

# Direct synthesis of hydrogen peroxide on palladium catalyst supported on sulfonic acid-functionalized silica†

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**The direct synthesis of H<sub>2</sub>O<sub>2</sub> has been successfully achieved at high-concentration and high selectivity on Pd-loaded sulfonic acid-functionalized silica using non-acidic solutions and a reaction temperature of 313 K.**

Hydrogen peroxide is a clean oxidizing and bleaching agent that is widely used for water purification/wastewater treatments as a whitening agent and disinfectant, and so is a basic product in the chemical industry.<sup>1</sup>

Recently, H<sub>2</sub>O<sub>2</sub> has drawn growing interest in green chemistry because it acts as a direct and environmentally benign oxidant in organic synthesis,<sup>2</sup> and because its high cost limits the use for the production of bulk organic chemicals. The synthesis of hydrogen peroxide by direct reaction between H<sub>2</sub> and O<sub>2</sub> is a very attractive alternative to the traditional anthraquinone process. Direct synthesis over a Pd-based catalyst was first reported by Henkel and Webel in 1914<sup>3</sup> and several studies have been published since then.<sup>1</sup> However this process has yet to be put into practice. There are two major drawbacks: (i) the explosive limits of H<sub>2</sub>/O<sub>2</sub> gas mixtures are very wide<sup>4</sup> and are further widened with increasing pressure; and (ii) another major problem is to achieve good selectivity for H<sub>2</sub>O<sub>2</sub>. To remain outside the explosive region mixtures of H<sub>2</sub> and O<sub>2</sub> should contain less than about 4% hydrogen.

Acids are often incorporated into the reaction medium to delay or prevent the decomposition of hydrogen peroxide, which indeed takes place in the presence of bases.<sup>5</sup> For hydrogen peroxide formation, certain compounds, *i.e.* some of the halides, have to be added to delay water production, with the subsequent increase in hydrogen peroxide selectivity.<sup>5–10</sup> Although halides have good selectivity toward H<sub>2</sub>O<sub>2</sub> formation, they cause some delay in hydrogen conversion,<sup>5,8</sup> suggesting that halide ions are adsorbed on metal centres that indeed participate in the surface reaction between hydrogen and oxygen.<sup>7</sup> Among the halides, chlorides and bromides are most often used for this purpose.<sup>1,5,7,9</sup> The presence of acid solutions and halide ions in the reaction medium also has a detrimental effect by facilitating the corrosion of reactor material and producing the solution of active metals.<sup>11,12</sup>

**Table 1** Palladium concentration and BE of Pd core level spectra

Sample	Pd (wt%)	BE Pd 3d <sub>5/2</sub> /eV
PdSiTA-1	1.92	338.1 (89), 336.2 (11)
PdSiTA-2	0.97	338.1 (90), 336.2 (10)
PdSiTA-3	0.50	338.1 (91), 336.2 (9)
PdSiTA-4	0.26	338.1 (90) 336.2 (10)

The numbers in parentheses are peak proportions.

Organic solvents, especially alcohols, are better suited than water because of the greater solubility of H<sub>2</sub> and O<sub>2</sub>.<sup>13</sup> Methanol gives the highest rate of reaction.<sup>14,15</sup> Recent studies showed that the functionalization of supports result in an enhancement of hydrogen peroxide yields.<sup>16</sup> This observation is related to our earlier studies<sup>17,18</sup> in which we reported a new catalytic system, consisting of anchoring Pd(II) ions onto ion-exchange resins functionalized with sulfonic groups. This system produces hydrogen peroxide by direct reaction between H<sub>2</sub> and O<sub>2</sub> in methanol, and yields high-concentration, non-corrosive H<sub>2</sub>O<sub>2</sub> solutions with high selectivity.<sup>17,18</sup> The high yield attained with these catalysts is related to the interaction of sulfonic groups with palladium moieties. However, resin-based catalysts suffer from a lack of mechanical strength, thermal stability, and low specific area. An alternative support is amorphous silica, which has high specific area and very high mechanical strength, as the silica surface can be properly functionalized with sulfonic acid groups<sup>19</sup> similarly to sulfonic resins. A catalytic system based on this concept has been recently patented.<sup>20</sup>

Here we report a study of a catalytic system consisting of supported palladium nanoparticles deposited on commercial silica functionalized with sulfonic acid groups for the production of H<sub>2</sub>O<sub>2</sub> by direct synthesis between H<sub>2</sub> and O<sub>2</sub> in non-acidic solutions outside the explosive limits of H<sub>2</sub>/O<sub>2</sub> mixtures. The use of this catalyst yields a high-concentration hydrogen peroxide solution with high selectivity.

In a first step, a sample of functionalized commercial silica (Silicycle Tosic Acid) (10 g) was stirred with 125 mL of acetone. To this suspension, a palladium(II) acetate (Johnson Matthey) solution in acetone (50 mL) was dropwise added. The suspension was stirred for 1 h. The remaining solution was filtered off and the solid obtained was washed and air-dried at 333 K for 2 h. Four catalysts with different palladium loadings were prepared according to this procedure (Table 1). In all cases, the amount of Pd incorporated, determined by ICP-AES (Perkin-Elmer Optima 3300 DV) to the silica was similar to the nominal one.

The XRD profiles (X'Pert Pro PANalytical) of the samples showed only a broad peak due to silica substrate, but no

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diffraction lines of palladium species were observed. This fact indicates that the size of palladium particles is very small or non-crystalline. Samples were analyzed by TEM (JEOL 2100F $\times$ ), being difficult to measure in transmission mode, mainly due to the small particle size. It was therefore necessary to analyze in STEM mode, which magnifies the contrast between support and the palladium species (see Fig. 1 and the ESI $^\dagger$ ). All samples showed a homogeneous distribution of Pd particles with a size around 3–4 nm.

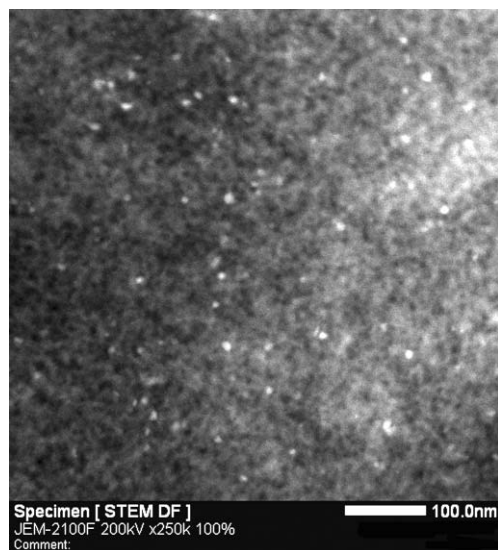


Fig. 1 STEM image of PdSiTA-1 sample.

Catalysts were tested for the direct synthesis of hydrogen peroxide. In a typical run, 1.6 g of the catalyst was put inside an autoclave with 150 g of methanol and HBr as promoter. The reactor was pressured with nitrogen to 9.5 MPa. The mixture was heated to 313 K. Then, the reaction gas mixture was fed ( $\text{H}_2:\text{O}_2:\text{N}_2 = 3.6:46.4:50$ ) with a total flow of 2500 mL(N)  $\text{min}^{-1}$ , and then the suspension was stirred (1500 rpm) to initiate the reaction. The reproducibility of the results is very high as demonstrated by replica experiments in which differences in product concentration smaller than 0.2 wt% were observed (see error bar in Fig. 2). Two blank experiments have been performed using the support and palladium(II) acetate. In both cases no hydrogen peroxide formation was detected.

There is a strong influence in the yield to hydrogen peroxide and the promoter concentration (bromide).<sup>5–8</sup> For this reason, different HBr/Pd weight ratios have been studied. The concentration studied was around the optimum one found previously for catalysts based on sulfonic resins.<sup>17,18</sup> The concentration of hydrogen peroxide clearly increases linearly in all experiments (Fig. 2), but the final  $\text{H}_2\text{O}_2$  concentration changes with the HBr/Pd ratio. The final hydrogen peroxide concentration increased with the HBr/Pd ratio peaking at around 0.160, then decreasing slightly at a higher HBr/Pd value. Selectivity to  $\text{H}_2\text{O}_2$  decreased with the time of reaction (concentration of  $\text{H}_2\text{O}_2$ ) in all cases. But this drop became more evident when the HBr/Pd ratio is lower than 0.150 (Fig. 2). Consequently, the maximum yield to hydrogen peroxide found for the HBr/Pd = 0.160 is due to a high selectivity to  $\text{H}_2\text{O}_2$  and hydrogen conversion. In all

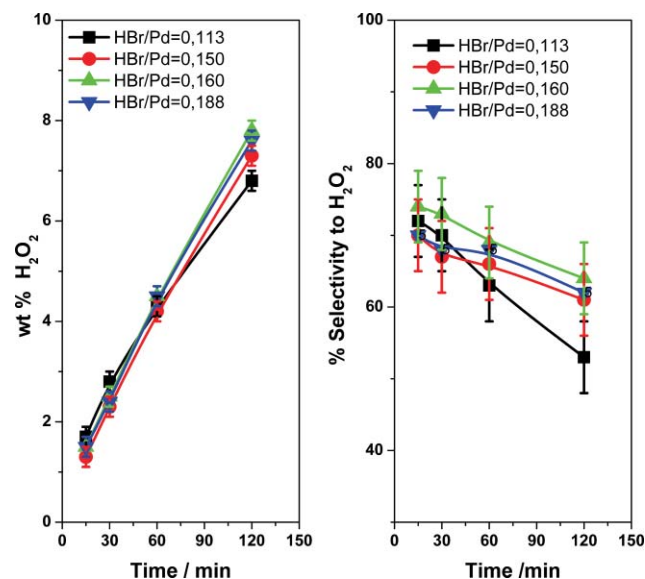


Fig. 2 Influence of the weight ratio HBr/Pd in the PdSiTA-2 catalyst on its performance in the  $\text{H}_2\text{O}_2$  concentration and selectivity profile versus time along the direct reaction of hydrogen and oxygen at 313 K.

cases the hydrogen conversion was above 90%. This optimum value corresponds to 24 ppm of HBr, which implies an almost neutral solution.

The effect of palladium loading in the catalyst was studied. Pd-loadings ranged from 1.92 wt%, corresponding to the exchange capacity of the support, to 0.26 wt%, about 8 times lower. These catalysts were analyzed by XPS. The photoelectron spectra of the Pd 3d core-levels showed the characteristic spin–orbit splitting of Pd 3d levels. Each component of the Pd 3d doublet appeared broad and asymmetric, suggesting that two palladium species are present. The peaks were fitted by a non-linear least square fitting routine using a properly weighted sum of Lorentzian and Gaussian component curves after background subtraction with Shirley line. By applying peak fitting procedures, two palladium species were identified (Fig. 3, Table 1).

For the most intense  $\text{Pd}3d_{5/2}$  level, one of these components appeared at 336.5 eV, which is usually assigned to PdO clusters, and the second one at 338.2 eV, corresponding to Pd(II) ions interacting with the  $-\text{SO}_3\text{H}$  anchored to the silica substrate. All catalysts exhibited a higher amount of Pd(II) species interacting with  $-\text{SO}_3\text{H}$  groups and a lower quantity of PdO species, which affords a high selectivity and conversion of  $\text{H}_2\text{O}_2$  in liquid phase.<sup>17,18</sup> No significant differences were observed in the proportion of palladium species.

These catalysts were used in the direct synthesis of hydrogen peroxide, using the same amount of palladium. This was achieved by adjusting the weight of catalyst. The performance in reaction was practically identical for all catalysts (Fig. 4). For the sake of simplicity, only two curves are shown. The concentration of  $\text{H}_2\text{O}_2$  and selectivity to hydrogen peroxide profiles are very similar. This observation suggests that the active species are identical in all catalysts and proves that selectivity and activity data are in agreement with the nature of palladium species<sup>17,18</sup> as revealed by XPS.

In general, reaction data are difficult to compare with those published in open literature because reaction conditions are

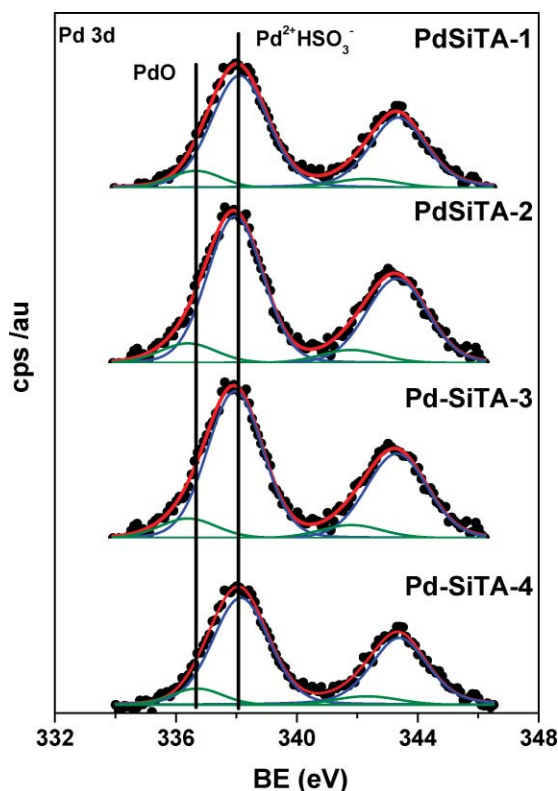


Fig. 3 Pd3d core-level spectra of prepared samples.

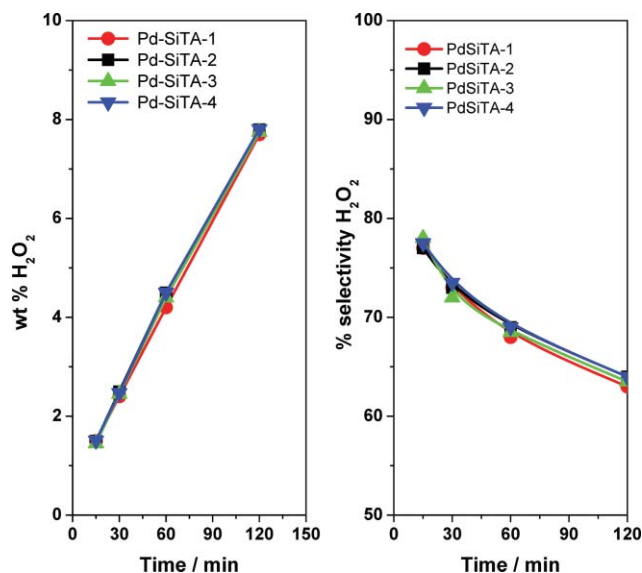


Fig. 4 Dependence between  $\text{H}_2\text{O}_2$  concentration/selectivity and reaction time for catalysts with different palladium loading.

different. In the present work, we have used a reaction temperature of 313 K, which is much more attractive from an industrial perspective and differs substantially from those used in most of the published works (273–278 K). The higher temperature used in this work has a twofold effect: (i) a high reaction temperature determines a high reaction rate, and therefore much higher hydrogen peroxide concentrations are obtained for shorter reaction times (7–8 wt% in this work), which contrasts with the much lower concentrations usually reported in the

Table 2 Selectivity and yield towards  $\text{H}_2\text{O}_2$  for different catalysts

Sample	Selectivity to $\text{H}_2\text{O}_2$ at 0.5 wt% $\text{H}_2\text{O}_2$	$\text{H}_2\text{O}_2$ yield <sup>a</sup> /mol kg <sub>cat</sub> <sup>-1</sup> h <sup>-1</sup>
PdSiTA-1	83	335
PdSiTA-2	84	165
2.5%Pd-2.5%Au/Carbon <sup>b</sup>	98	175

<sup>a</sup> Data taken at 1.5 wt%  $\text{H}_2\text{O}_2$ . <sup>b</sup> Data from reference 16.

literature; and (ii) the reaction temperature of 313 K selected in this work is closer to industrial application because the reaction  $\text{H}_2 + \text{O}_2 \rightarrow \text{H}_2\text{O}_2$  is highly exothermic and hence the heat released must be removed, this being easier at 313 K than at 278 K.

From Fig. 4 it is clear that the values of  $\text{H}_2\text{O}_2$  selectivity depend strongly on hydrogen peroxide concentration levels. In order to compare the performance of our catalysts with that reported in the literature,  $\text{H}_2\text{O}_2$  selectivity values in Table 2 have been extrapolated to the  $\text{H}_2\text{O}_2$  concentration region below 1 wt%. This simple procedure allowed us to make a reliable comparison of  $\text{H}_2\text{O}_2$  productivity. The data collected in Table 2 allow us to conclude that this family of catalysts supported on  $\text{HSO}_3^-$ -functionalized silica, and specifically PdSiTA-1, produce high  $\text{H}_2\text{O}_2$  yields with a high selectivity to  $\text{H}_2\text{O}_2$ , and thus they are promising for industrial exploitation.

Finally, the reuse of the catalysts was studied for PdSiTA-1 sample. No changes in the catalytic activity were observed after 15 operation cycles. Reactor effluent was analysed and no measurable amount of leached palladium was observed.

In short, the new catalyst system of supported palladium nanoparticles deposited on  $\text{HSO}_3^-$ -functionalized commercial silica used here produces hydrogen peroxide with a high yield (335 mol kg<sup>-1</sup> h<sup>-1</sup>) by feeding a non-flammable  $\text{H}_2/\text{O}_2$  mixture into a non-acidic catalyst-methanol suspension at 313 K. The advantages provided by this approach offer the possibility of industrial application.

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