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Functional Resins as Hydrophilic Supports for Nanoclustered Pd(0) and Pd(0)-Au(0) Catalysts Designed for the Direct Synthesis of Hydrogen Peroxide

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Abstract: The commercial macroreticular cation exchanger resin Lewatit K2621/H^+ and two gel-type resins bearing $-SO_3H$ and $-SMe$ functionalities are used to produce two acidic Pd(0)/resin(H^+) and one non-acidic Pd(0)-Au(0)/resin catalysts that are tested in the direct synthesis of H_2O_2 in methanol/water (2.5:1) at $-10\,°C$ and moderate H_2 and O_2 pressures. Molar yields in H_2O_2 after 1.5 hours, range from 12.9% [Pd(0)-Au(0)/resin] to 46% [Pd(0)/K2621/H^+].

Keywords: functional cross-linked polymer; hydrogen; hydrogen peroxide; oxygen; palladium

The direct synthesis of hydrogen peroxide from dihydrogen and dioxygen is attracting considerable attention in academic[1–8] and industrial[9] laboratories. The prospect of achieving small and medium capacity plants for the synthesis of H_2O_2 is in fact extremely appealing for the application of this clean oxidizing agent both in organic synthesis[9–11] and in the production of commercial items dealing with everyday life needs, i.e., detergency, cosmetics and sanitizing.

It is well known that the basic problem to be solved is the tuning of catalyst activity among the "simple" addition of O_2 to H_2, the disproportionation of the so-formed H_2O_2 and the over-reduction of O_2 to water. In this connection, the remarkable synergistic action of nanoalloyed Au(0) and Pd(0) in contrasting the over-reduction of O_2 and/or the disproportionation of H_2O_2 leads to promising results as reported by Hutchings et al. in refs.[1,2]

Early last year, Fierro and co-workers reported[3] on a very effective catalyst allegedly (and surprisingly for us) based on "Pd^{2+} centres" dispersed inside the polymer framework of a commercially available macroreticular resin bearing sulfonic groups (Lewatit K 2621/H^+). The liquid medium was similar to that employed by Hutchings et al., i.e., methanol/water mixtures, the major difference in the two approaches being the total pressure of the gaseous reagents, i.e., 100 bar in Fierro's system and 36.5 bar in Hutchings' one.

The very reason of our surprise stems from our long-standing and extensive experience[12–14] with the low chemical stability of "Pd^{2+}" ionically connected to SO_3^- groups hanging from the chains of cross-linked polymer frameworks. On the basis of the above, we hypothesize that in Fierro's catalyst, "Pd^{2+}" is unable to survive as such under the action of H_2 and methanol, albeit in the presence of O_2. Indeed, Fierro does not state what is the fate of Pd(II) at the end or during the catalytic run and does not report on catalyst reusability, if any. We herein confirm the remarkable data reported by Fierro but we raise questions on the very nature of Pd during the course of the catalyzed reaction, while we observe that Fierro's catalyst is reusable indeed.

We have recently reported[15] on an innovative protocol useful to produce size-controlled palladium nanoclusters (Template Controlled Synthesis, TCS, approach, see Figure 1 below) supported on designed gel-type resins. We have applied our expertise to obtain potential catalysts related both to Hutching' and Fierro's approaches, i.e., based on i) nanometer-sized, expectedly (see below) nanoalloyed Au(0) and Pd(0) supported on gel-type resins[16] and ii) designed gel-type sulfonic resins bearing either "Pd^{2+}" ions or Pd(0) nanoclusters to be possibly employed in water and featured by good stability and consequently reusability.

In essence, we designed our contribution along the following lines of reasoning:

i) Hutchings et al. employ a Pd-Au nanoalloy supported on alumina and we do produce a similar nanoalloy supported on a hydrophilic resin (**MTEMA-DMAA-MBA-10-4**, Scheme 1), potentially suitable to provide catalysts able to effectively work in pure water.

ii) Fierro et al. employ a macroreticular commercial strongly acidic resin (*ca.* 2.8 meq H^+/g) featured

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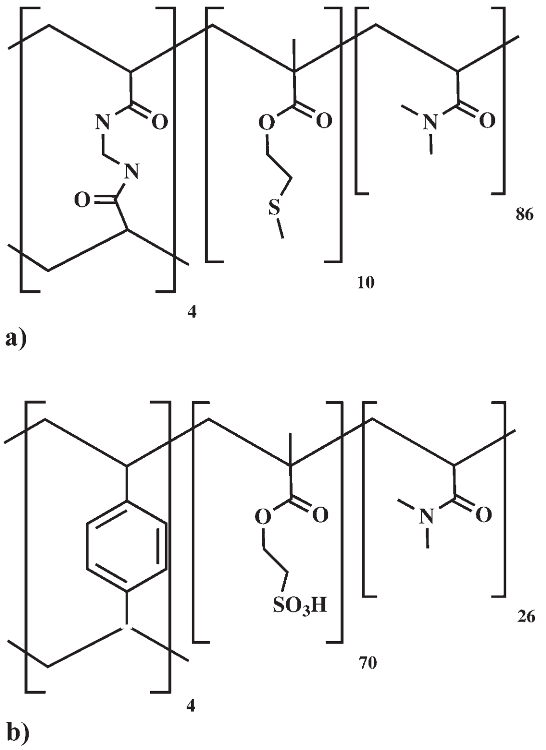

Scheme 1. Sketch of the primary structure of resin **MTEMA-DMAA-MBA 10–4** (10% mol – 86% mol – 4% mol) (**a**) and of resin **SEMA-DMAA-DVB** (26% mol, 70% mol, 4% mol) **(b)**.

by a substantial molar percentage of "Pd^{2+}", i.e., *ca* 10% of the initial H^+ functionality. In order to test our hypothesis that the active metal centre in Fierro's catalyst is in fact Pd(0) that is formed in the course of the catalytic run (if not even during its preparation[12]) we tested one of Fierro's catalysts in a pre-reduced protonated form, coded as **Pd(0)/Ⓟ$_F$-SO$_3^-$H$^+$** (**Ⓟ$_F$-SO$_3^-$H$^+$** is Lewatit K2621, see below) and we tested also new catalysts based on a tailor-made sulfonated resin (**SEMA-DMAA-DVB**, Scheme 1), which is a classic gel-type nanoporous resin prepared with our well established γ-rays sustained polymerization protocol of methacrylate monomers.[13]

The primary structure of our employed resins is depicted in Scheme 1. For sake of further simplification, we code occasionally **MTEMA-DMAA-MBA 10–4** also as **Ⓟ-SMe** and **SEMA-DMAA-DVB** also as **Ⓟ-SO$_3^-$H$^+$**. **MTEMA-DMAA-MBA 10–4** is a macromolecular ligand chemically and structurally very close to **MTEMA-DMAA-MBA 4–4** (4% mol – 92% mol – 4% mol), which resin was thoroughly investigated by us both as a ligand towards Pd(II) and Au(III) and as a macromolecular "mold" for the generation of size-controlled Pd(0) and Au(0) nanoclusters,[15,16] Figure 1.

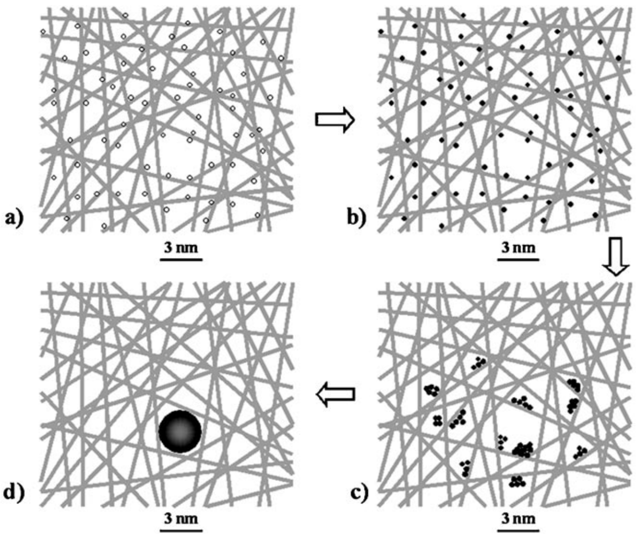

Figure 1. Model for the generation of size-controlled metal nanoparticles inside metallated resins. **a)** Pd(II) is homogeneously dispersed inside the polymer framework; **b)** Pd(II) is reduced to Pd(0); **c)** Pd(0) atoms start to aggregate; **d)** a single 3 nm nanocluster is formed and "blocked" inside of the largest mesh present in that "slice" of polymer framework (reproduced from *Angewandte Chemie*[15]).

MTEMA-DMAA-MBA 10–4 does swell considerably in water (1.78 mL/g) and it turns out to be suitable for the facile co-ordination of both metal centres. Thus, the resin undergoes facile metallation with Pd(OAc)$_2$ in acetonitrile and with HAuCl$_4$ also in acetonitrile to give **Pd(II)/Ⓟ-SMe** and **Au(III)/Ⓟ- SMe** macrocomplexes.[16] A quite similar reaction under similar conditions leads to the **Pd(II)-Au(III)/Ⓟ-SMe** macrocomplex. Treatment of the three macrocomplexes with excess NaBH$_4$ in water leads to the very rapid (seconds) formation of **Pd(0)/Ⓟ-SMe** black, **Au(0)/Ⓟ-SMe**, burgundy red, **Pd(0)-Au(0)/Ⓟ-SMe**, black,[16] tentatively considered to be a nanoalloy. This expectation is based on the following rationale (see Figure 1 and the relevant caption). **Ⓟ-SMe** undergoes equally facile metallation with both Pd(II) and Au(III) in acetonitrile under identical conditions and apparently with the same rate (visual estimate). In view of the isotropic nature of the **Pd(II)-Au(III)/Ⓟ-SMe** macrocomplex, the composition of the metal nanoclusters stemming from the simultaneous reduction of the two metal centres should reflect the statistical composition of the precursor macrocomplex itself. On the basis of the above, the formation of a homogeneously dispersed (*vide infra*) nanoalloy should not be surprising.

SEMA-DMAA-DVB is a tailor-made, gel-type ion-exchanger (2.1 meq H^+/g). The resin was loaded with Pd using a protocol fully analogous to that reported by Fierro et al. in ref.[3] After swelling in methanol, the resin undergoes facile palladiation with Pd(OAc)$_2$ dissolved in acetone to give **Ⓟ-SO$_3^-$ Pd^{2+}/2**, which in its turn un-

Table 1. Direct synthesis of H_2O_2 from H_2 and O_2 in the liquid phase.[a]

Entry	Catalyst	Residual cationic functionality	Pd [%]	Molar yield[b] [%]	Colour[c]
1	**Ⓟ$_F$-SO$_3^-$ Pd^{2+}/2**	H^+	1.1	35.0	beige
2	**Pd(0)/Ⓟ$_F$-SO$_3^-$**	H^+	1.1	46.0	gray
3	**Pd(0)/Ⓟ$_F$-SO$_3^-$**	Na^+	1.1	10.1	gray
4	**Ⓟ-SO$_3^-$ Pd^{2+}/2**	H^+	1.0	28.5	yellow
5	**Pd(0)/Ⓟ-SO$_3$**	H^+	1.0	26.2	dark brown
6	**Pd(0)-Au(0)/Ⓟ-SMe**	none	0.8[d]	12.9	black

[a] MeOH/H_2O = 2.4 (vol); P_{tot} = 20 bar [$P(H_2)$ = 0.25 bar; $P(O_2)$ = 3.7 bar; $P(CO_2)$ = 16.05 bar; $P(O_2)/P(H_2)$ = 15]; T = −10 °C; reaction time = 1.5 h; [Au(0)] = 2×10^{-4} M (analytical); [Pd(0)] = 1×10^{-4} M (analytical); liquid phase volume = 5.0 mL.

[b] Based on the moles of H_2 as limiting reagent.

[c] Before the occurrence of the first run.

[d] [Au] = 2.7%.

dergoes facile reduction to **Pd(0)/Ⓟ-SO$_3^-$ H$^+$**, upon treatment with refluxing ethanol. Such resins, both in unreduced and in pre-reduced form, are used (Table 1) for comparison purposes with **Ⓟ$_F$-SO$_3$-Pd^{2+}/2**, Fierro's catalysts, in which the non-palladiated cationic sites are in the H^+ form, and with **Pd(0)/Ⓟ$_F$-SO$_3^-$ H$^+$**, prepared by us from **Ⓟ$_F$-SO$_3$-Pd^{2+}/2** upon pre-reduction with ethanol, in which the non-palladiated cationic sites are also in **H$^+$** form.

To summarize, we have tested the following catalysts **Pd(0)-Au(0)/Ⓟ-SMe**, **Ⓟ$_F$–SO$_3^-$ Pd^{2+}/2**, **Pd(0)/Ⓟ$_F$-SO$_3^-$ H$^+$**, **Ⓟ-SO$_3^-$ Pd^{2+}/2**, **Pd(0)/Ⓟ-SO$_3^-$ H$^+$** and, by practical choice, we have selected the moderate total pressure of 20 bar. We have employed a standard batch laboratory reactor. Reaction conditions are listed in Table 1. They stem from an optimization screening centred on catalyst **Pd(0)-Au(0)/Ⓟ-SMe**, the protocol of which will be described elsewhere. The molar yield values reported in the Table are measured on the basis of the peroxide produced with respect to the initial amount of the limiting reagent (H_2). Since with the exploited simple apparatus the determination of H_2 conversion is not feasible, the values reported represent a lower limit for the hydrogen conversion to hydrogen peroxide (see also the Experimental Section).

It is seen that catalyst **Pd(0)/Ⓟ$_F$-SO$_3^-$ H$^+$** (entry 2) is the most active one among those tested by us, under our conditions. Fierro's catalyst (entry 1) is somewhat less active and we find that the colour of the catalyst after the first run is definitely gray, thus suggesting the occurrence of at least a partial reduction of Pd(II) to Pd(0). This perception finds a punctual support by TEM analysis of the catalyst just after the first catalytic run as shown by Figure 2. Furthermore, quite in line with our suspects (see above) *ca.* 5 nm Pd(0) nanoclusters (HRTEM control) are present (Figure 2) also in the as prepared catalyst. On the basis of elementary considerations based on the colours of the catalysts before and after the first catalytic run, we may safely propose that the percentage of reduction of Pd(II) to Pd(0) has to be very limited before the first catalytic run and significant thereafter. Most remarkably and again, as expected by us in view of the presumed formation of Pd(0) after the first run, Fierro's catalyst is found to be quite re-usable for at least two further runs with yields equal to 35.4% (second run) and 35.9% (third run). As to the positive role played by acidity in the catalyst activity, we checked this important point upon comparing the activity of pre-reduced **Pd(0)/Ⓟ$_F$–SO$_3^-$** in the H^+ and in Na^+ forms and we observe that the catalytic activity (conditions of Table 1) is quite appreciable also in the Na^+ form (*ca.* the half of the acidic one). Not only, but quite interestingly, we find that **Pd(0)/Ⓟ$_F$–SO$_3^-$** Na$^+$ is moderately active also in pure water (molar yield = 9.2%), under the conditions of Table 1, but at 2 °C.

As to the catalyst derived from **SEMA-DMAA-DVB** (entry 4) and functionalized with "Pd^{2+}", we observe that its activity does not appear to be affected by pre-reduction.

Finally, the bimetallic catalyst derived from **MTEMA-DMAA-MBA 10–4** exhibits a somewhat lower activity compared to the other catalysts. However, it has to be re-

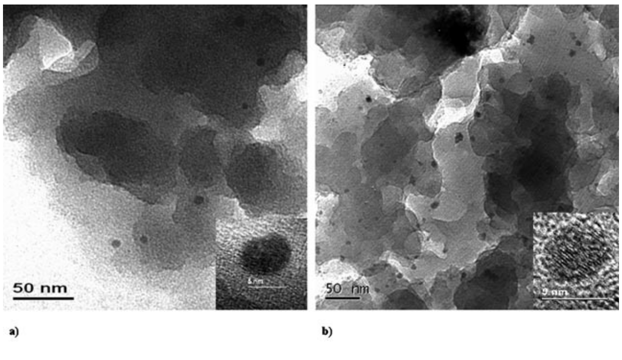

Figure 2. TEM micrographs of **Ⓟ$_F$-SO$_3^-$ Pd^{2+}/2** in the as prepared catalyst (*left*) and in the same after the first catalytic run (*right*). Pd(0) nanoclusters appear, albeit less numerous per "visual" field, also before the catalytic run and as well-spaced individual metal nanoclusters after the first run. HREM analysis confirms that the observed nanometer-sized spots are just Pd(0) nanoclusters.

marked that this catalyst lacks *a priori* acidic groups in the polymer backbone, which thus confirms that the acidity of the polymer framework does not appear to be essential to the catalytic process. The catalytic activity of the bimetallic catalyst appears indeed to be comparable to that reported by Hutchings et al. for Pd-Au nanoparticles dispersed on silica,[1,2] although in that case the catalytic tests were performed under slightly different reaction conditions (2 °C, 36.5 bar total pressure, O_2/H_2 ratio 1.2). We are currently attempting to prepare bimetallic Pd-Au catalysts inside acidic ion-exchangers: this task is not trivial, owing to the difficulties in incorporating Au precursors inside such resins and also to the lack of redox stability of the intermediate polymer-bound palladium(II) sulfonates, which we have demonstrated in a previous publication[l]12] and also in the present paper.

In conclusion, we confirm the remarkable catalytic potency of Fierro's catalyst in the direct synthesis of hydrogen peroxide, under conditions somewhat different from those employed in the work depicted in ref.[3] We find that the catalyst is definitely more active after pre-reduction of Pd(II) to Pd(0) and remarkably stable (re-usable in character). The catalyst, in the Na^+ form, turns out to be fairly active also in pure water. Finally, the presence of polymer-bound acidic groups in the support appears to have a positive influence on catalytic performance but support acidity is not essential for catalytic success. For technological applications, we envisage the opportunity to move from the batch type approach employed so far to one involving our best Fierro-like catalyst in a semi-continuous or a continuous microreactor.

Experimental Section

The catalytic reactions were carried out in a jacketed stainless steel reactor of 17.4-mL total available volume, including dead volumes due to connection lines, gauges and digital manometer, thermostatted at $-10\,^{\circ}C$ by an external liquid circulation thermostat. The vessel contains a glass beaker with an external diameter very close to the internal one of the reactor, which was loaded with the solvent (normally water:methanol 1:2.4, 5.0 mL), catalyst (50.0 mg) and a magnetic bar for stirring. In the absence of stirring, the reactor was pressurized first with a 25% O_2/CO_2 mixture (15.0 bar) and then with a 5% H_2/CO_2 mixture (5.0 bar) thus yielding a mixture of 2.98×10^{-3} O_2 and 1.99×10^{-4} H_2 moles. The catalytic process was triggered by stirring which allows the gases to rapidly dissolve in the liquid phase. Once the desired reaction time has elapsed, the vessel was vented off, the catalyst isolated by filtering and washed with water. The re-united aqueous layers were then analysed by iodometric titration in order to determine the amount of hydrogen peroxide formed. Scout experiments were carried out to check the effect of reaction time (30, 60, 90, 120 minutes) on the amount of hydrogen peroxide formed. The best yields were usually obtained after 90 minutes and this reaction time was maintained for all the experiments of Table 1. Indeed, in view of the fact that with the apparatus exploited the determination of H_2 conversion is not feasible, the hydrogen peroxide molar yields reported in Table 1 were measured supposing a complete hydrogen conversion. Therefore, the molar yields reported in Table 1 represent, as a matter of fact, a lower limit of the hydrogen conversion to hydrogen peroxide. From a practical point of view, the concentration of the hydrogen peroxide solutions thus obtained ranges from 3.83×10^{-3} M (entry 3) to 1.83×10^{-2} M (entry 2).

Reagents and solvents were of reagent grade from different commercial sources, and were used as received.

TEM analysis was carried out with a Philips CM 200 FEG apparatus equipped with a Supertwin-Lens operated at an accelerating voltage of 200 keV. Lens parameters: f = 1.7 mm, Cs = 1.2 mm, Cc = 1.2 mm, giving a point resolution of 0.24 nm and a line resolution of 0.1 nm. The preparation of samples for TEM analysis was carried out by mechanical milling of the as prepared solid sample and subsequent dispersing in ethanol with a ultrasonic bath for 0.5 h. One drop of the so-obtained suspension was brought onto a carbon-coated copper grid, dried at room temperature and then put into the microscope.

Resin Lewatit K2621 was obtained from Bayer AG and was thoroughly washed with 10% w/w aqueous ammonia solution and 10% w/w HCl solution. In practice, 2 g were treated with 4 portions of 5 mL each of ammonia solution and subsequently washed with excess water to neutrality of the supernatant; identical treatment was carried out with HCl solution.

The resin was then dried at 60 °C, and 6 mm Hg for one night, and stored in a closed glass vessel at ambient conditions.

Resins **MTEMA-DMAA-MBAA 10–4**[16] was available in the laboratory.

SEMA-DMAA-DVB was prepared upon irradiation of a mixture of 2-methacryloyl ethanesulfonic acid (5.1 g), *N,N*-dimethylacrylamide (7.2 g), divinylbenzene (1.0 g, technical grade) under dinitrogen with a γ-ray ^{60}Co source at room temperature for 18 hours at a distance of 17 cm from the source (total radiation dose was *ca.* 10 kGy). The so-obtained reddish rod was triturated with an impact grinder and then washed for 48 hours with methanol in a Soxhlet apparatus. After filtration, the pale red material was preliminarily dried, sieved to 180–400 μm and fully dried at 60 °C, 6 mmHg to constant weight. Anal. (%): C = 51.54, H = 7.89, N = 7.21, S = 5.24; estimated yield: *ca.* 98%.

Catalyst **Pd(0)-Au$^{(0)}$/Ⓟ-SMe** was also available in the laboratory.[16] **Ⓟ$_F$-SO_3^- Pd^{2+}/2** was obtained with the protocol published by Fierro et al.[3] after scaling down to 1/8 (mass). **Ⓟ-SO_3^- Pd^{2+}/2** was obtained with a protocol identical to that employed for **Ⓟ$_F$-SO_3^- Pd^{2+}/2**. **Pd(0)/Ⓟ$_F$-SO_3^-** (dark gray) and **Pd(0)/Ⓟ-SO_3^-** (dark brown) were obtained from **Ⓟ$_F$-SO_3^- Pd^{2+}/2** and **Ⓟ-SO_3^- Pd^{2+}/2**, respectively, upon treatment with boiling ethanol for 12 hours.

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