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Direct synthesis of hydrogen peroxide solution with palladium-loaded sulfonic acid polystyrene resins

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Received (in Cambridge, UK) 19th February 2004, Accepted 29th March 2004
First published as an Advance Article on the web 22nd April 2004

Anchorage of Pd^{II} ions into mesoporous ion-exchange resins functionalized with sulfonic groups is highly effective for the direct synthesis of hydrogen peroxide using methanol as a solvent at 313 K. The high performance of these catalytic systems is due to the ability of sulfonic acid groups of the resin to interact and stabilize Pd^{II} ions without further reduction to metallic palladium, as revealed by photo-electron spectroscopy.

Hydrogen peroxide is a clean oxidizing agent that is useful for a large variety of processes, such as use as a whitening agent in the textile or paper industries, as a disinfectant, and as basic product in the chemical industry, *e.g.* in the production of peroxide compounds (sodium perborate, sodium percarbonate, metallic peroxides or percarboxylic acids), in oxidation reactions (manufacture of amine oxides), epoxidation and hydroxylation (manufacture of plasticizers and stabilizers). It is further used for cleaning surfaces in the semiconductor industry, the chemical polishing of copper, tin and other copper alloy surfaces, and for etching electronic circuits, *etc.* However, because of the high cost of its production by the standard anthraquinone process,[1] hydrogen peroxide cannot be used for the production of bulk organic chemicals or for water treatments. Moreover, the anthraquinone method is not a green process. A very attractive alternative to this process is the production of hydrogen peroxide directly from the reaction between hydrogen and oxygen.

Although the formation of hydrogen peroxide in the palladium-catalyzed liquid-phase oxidation of hydrogen has been known since 1914,[2] and indeed several patents have been issued since then,[3,4] this process could not be put into practice. This is mostly because of its very hazardous nature[3] (the explosive limits of hydrogen/oxygen gas mixtures are very broad and are further increased with increasing pressure), and/or poor hydrogen peroxide selectivity and yield.[4,5] In this process, high concentration of H$^+$ and Br$^-$ ions is necessary in the reaction medium to obtain high concentrations of hydrogen peroxide. These ions are obtained from strong acids, such as sulfuric, phosphoric, hydrochloric or nitric and inorganic bromides.[6] Nevertheless, working with solutions of high acid concentration requires the use of special equipment to avoid corrosion. Furthermore, the presence of acid solutions and halogen ions favors the solution of active metals[7] (platinum group) which first causes deactivation of the catalyst and, due to the very low dissolved metal concentration, its recovery is non-viable.

Here we report a new procedure, based on the use of sulfonic acid-functionalized resins that permits the production of hydrogen peroxide by means of a direct reaction between hydrogen and oxygen, yielding high-concentration, non-corrosive hydrogen peroxide solutions with high selectivity.

Two palladium catalysts were prepared using mesoporous ion-exchange resins functionalized with sulfonic groups. Catalysts were prepared from two commercial resins functionalized with sulfonic groups Lewatit K2621 and K2641, kindly provide by Lewatit (Bayer AG). In a first step, the resin was washed three times with acetone, using equal volumes of solvent and resin. Then, a resin suspension (4 g) was stirred with 50 ml of methanol. To this suspension, a Pd(II) acetate solution (86 mg) in acetone (20 ml) was added dropwise. The suspension was concentrated to half of the solvent in a rotary evaporator; the temperature of the bath was 318 K. The remaining solution was filtered off and the solid obtained was washed and air-dried at 333 K for 2 h. A bimetallic catalyst was prepared using a Pd:Pt atomic ratio of 10:1. The Pt salt employed was tetra-ammine platinum(II) nitrate. An account of the catalysts prepared, resins characteristics and results of chemical analysis is given in Table 1.

Both functionalized resins showed moderate specific surface areas of approximately 40 m^2 g^{-1} and a high degree of cross-linking. Neither property seems to be detrimental to the liquid-phase reaction because the resins become swollen in the presence of a solvent and, therefore, access of the reagents (H_2 and O_2) to the active sites is facilitated.[8] In all cases, the amount of palladium incorporated, determined by ICP-AES (Perkin-Elmer Optima 3300 DV), to the resins was similar and similar to that added to the solutions employed in the preparations.

The photoelectron spectra (VG Escalab 200R spectrometer) of the Pd 3d core-levels showed the characteristic spin–orbit splitting of Pd 3d levels, the most intense 3d$_{5/2}$ component being located at lower binding energies and the least intense 3d$_{3/2}$ one located at higher binding energies (Fig. 1). Since chemical information can be extracted from each of these components, in what follows attention will only be paid to the most intense one (Pd 3d$_{5/2}$). Upon applying a peak fitting procedure to the experimental Pd 3d$_{5/2}$ spectra, two palladium species were detected. One appeared at a binding energy of 336.5 eV, which was assigned to PdO clusters, and the second one appeared at 338.2 eV, corresponding to Pd^{II} ions interacting with the –SO$_3$H groups of the resins. The percentage of these species was found to be a function of the resin employed in the

Table 1 Characteristics of the supports, catalysts prepared, binding energy of Pd 3d core-levels and Pd/S surface atomic ratio as determined by XPS

Catalyst	Resin	Exchange capacity (eq l^{-1})	Pore diameter (nm)	Pore volume (ml g^{-1})	BET Surface (m^2 g^{-1})	% wt. Pd	BE Pd 3d$_{5/2}$ (eV)	Pd/S at
Cat1	K2641	4.8	70	0.30	35	1.49	336.5 (29) 338.3 (71)	0.041
Cat2	K2621	1.4	70	0.60	40	1.34	336.6 (56) 338.1 (44)	0.060
Cat3[a]	K2621	1.4	70	0.60	40	1.37 (0.14 Pt)	336.4 (52) 338.2 (48)	0.059

[a] Bimetallic catalyst with palladium/platinum.

DOI: 10.1039/b402530j

preparation, *i.e.* the resin with the higher surface density of sulfonic acid groups (K2641) led to a higher amount of Pd^{II} ions interacting with the –SO_3H groups. In addition, a slight increase in the amount of Pd^{II} ions interacting with the sulfonic group was found in the bimetallic system (Cat 3). Quantitative XPS analysis revealed that the Pd/S atomic ratio (Table 1) was also dependent on the resin employed. As expected, Cat 1 displayed a lower Pd/S ratio than catalysts Cat2 and Cat3 due to its higher density of sulfonic acid groups, although the drop in the Pd/S ratio was even smaller than that expected merely from the sulfur content of the resin. Thus, it may be inferred that palladium is still more dispersed in Cat1 than in the other two catalysts.

These catalysts were tested in the direct synthesis of hydrogen peroxide. In a typical run, 0.80 g of the catalyst was placed in an autoclave with 150 g of a methanol:water mixture (96:4) and 12 ppm of HBr, and the mixture was heated to 313 K. Then, the system was pressurized with a H_2:O_2:N_2 (2:48:50) mixture with a total flow of 2500 ml N min^{-1} at 10 MPa without stirring, after which stirring was started (1500 rpm) to initiate the reaction. Hydrogen consumption was determined by GC–TCD using an Agilent 6850 equipment. Hydrogen peroxide and water concentrations were measured by iodometric and Karl-Fischer standard titrations, respectively.

Hydrogen consumption was in all cases fairly high ($> 90\%$). The concentration profiles of H_2O_2 were found to depend linearly with the time of reaction, indicating that reaction proceeds at a constant rate (Fig. 2). The hydrogen peroxide production rate was very high (Table 2), and clearly higher than data reported previously when an acid-free solvent was employed.[5e] Table 2 shows that the hydrogen peroxide concentration depends on the type of resin employed as the support of the palladium phase. The catalyst prepared with resin K2641 (Cat1) exhibited the largest yield to hydrogen peroxide. As may be seen in Table 2, this result is at least partly due to the increase in hydrogen peroxide selectivity. Photoelectron spectra of used catalysts were virtually identical to the fresh counterparts. The activity data are in good agreement with the nature of the palladium species, as revealed by photoelectron spectroscopy. The catalyst with the lowest proportion of PdO, and hence with the highest amount of Pd^{II} ions interacting with the –SO_3H groups (Cat1), afforded the highest selectivity and highest concentration of hydrogen peroxide in the liquid phase. A similar effect, although less marked, was noted in the bimetallic catalyst (Cat3). These findings point to Pd^{II} species interacting with –SO_3H groups as being the site responsible for H_2O_2 formation.[5a] Otherwise, a large proportion of PdO species may result in the formation of metallic Pd clusters during the reaction, which, in turn, catalyze the subsequent decomposition of hydrogen peroxide to water.[8]

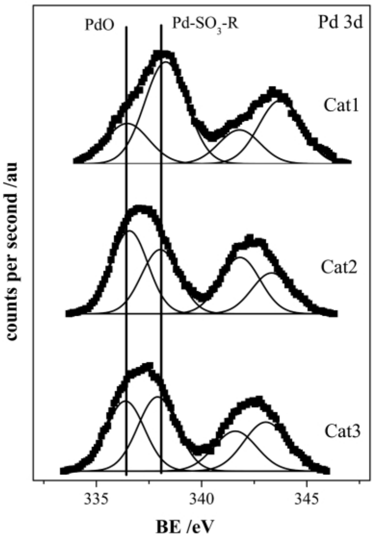

Fig. 1 Photoelectron spectra of the Pd 3d region of catalysts.

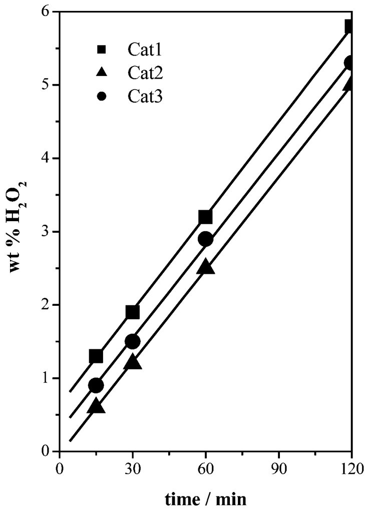

Fig. 2 Hydrogen peroxide concentration profile *versus* time along the direct reaction of hydrogen and oxygen at 313 K.

Table 2 Catalytic activity results of the catalysts in the direct synthesis of hydrogen peroxide

Catalyst	wt % H_2O_2[a]	% Selectivity of H_2[a]	H_2O_2 Production rate (mol H_2O_2 h^{-1} mol Pd^{-1})
Cat1	5.8	77	1105
Cat2	4.9	72	1070
Cat3	5.2	74	1155
Pd:Au/Al_2O_3[b]	0.1[c]	14[c]	10

[a] Data at 2 h of reaction [b] From reference 5e. [c] At 60 min of reaction.

In sum, palladium-loaded sulfonic acid-functionalized resins prove to be efficient in the synthesis of hydrogen peroxide by the direct reaction between hydrogen and oxygen in a solvent. The most effective resin was the one exhibiting the highest surface density of sulfonic-acid groups (K2641). The high performance of this catalyst is due to the presence of a larger fraction of Pd^{II} ions interacting with the –SO_3H groups of the resin.

The authors acknowledge financial support from Repsol-YPF (Spain). JMCM acknowledges a fellow awarded by the MCYT (Spain) in the Ramon y Cajal Program. GBB and ECS gratefully acknowledge fellowships granted by Repsol-YPF.

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