd^{II} to Pd⁰ (Scheme 1).

 $P-SO_3H + \frac{1}{2} [Pd(NH_3)_4]SO_4 \rightarrow P-SO_3[Pd(NH_3)_4]_{/2} + H^+ + \frac{1}{2} SO_4^{2-1}$

$$\mathbb{P}$$
-SO₃[Pd(NH₃)₄]/2 + H₂ \rightarrow Pd/ \mathbb{P} -SO₃H + 4 NH₃

Scheme 1. Ion-exchange and reduction reactions in the preparation of the catalysts.

The sulfonated resins were prepared from a commercial macroreticular pSDVB (15% cross-linked, Spolchemie, Czech Republic, hereafter referred to as m-pSDVB) and from μ -pDVB according to a standard procedure with concentrated H₂SO₄ [44]. μ -pDVB was prepared upon polymerization of technical grade DVB (85%, the complement to 100% is ethylbenzene) under 'solvothermal' conditions which ensure the peculiar morphology described in the Introduction. The ion-exchange capacity of the supports ranged from ca 1.0 to 2.5 mmol·g⁻¹ of a di-cation, corresponding to ca 100 to 250 mg of palladium, much more than needed to obtain a load of the supported metal of 5% (w/w) or lower. Some analytical data concerning the supports and the resin supported catalysts are reported in Table 1.

| Table 1. Selected analytical data on th | e resin-supported Pd cata | lysts empl | oyed in this work |
|---|---------------------------|------------|-------------------|
|---|---------------------------|------------|-------------------|

| | Ion-Exchange Cap | Pd | |
|---------------------------|------------------|-----------------|----------|
| | M+ | M ²⁺ | (%, w/w) |
| Pd/µS-pSDVB10 | 5.0 | 2.5 | 1.0 |
| Pd/µS-pDVB10 ^a | 2.0 | 1.0 | 1.0 |
| Pd/µS-pDVB35 ª | 3.2 | 1.6 | 3.6 |

 a the 1% and the 3.6% catalysts supported on $\mu S\text{-pDVB}$ were obtained from two different batches of the support.

The catalysts were generally used within 24 h from the final step of their preparation (reduction and drying). The leftovers of some of them were then divided into three batches, which were stored under different conditions before use. Coding of the different batches and their ageing histories are summarized in Table 2.

| | Age (weeks) ^a | Storage Atmosphere | Re-Activation |
|---------------------------------------|--------------------------|-------------------------|---------------------------------|
| Pd/mS-pSDVB10-2A Pd/µS-pDVB35-2A | 2 | Air (closed desiccator) | none |
| Pd/mS-pSDVB10-3N Pd/µS-pDVB35-3N | 3 | Nitrogen (dry-box) | none |
| Pd/mS-pSDVB10-4AR Pd/µS-pDVB35-4AR | 4 | Air (laboratory) | H ₂ , 506 kPa, 60 °C |

Table 2. History and coding of the catalysts' leftovers tested after ageing.

^a time from the end of the preparation and the use of the batch in the catalytic tests.

One batch was stored for two weeks in a closed desiccator under air to protect it from environmental humidity. The second one was stored for three weeks in a dry-box under nitrogen atmosphere ($O_2 < 10$ ppm; $H_2O < 0.1$ ppm). The third one was stored for four weeks under laboratory conditions and regenerated upon the very same reduction treatment used during its preparation.

2.2. Catalytic Runs: Fresh Catalysts

The catalytic tests reported herein were carried out at 25 °C and 101 kPa in a semi-continuous reactor containing the catalyst suspended in the alcoholic (CH₃OH) solution of the reagents (H₂, O₂) and products (H₂O₂, H₂O). The reaction mixture was kept under stirring, which was vigorous enough to ensure the kinetic regime. The reagents (4% H₂, 96% O₂) were continuously fed through separate mass-flow controllers at ambient pressure and temperature. Volatile species (mainly the solvent, if any) were abated with a condenser (-9 °C) and returned to the reactor prior to the analysis of the offgas with an on-line micro-gaschromatograph (μ GC). This set-up allowed to monitor the consumption of H₂ in real time, which was taken in this work as the measure of the catalytic activity. Representative curves are illustrated in Figure 3.



Figure 3. Kinetic plots of the overall H_2 consumption in the DS with Pd/mS-pSDVB10-3N (51.5 mg, diamonds; 100.3 mg, circles).

There is an initial delay (shaded area in Figure 3) between the start of the reaction (introduction of the catalyst into the reaction mixture) and the first detection of gas consumption, which we interpret as the time to the μ GC of the off-gas. The catalysts then generally underwent an activation period

and eventually reached a steady-state condition in which the apparent rate of H₂ consumption was constant (pseudo-zero order). The slopes of the steepest linear portions of these kinetic plots could be readily obtained and used to compare the catalytic activity. The plots in Figure 3 were obtained with different amounts of the same catalyst (51.5 and 100.3 mg) and the respective apparent rates (0.114 and 0.222 mmol_{H2}·h⁻¹) are in the same ratio as the amounts: This clearly demonstrates that the reaction is proceeding under kinetic regime, with a specific consumption rate of 23.6 mol_{H2}·mol_{Pd}⁻¹·h⁻¹. In some cases, the rate of H₂ declined at relatively long time on-stream and a plateau was observed depending on the catalyst stability. The amount of H₂O₂ produced was measured by indirect iodometric titration of small samples of the liquid phase periodically withdrawn from the reactor. The number of samples and their volume was small enough to have a negligible variation of the liquid-to-catalyst ratio (v/m). As the consequence, the kinetic plots of the production of H₂O₂ are much less time-resolved than those of the H₂ consumption. This way of collecting the catalytic data allows to readily calculate the selectivity and is much simpler than methods based on the Karl Fischer titration of water, which require a very strict control of the interference of environmental water.

Figure 4 represents the consumption of H₂ (top) and the production of H₂O₂ (bottom) with time over 100 mg of the catalysts, employed shortly after their preparation. The highest apparent reaction rate was achieved with Pd/µS-pDVB35, which is not unexpected in view of its relatively high metal load (3.6%). Pd/µS-pDVB10 and Pd/C were apparently almost as active as each other, with comparable apparent rates and the same metal load (1%, w/w). Pd/mS-pSDVB10 was very little active: this shows how important is the morphology of ion-exchanger resins when they are used as catalysts or catalytic supports.

In this case, it is well known that in macroreticular resins there is a more or less thick gel-phase beneath the surface of the permanent pores [27,45]: as a rule of thumb the higher the cross-linking degree the thinner is the layer (and smaller its proportion in the polymeric material) [45]. The sulfonic groups in the gel phase can be made accessible only upon swelling, which is relatively very effective in water in view of the hydrophilic nature of the –SO₃H groups. As the consequence if the ion-exchange process is carried out in aqueous environment, a part of the ions exchanged for H⁺ (or Na⁺ in this work) are taken up in the gel-phase. In Pd/mS-pSDVB10 this likely occurred to the [Pd(NH₃)₄]²⁺ ions during the preparation of the catalyst, so that they could have been excluded to some extent from the contact with H₂ during the reduction step in THF. In addition, the palladium nanoparticles formed in the gel phase, if any, could be excluded from the contact with the reagents of the DS due to less effective swelling in CH₃OH in comparison with water.



Figure 4. Cont.



Figure 4. Overall amount of H_2 consumed (mmol) and of H_2O_2 formed (bottom, mmol) over 100 mg of freshly prepared catalysts (used within 24 h from the end of preparation) as a function of time (lines in the bottom panel are intended to serve only as guides to the eye).

If the initial delay is neglected, all the curves in the top part of Figure 4 are practically always linear up to 4 h and those of the bottom part as well up to 80 min. This allowed to readily obtain their initials slopes, $-\left(\frac{\partial n_{H_2}}{\partial t}\right)_{80'}$ and $-\left(\frac{\partial n_{H_2O_2}}{\partial t}\right)_{80'}$ also used to calculate the initial specific apparent rates of H₂ consumption ($R_{s,H_2}^{80'}$) and H₂O₂ formation ($R_{s,H_2O_2}^{80'}$) (Table 3).

| | | | Pd/µS-pDVB10 | Pd/µS-pDVB35 | Pd/mS-pSDVB10 | Pd/C |
|----------|--|--|--------------|--------------|---------------|------|
| 1 | H ₂ feed rate (| µmol∙h ^{−1}) ^a | | 2452 | | |
| 2 | n _{Pd} (μ | mol) | 9.92 | 34.34 | 9.98 | 9.44 |
| 3 | $-\left(\frac{\partial n_{H_2}}{\partial t}\right)_{80\prime}$ (| umol·h ⁻¹) ^b | 792 | 1674 | 162 | 714 |
| 4 | $-\left(rac{\partial n_{H_2O_2}}{\partial t} ight)_{80\prime}$ | $(\mu mol \cdot h^{-1})^{c}$ | 739 | 1757 | 161 | 646 |
| 5 | $-\left(\frac{\Delta n_{H_2}}{\Delta t}\right)_{240\prime}$ (| μ mol·h ⁻¹) ^d | 414 | 720 | <54 | <60 |
| 6 | $\left(\frac{\Delta n_{H_2O_2}}{\Delta t}\right)_{240\prime}$ (| µmol·h ⁻¹) ^e | 396 | 174 | 58 | 39 |
| 7 | D_{1} (1, -1) | 80' ^f | 79.8 | 48.7 | 16.2 | 75.6 |
| 1 | κ_{s,H_2} (II –) | 240′ g | 75.5 | 51.2 | 16.1 | 75.6 |
| 0 | p $(h-1)$ | 80′ ^h | 41.7 | 21.0 | <5.4 | <6.4 |
| 0 | K_{s,H_2O_2} (II) | 240′ ⁱ | 39.9 | 5.1 | 5.8 | 4.1 |
| | C(0/) | 80′ ^j | 32.3 | 68.3 | 6.6 | 29.1 |
| 9 | C (%) | 240' ^k | 30.1 | 71.7 | 6.6 | 26.3 |
| 10 | C (9/) | 80′ ¹ | 52.2 | 43.1 | <33 | <8.5 |
| 10 S (%) | 5 (%) | 240′ ^m | 53.6 | 10.0 | 36.0 | 5.4 |

Table 3. Apparent and specific rates of H_2 consumption and H_2O_2 formation and the respective conversions and selectivities over different catalysts.

^a ca 9.8 mmol of H₂ are fed per single run overall; ^b initial slopes of curves up to 80 min in Figure 4 measured from the end of the delay and induction time; ^c total amount of H₂ consumed in the run (ΔnH_2) over the total reaction time (Δt); ^d initial slopes of curves in Figure 5 measured from the end of delay and induction time up to 80 min; ^e total amount of H₂O₂ formed in the run (ΔnH_2O_2) over the total reaction time (Δt); ^f calculated as the ratio of entry 3 over entry 2 in the same column; ^g calculated as the ratio of entry 4 over entry 2 in the same column; ^h calculated as the ratio of entry 5 over entry 2 in the same column; ⁱ calculated as the ratio of entry 4 over entry 1 in the same column; ¹ calculated as the ratio of entry 5 over entry 3 in the same column; ^m calculated as the ratio of entry 6 over entry 4 in the same column.



Figure 5. Representative HAADF-STEM (**top**) and TEM (**bottom**, **left**) microphotographs of Pd/µS-pDVB10 and HR-TEM of a Pd NP with corresponding FFT pattern (**bottom**, **right**).

The final rate values $\left(\left(\frac{\Delta n_{H_2}}{\Delta t}\right)_{240'}\left(\frac{\Delta n_{H_2O_2}}{\Delta t}\right)_{240'}, R_{s,H_2}^{240'}, R_{s,H_2O_2}^{240'}, \text{Table 3}\right)$ were simply obtained from the ratios between the number of moles of H₂ consumed and H₂O₂ formed at the end of the reaction, respectively, and the reaction time (4 h). The values of Δt employed for this calculation included also the initial delay and/or induction times, but they were apparently short enough to have a negligible effect on the results. In fact, the initial rate values of H₂ consumption, hence of conversions, are strictly comparable to the final ones as expected for catalysts working under steady state conditions.

Pd/mS-pSDVB10 turns out to be the least active catalysts by a great deal even when the specific rates are compared. In spite of this, the least productive one is Pd/C, because it produces H_2O_2 at the smallest rate. At the beginning of the reaction, Pd/mS-pSDVB10, Pd/µS-pDVB10, and Pd/µS-pDVB35 are therefore four to six times more selective than Pd/C (Table 3, #7). With Pd/µS-pDVB10 the selectivity in the first 80 min is a bit higher than 50% (at room temperature and with no promoters), with a conversion slightly above 30%.

These data show that the cross-linked sulfonated resins were better supports than carbon for the palladium catalysts for the DS, at least under the mild pressure conditions employed in this work. This was especially true for μ S-pDVB, which gave the most active and the most selective catalyst. This support was employed to prepare two catalysts, Pd/µS-pDVB35 and Pd/µS-pDVB10, with different metal loads (respectively 1.0% and 3.6%, w/w). R_{s,H_2} of Pd/µS-pDVB35 (ca 50 h⁻¹) was always smaller Pd/ μ S-pDVB10 (75–80 h⁻¹), which is compatible with a smaller proportion of active metal. $Pd/\mu S$ -pDVB10 is particularly interesting in that it was the only catalyst stable from the point of view of both activity and selectivity. We speculate that this was the consequence of the very open pore structure of this resin, which allow at the same time a fast inwards diffusion of the reagents and a fast outwards diffusion of H_2O_2 . This circumstance likely limited the transformation of H_2O_2 . into water, provided that the palladium load is was not too high. In fact Pd/µS-pDVB35 is much less selective at relatively long time. The bottom part of Figure 4 shows that the actual selectivity to H_2O_2 of Pd/μ S-pDVB35 approached zero after about 90 min, when a very slight decrease of the concentration of H_2O_2 started to be observed. In this case H_2O_2 was transformed into water (hydrogenation + dismutation) slightly faster than it was formed, which could be caused by the transformation of the catalyst into a still active, not selective form or by the onset of some transport limitations. The build-up of the concentration of H₂O₂ in the liquid could have increased the rate of the chemical reaction inside the catalyst and decreased the rate of its diffusion from the catalyst to the liquid phase, making them comparable. In this connection, the catalytic activities of Pd/µS-pDVB35 and Pd/µS-pDVB10 are in a slightly smaller ratio than the respective palladium loads (2.4 vs. 3.5), a hint that some mass transport limitations might be in operation with Pd/ μ S-pDVB35. As the result at the end of the catalytic run with Pd/ μ S-pDVB10 H₂O₂ was more than twice concentrated (and its yield proportionally higher) in comparison with Pd/µS-pDVB35, showing that the increase of the palladium load was detrimental to the catalytic performance altogether. Pd/C and Pd/mS-pSDVB10 seemed also stable, but because of their low selectivity (Pd/C) or activity (Pd/mS-pSDVB10) the final yield of H_2O_2 was so low that it was difficult to appreciate changes in the catalysts' performance, if any. For Pd/mS-pSDVB10, the possible confinement of palladium in the gel phase beneath the surface of the permanent pores could have made both its participation to the catalytic reaction and the removal of H_2O_2 away from the active surface with adverse effects on the selectivity and, above all, the activity.

In summary, Pd/ μ S-pDVB10 was the most productive among the catalysts investigated herein, Its productivity (specific rate of H₂O₂ formation) and the final H₂O₂ concentration in MeOH respectively corresponded ca 375 mol_{H₂O₂ ·kg⁻¹_{Pd}·h⁻¹ to 0.02% (w/w). This value is pretty low in comparison with previously reported literature values [46]. However, whereas our data were achieved with a total pressure as low as 101.3 kPa and 25 °C the literature ones were generally obtained at higher pressure and/or temperature. The observed difference of productivity can be therefore easily attributed to the difference in the experimental conditions. Moreover, Pd/ μ S-pDVB10 turned out to be as active as Pd/C, converting ca 750 in comparison with 710 mol_{H₂O₂ ·kg⁻¹_{Pd}·h⁻¹. As the result it showed a selectivity slightly above 50% stable with time, which is quite satisfactory for a unpromoted, monometallic palladium catalyst.}}

2.3. TEM Characterization

The best catalysts for the DS tested herein was Pd/ μ S-pDVB10. It gave the highest final absolute concentration (yield) in H₂O₂ and even more so relative to the amount of the active metal. This was the result of its higher selectivity, which was retained for a much longer time in comparison with the other catalysts, and of its stability leading to the longest useful lifetime found in this work. For this reason it was characterized by transmission electron microscopy (TEM), high angular annular dark field scanning electron microscopy (HAADF-STEM) and high resolution transmission electron microscopy (HRTEM) (Figure 5) along with the commercial Pd/C catalyst (Figure 6), which was taken as a benchmark. According to the supplier, this is an egg-shell catalyst and in fact metal nanoparticles (NPs) are clearly visible in its STEM image (Figure 6 top) close to the edge of the grain, but almost none was found close to the center. By contrast, the NP distribution is pretty homogeneous in Pd/ μ S-pDVB10 (Figure 5, top). The STEM microphotograph of Pd/ μ S-pDVB10 also highlights the very open pore

system of the support, where mesopores down to a few nanometers are also clearly visible. The size distribution analysis, carried out on the TEM microphotographs, showed a broad log-normal particle size distribution for both analysed samples (Figure 7).



Figure 6. Representative HAADF-STEM (**top**) and TEM (**bottom**, **left**) microphotographs of Pd/C and HR-TEM of a Pd NP with corresponding FFT pattern (**bottom**, **right**).

Pd/C is featured by a relatively narrow size distribution centred in the 1–3 nm range, a small fraction of NP up to 6 nm and none above this value. The mean NP size of this catalyst is 2.1 nm. Pd/ μ S-pDVB10 has a broader distribution, centered in the 3–6 nm range. The NP larger than 6 nm, topping 21 nm in diameter, are 21% of their total number. The presence of relatively large NPs in Pd/ μ S-pDVB10 is compatible with the features of the pore system of the support, because they can also be formed in relatively large mesopores. The HRTEM characterization of the catalysts provided a better insight on the structure of the nanoparticles. Lattice fringe analysis carried out on Pd NPs for Pd/C and Pd/ μ S-pDVB10 samples exhibit spots in the FT pattern at 2.2 Å and 2.0 Å that are ascribed to the spacing of {111} and {200} planes, respectively, of face centered cubic (fcc) structure of metallic



Pd [47–49]. This result shows that nanoparticles are formed by zerovalent palladium, but the presence of a thin layer of PdO at the surface cannot be ruled out.

Figure 7. Particle size distribution for Pd/C (122 NPs) and Pd/ μ S-pDVB10 (74 NPs).

Interestingly Pd/C was not more active than Pd/ μ S-pDVB10, although its NPs are smaller. The respective apparent rates of H₂ differed from each other by about 10%, but the specific rates were much closer. This suggests that the activation of H₂ was not structure sensitive, hence it did not depend on the morphological features of the metal phase. For this reason, the characterization of the metal phase was limited to these two catalysts only. Moreover, TEM was the only technique applied because CO chemisorption, commonly employed for this kind of investigation, is not suitable for polymer-supported materials [22]. As recalled above, in metal catalysts supported by ion-exchange sulfonated resins the NP can be located into domains of the polymer framework which are accessible only upon swelling. Therefore, gas–solid contact in dry conditions can be prevented to different extents (sometimes even completely, [50]) according to the support physico-chemical features. Even more interestingly, Pd/ μ S-pDVB10 was much more selective than Pd/C, which fully supports our hypothesis that the diffusion of H₂O₂ from Pd/ μ S-pDVB10 to the liquid phase is so fast to prevent its transformation into H₂O over the metal surface.

2.4. Catalytic Runs: Aged Catalysts

Ageing under different conditions was investigated for Pd/ μ S-pDVB35 and Pd/mS-pSDVB10. Figures 8 and 9 respectively illustrate the kinetic plots of consumption (top) and of the H₂O₂ formation (bottom) over different batches of these two catalysts. For the batch of Pd/ μ S-pDVB35 stored under the air and in a closed desiccator, the initial rate of H₂ consumption was decreased by about 17% (the comparison of fresh Pd/ μ S-pDVB35 with its aged forms will be hereafter limited to the beginning of the reaction, as it did not produce H₂O₂ any longer after 90 min). By contrast, the performances were closely comparable for the batches stored under the strictly inert N₂ atmosphere of a dry-box or under the environmental conditions of the laboratory and regenerated with the same treatment employed during the reduction step of its preparation (Table 4).





Figure 8. Overall amount of H₂ consumed (**top**, mmol) and of H₂O₂ formed (**bottom**, mmol) over 100 mg of aged batches of Pd/ μ S-pDVB35 as a function of time (lines in the bottom panel are intended to serve only as guides to the eye).





Figure 9. Overall amount of H_2 consumed (**top**, mmol) and of H_2O_2 formed (**bottom**, mmol) over 100 mg of aged batches of Pd/µS-pSDVB10 as a function of time (the point connected with lines refer to the fresh catalyst).

In these two cases, the activity was increased by about 24% in comparison with the fresh catalyst. These data show that ageing of Pd/ μ S-pDVB35 under oxidative conditions should be better avoided for the sake of the preservation of the activity. However, all the aged batches of this catalyst showed a 20–25% lower rate of H₂O₂ formation in the first 80 min. This leads to a drop of the selectivity, which was relatively moderate (from 43 to 28%) for Pd/ μ S-pDVB35-2A (aged under air in a closed desiccator), but much higher (from 43 to less than 10%) for Pd/ μ S-pDVB35-3N (aged under non-oxidative conditions) and Pd/ μ S-pDVB35-4AR (regenerated upon reduction). However, Pd/ μ S-pDVB35-2A turned out to be more stable than fresh Pd/ μ S-pDVB35: in fact, the final plateau in the concentration makes of H₂O₂ started after about 180 min (instead of 90 min) and the overall production of H₂O₂ was doubled in comparison with the fresh catalyst and its other aged batches. This indicates that, although the exposure of the catalyst to an oxidative environment made it less active and selective, it also decreased its rate of deactivation and made its useful lifetime long enough to give a higher final yield in comparison with the fresh catalyst. This is an intriguing finding, because the oxidation state of

palladium in the catalysts for the DS has been a vividly debated issue since long [2,14] and our results suggest that conflicting conclusions on its effect could be obtained with the same system depending on the design of the experimental set-up.

Table 4. Apparent and specific rates of H_2 consumption and H_2O_2 formation (values relative to the fresh catalyst in parentheses) and the respective conversions and selectivities over aged Pd/ μ S-pDVB35 batches.

| | Catalyst | | Pd/µS-pDVB35-2A | Pd/µS-pDVB35-3N | Pd/µS-pDVB35-4AR |
|----|--|---------------------------------------|---------------------|---------------------|---------------------|
| #1 | H ₂ feed rate (µmol·h | $(1^{-1})^{a}$ | | 2452 | |
| #2 | n _{Pd} (μmol) | | 36.0 | 35.3 | 33.1 |
| #3 | $\frac{-\partial n_{H_2}}{\partial t} (\mu \text{mol} \cdot \text{h}^{-1})$ | 80′ ^b 240′ ^c | 1386 (0.83) 1320 | 2124 (1.27) 2088 | 2070 (1.24) 2034 |
| #4 | $rac{-\Delta n_{H_2O_2}}{\Delta t} \ (\mu { m mol} \cdot { m h}^{-1})^{ m d} = rac{80'}{240'}$ | | 554 (0.77) 359 | 532 (0.74) 188 | 585 (0.81) 193 |
| #5 | R_{s,H_2} (h ⁻¹) ^e | 80' 240' | 38.5 (0.79) 36.7 | 60.2 (1.23) 59.2 | 62.5 (1.28) 61.5 |
| #6 | R_{s,H_2O_2} (h ⁻¹) ^f | 80' 240' | 15.4 (0.73) 10.0 | 15.1 (0.72) 5.3 | 17.7 (0.84) 5.8 |
| #7 | C (%) ^g | 80' 240' | 56.5 53.8 | 86.6 85.2 | 84.4 83.0 |
| #8 | S (%) ^h | 80' 240' | 40.0 27.2 | 25.0 9.0 | 28.3 9.5 |

^a ca 9.8 mmol of H₂ are fed per single run overall; ^b initial slopes (from the end of the delay+induction time to 80 min) of the curves in the top of Figure 5; ^c final slopes (80–240 min) of the curves in the top of Figure 5; ^d amount of H₂O₂ formed (ΔnH_2O_2) after the reaction time ($\Delta t = 80$ or 240 min) over Δt ; ^e calculated as the ratio of entry 3 over entry 2 in the same column; ^f calculated as the ratio of entry 4 over entry 2 in the same column; ^g calculated as the ratio of entry 3 in the same column.

This serves as an example of how much delicate the comparison of the performances of different catalysts for the DS can be, even when the experimental conditions are apparently similar and well controlled. This is especially true when the catalysts are tested in batch as to provide only 'single point' data at a given time. For instance, if the data of H_2O_2 formation of Figure 8 were compared taking only the 30 min values of conversion and selectivity, it might have been concluded that any ageing process is generally beneficial from the point of view of the selectivity, and that there is no difference between Pd/µS-pDVB35-2A and the other two aged batches (Pd/µS-pDVB35-3N, Pd/µS-pDVB35-4AR). However, Pd/µS-pDVB35 had an induction time and the aged samples had not, but from the end of the induction time on its kinetic plot for the formation of H_2O_2 was practically superimposable to those of Pd/µS-pDVB35-3N and Pd/µS-pDVB35-4AR in the whole run and to that of Pd/µS-pDVB35-2A in the first 40 min.

It is also clear from Figure 8. that for reaction times longer than 1 h Pd/ μ S-pDVB35-2A is better than the other aged catalysts and of the fresh catalyst too. All of them undergo of a decrease of selectivity with time (Table 4), but for Pd/ μ S-pDVB35-2A this is small enough to produce a larger amount of H₂O₂.

The interpretation of the results of the ageing experiments on Pd/mS-pSDVB10 (Table 5, Figure 9) is less straightforward, because this catalyst is little active and its aged batches as well, especially at the beginning of the reaction.

| | Catalyst | | Pd/mS-pSDVB10-2A | Pd/mS-pSDVB10-3N | Pd/mS-pSDVB10-4AR |
|----|---|---------------------|------------------|------------------|-------------------|
| #1 | H ₂ feed rate (μmol·h | 1 ⁻¹) a | | 2452 | |
| #2 | n _{Pd} (μmol) | | 9.63 | 9.42 | 9.57 |
| #3 | $\frac{-\partial n_{H_2}}{\partial t}$ (µmol·h ⁻¹) | 240' ^b | 53.0 (0.32) | 220 (1.36) | 155 (0.97) |
| #4 | $rac{-\Delta n_{H_2O_2}}{\Delta t}$ (µmol·h ⁻¹) ^c | 240′ | 17.6 (0.31) | 102 (1.76) | 55.6 (0.96) |
| #5 | R_{s,H_2} (h ⁻¹) ^d | 240′ | 5.5 (0.34) | 23.4 (1.45) | 16.2 (1.01) |
| #6 | R_{s,H_2O_2} (h ⁻¹) ^e | 240′ | 1.8 (0.31) | 10.8 (1.86) | 5.8 (1.00) |
| #7 | C (%) ^f | 240' | 2.2 | 9.0 | 6.3 |
| #8 | S (%) ^g | 240′ | 33.2 | 46.4 | 35.8 |

| Table 5. | Apparent | and | specific | rates | (values | relative | to | the | fresh | catalys | st in | parer | these | s) of |
|----------------------|------------|-------|----------------------|---------|-----------|-----------|------|------|---------|---------|--------|--------|-------|-------|
| H ₂ consu | mption and | H_2 | O ₂ forma | ation a | and the i | respectiv | e co | onve | ersions | and se | electi | vities | over | aged |
| Pd/mS-pS | SDVB10 bat | ches. | | | | | | | | | | | | |

^a ca 9.8 mmol of H₂ are fed per single run overall; ^b final slopes (120–240 min) of the curves in the top of Figure 6; ^c amount of H₂O₂ formed (Δn H₂O₂) at the end of the reaction (Δt = 240 min) over Δt ; ^d calculated as the ratio of entry 3 over entry 2 in the same column; ^e calculated as the ratio of entry 4 over entry 2 in the same column; ^f calculated as the ratio of entry 4 over entry 3 in the same column; ^g calculated as the ratio of entry 4 over entry 3 in the same column.

Therefore, we will compare these catalysts on a quantitative basis only for relatively long reaction time. In particular, the kinetic plots in the upper part of Figure 9 show that after 120 min all the catalysts attained the steady state and converted H₂ at constant rates. The final rates reported in Table 5 were calculated for $t \ge 120$ min from the slopes of the plots. The data show that ageing under oxidative conditions was detrimental to the activity (the consumption rate of H₂ clearly decreased with time for Pd/µS-pSDVB10-2A), but not to the selectivity. In this case the activity could be restored upon regeneration with a reducing agent and Pd/mS-pSDVB10-4AR practically replicated the performance of the fresh catalyst also from the point of view of the selectivity. Pd/mS-pSDVB10-3N, which was aged under inert atmosphere, was better than Pd/mS-pSDVB10, Pd/mS-pSDVB10-2A, and Pd/mS-pSDVB10-4AR. The reason why it was so is unclear at the moment.

The comparison of fresh and aged Pd/mS-pSDVB10 with fresh and aged Pd/mS-pDVB35 shows that the former ones were less affected by the exposure to oxidative conditions. This could be at least in part accounted for the protection from O_2 of the metal NPs of Pd/mS-pSDVB10. As recalled above, the morphology of the support implies that a proportion of the metal NPs are embedded in the polymer framework beneath the pore walls (the gel-phase) in the dry, unswollen support. As it can be reasonably assumed that these NPs gave a major contribution to the catalytic performance [27,51]. Pd/mS-pSDVB10 was apparently less affected by the storage in the presence of air and it was easier to restore the activity upon regeneration. However, great care must be taken in drawing such a conclusion because Pd/mS-pSDVB10 and its aged batches were pretty little active (about one order of magnitude less active than Pd/ μ S-pDVB35).

3. Experimental

Full experimental details, methods, materials, and equipment are illustrated in the Supplementary Materials to this article.

4. Conclusions

The results collected in this work show that mesoporous poly-divinylbenzene, transformed into a sulfonated ion-exchange resin, was a good support for monometallic, unpromoted palladium catalysts for the DS of H_2O_2 . Due to its open pore system it ensured a fast removal of this product away from the active metal, which was beneficial to the selectivity towards H_2O_2 (an unstable intermediate species in this system). Microporous active carbon was much less effective under this point of view, in spite

of the egg-shell distribution of the metal in the Pd/C catalyst investigated for comparison. Even a macroreticular ion-exchange resin, with a lower surface area, pore volume and pore diameter was not as effective as mesoporous poly-divinylbenzene. This can be attributed to its morphology which made more difficult the participation of the metal to the catalytic transformation. As a matter of fact, Pd/mS-pSDVB10 was the least active catalyst tested in this work and more or less as productive as Pd/C.

By contrast Pd/ μ S-pDVB10 was not only the most selective catalyst found in this work, but also the most active and the most stable one. It consumed H₂ as fast as an egg-shell Pd/C (or even slightly faster) and its selectivity at the end of the catalytic run (4 h on-stream) was the same as at the beginning (ca 50%). Its comparatively high activity is remarkable in view of the larger size of the palladium nanoparticles and of their 'unfavorable' radial distribution throughout the catalyst grains in comparison with Pd/C.

The strong differences in the catalytic performance observed for Pd/ μ S-pDVB10 and for Pd/mS-pSDVB10 are of particular interest, in that the macroreticular ion-exchange resins, just like mS-pSDVB, have been so far the most commonly employed as supports for the DS catalysts. It is worth mentioning that μ S-pDVB can be readily obtained from monomers already available for the preparation of commercial styrenic resins and from a well-established sulfonation procedure.

Ageing had different effects on the catalytic performance depending on the conditions of the storage of the catalysts. For Pd/ μ S-pDVB35 ageing under air implies a moderate reduction of the activity, but an improvement of the stability. Like the fresh catalyst it underwent a selectivity drop, but it was lower. If the catalyst was stored under inert atmosphere or was regenerated with H₂ the activity increased, but the selectivity was significantly lowered. The relatively poor activity of Pd/ μ S-pSDVB10 made the assessment of the effects of its ageing more uncertain. In the presence of air the catalyst was deactivated, but retained more or less the same selectivity and the regeneration restored its original performance. In this sense Pd/mS-pSDVB10 seemed less sensible to oxidative ageing than Pd/ μ S-pDVB. This is compatible with the difference in the morphology of the two supports: with its very open pore structure μ S-pDVB did not protect the metal NPs during ageing from the interaction with O₂ as effectively as mS-pSDVB. However, in view of the relatively low activities and selectivities (especially for Pd/mS-pSDVB10 and its aged forms), these conclusions must be taken with some care and further work to support them is under way.

Supplementary Materials: The following are available online at http://www.mdpi.com/2073-4344/9/2/124/s1, Materials and apparatus; Polymerization of DVB; Sulfonation of the macroreticular resin and of pDVB; Titration of sulfonated resins; Catayst preparation; Catalytic runs; On-line analysis of the off-gas.

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