

Contents lists available at ScienceDirect

Applied Catalysis A: General

journal homepage: www.elsevier.com/locate/apcata

New Pd–Pt and Pd–Au catalysts for an efficient synthesis of H₂O₂ from H₂ and O₂ under very mild conditions

Giulia Bernardotto^a, Federica Menegazzo^a, Francesco Pinna^a, Michela Signoretto^a, Giuseppe Cruciani^b, Giorgio Strukul^{a,*}^a Dipartimento di Chimica, Università di Venezia, and Consorzio INSTM, Dorsoduro 2137, 30123 Venezia, Italy^b Dipartimento di Scienze della Terra, Università di Ferrara, Via Saragat 1, 44100 Ferrara, Italy

ARTICLE INFO

Article history:

Received 19 November 2008

Received in revised form 15 January 2009

Accepted 3 February 2009

Available online 21 February 2009

Keywords:

Hydrogen peroxide synthesis

Hydrogen

Oxygen

Palladium

Platinum

Gold

Sulfated zirconia

Bimetallic catalysts

ABSTRACT

Bimetallic Pd–Pt and Pd–Au samples supported on sulfated zirconia were successfully tested for the direct synthesis of hydrogen peroxide under very mild conditions (1 bar and 293 K) and outside the explosion range. The effect of the addition of Pt to Pd in enhancing the yield of hydrogen peroxide is sensitive to the Pt amount: only using a low Pt content it is possible to improve H₂O₂ selectivity (from 55% to 70%) and productivity with respect to the monometallic sample. The addition of gold in 1:1 amount to palladium improved both the productivity and even more the selectivity of the process, producing a hydrogen peroxide concentration already useful for industrial applications and maintaining a stable selectivity (62%) after 12 h of time on stream.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

Hydrogen peroxide is a clean and excellent oxidizing reagent for the production of both fine and bulk chemicals, that finds applications also in the area of wastewater treatment and paper and pulp bleaching [1] although in these processes the cost of H₂O₂ may often be a limiting economic factor. Over 95% of the world's hydrogen peroxide is currently produced by the sequential hydrogenation and oxidation of an alkyl anthraquinone, a process essentially unchanged since the 1940s (AO process). This technology employs multiple unit operations, it generates considerable waste and requires significant energy input, lowering the sustainability of the process and raising the production costs. For hydrogen peroxide to successfully break into new markets, like e.g. commodity chemicals, the production should become cheaper. A distributed production based on on-site small scale plants would be a possible answer cutting transport costs. However the current AO process cannot be downsized for technical and economic

reasons. The direct synthesis of H₂O₂ from H₂ and O₂ is a possible way towards small scale plants that may potentially half the cost of hydrogen peroxide with respect to the commercial process [2]. Clearly, the contact between H₂ and O₂ is a significant safety hazard and, at present, no commercial processes have been developed despite several patents [3–9] and recent literature [10–15]. In addition another major problem associated with the process is the generally low H₂O₂ selectivity. Hydrogen peroxide is unstable with respect to both hydrogenation and radical decomposition, and the most thermodynamically favored reaction between hydrogen and oxygen is, by far, water formation (Fig. 1).

So far Pd has qualified as the best catalytic material [10,11,14,16–19]. However, it is well known that alloying or combining two metals can lead to materials with specific chemical properties due to an interplay of “ensemble” and “electronic” effects [20], and that a bimetallic surface can exhibit catalytic properties that are very different from those of the surfaces of the individual metals. It has also been demonstrated that the combination of Pd with Au [21–23], Ir [24], Ag [25], and Pt [21,25–27] can improve both the productivity and the selectivity of the process.

We have already shown [14] that sulfated zirconia is an excellent support for Pd-based catalysts for H₂O₂ direct synthesis, performing better than plain zirconia. It also allows to avoid the

* Corresponding author at: Dipartimento di Chimica, Università di Venezia, Dorsoduro 2137, 30123 Venezia, Italy. Tel.: +39 041 234 8931; fax: +39 041 234 8517.

E-mail address: strukul@unive.it (G. Strukul).

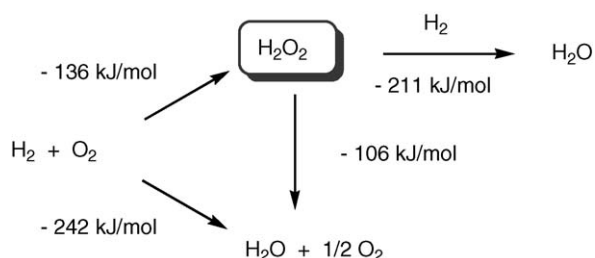


Fig. 1. Reactions involved in the direct production of H_2O_2 .

addition of halides as promoters to improve the selectivity of the catalytic system.

In the present work we report a detailed investigation on the influence of the presence and content of a second metal (Pt and Au) on H_2O_2 synthesis by preparing a series of sulfated zirconia supported bimetallic samples with various metal amounts and testing their performance under very mild conditions (1 bar and 293 K), outside the explosion range.

2. Experimental

2.1. Materials

ZrOCl_2 (Fluka) and $(\text{NH}_4)_2\text{SO}_4$ (Merck), were used as received for sample synthesis. All kinetic tests were performed in anhydrous methanol (SeccoSolv, Merck [H_2O] < 0.005%). Commercial standard solutions of $\text{Na}_2\text{S}_2\text{O}_3$ (Fixanal [0.01], Hydranal-solvent E, and Hydranal-titrant 2E, all from Riedel-de Haen) were used for iodometric and Karl–Fischer titrations.

2.2. Catalyst preparation

Sulfated zirconia was prepared by precipitation from ZrOCl_2 at pH = 10, aged under reflux conditions for 20 h [28,29], washed free from chloride (AgNO_3 test) and dried at 383 K overnight. This material was impregnated by incipient wetness method with ammonium sulfate, in amounts necessary to yield a nominal anion loading of 8% by weight. Impregnated supports were then calcined in flowing air (30 ml/min) at 923 K for 4 h. Metals were deposited on sulfated zirconia by incipient wetness (co)impregnation of H_2PdCl_4 and/or H_2PtCl_6 , HAuCl_4 aqueous solutions in different amounts. Samples were finally calcined at 773 K in flowing air (30 ml/min) for 3 h.

2.3. Methods

Surface areas and pore size distributions were obtained from N_2 adsorption/desorption isotherms at 77 K (using a Micromeritics ASAP 2000 analyser). Calcined samples (300 mg) were pretreated at 573 K for 2 h under vacuum. Surface area was calculated from the N_2 adsorption isotherm by the BET equation, and pore size distribution was determined by the BJH method [30]. Total pore volume was taken at $p/p_0 = 0.99$. The amount of sulfate was determined by ion chromatography (IEC) after dissolution of the materials [31]. All sulfate concentrations were calculated as the average of two independent sample analyses, and each analysis included two chromatographic determinations.

Actual metal loading was determined by atomic absorption spectroscopy after microwave disaggregation of the samples (100 mg). The differences between loaded and found metal content were always within $\pm 5\%$.

TPR experiments were carried out in a home-made equipment: samples (100 mg) were heated with a 10 K/min ramp from 298 to 1500 K in a 5% H_2/Ar reducing mixture (40 ml/min STP).

CO chemisorption measurements were performed at 298 K using a home-made pulse flow system. Prior to measurements, samples were subjected to a pretreatment involving exposure to hydrogen flow for 1 h at 298 K, followed by He purge for 2 h at the same temperature of reduction.

X-ray powder diffraction (XRD) patterns were measured by a Bruker D8 Advance diffractometer equipped with a Si(Li) solid state detector (SOL-X) and a sealed tube providing Cu K α radiation. Measuring conditions were 40 kV \times 40 mA. Apertures of divergence, receiving and detector slits were 1° , 1° , and 0.3° respectively. Data scans were performed in the 2θ range $20\text{--}80^\circ$ with 0.02° stepsize and counting times of 10 s/step. The normalized Reference Intensity Ratio (RIR) method and the Rietveld refinement, as respectively implemented in the Bruker EVA and TOPAS programs, were used to obtain the quantitative phase analysis and the crystal size of zirconia polymorphs and metals in the samples.

2.4. H_2O_2 synthesis

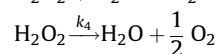
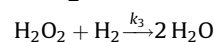
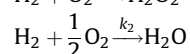
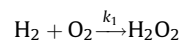
Catalytic tests were carried out at atmospheric pressure in a 293-K thermostatted glass reactor according to a previously described procedure [14,23]. Mixing was carried out with a Teflon[®]-made rotor operating at 1000 rpm. Oxygen and hydrogen were bubbled by a gas diffuser directly into the liquid phase with a total flow of 50 ml/min. A gas mixture with the following composition was used: $\text{H}_2:\text{O}_2$ 4:96 (nonexplosive and lower limit for nonflammable mixture) [32].

The reaction medium was 100 ml of a 0.03-M H_2SO_4 methanolic solution and was pre-saturated with the gas mixture before catalyst (135 mg) introduction. An activation process giving rise to a surface oxidized Pd particle was used: samples were pretreated in situ first by H_2 (15 min, 30 ml/min) and then by O_2 (15 min, 30 ml/min) flow. During catalytic tests small aliquots of the liquid phase were sampled through a septum and used for water and hydrogen peroxide determination. H_2O_2 concentration was measured by iodometric titration, whereas water was determined by volumetric Karl–Fischer method. The water content in the reaction medium before catalyst addition was determined prior to each catalytic experiment. H_2O_2 selectivity at time t was determined as follows:

$$S_{\text{H}_2\text{O}_2} = \frac{[\text{H}_2\text{O}_2]}{[\text{H}_2\text{O}_2] + [\text{H}_2\text{O}]}$$

Independent tests for hydrogen peroxide decomposition were carried out by placing the catalysts in contact with a slightly concentrated H_2O_2 solution (60 mM) in the same reactor used for synthesis, and replacing either H_2 or O_2 by N_2 , where appropriate.

A simple model was used to fit the kinetic data and find the apparent kinetic constants of the four reactions involved in the catalytic process:



$$\frac{dc_{\text{H}_2}}{dt} = -k_1 c_{\text{H}_2}^a c_{\text{O}_2}^b - k_2 c_{\text{H}_2}^c c_{\text{O}_2}^d - k_3 c_{\text{H}_2\text{O}_2} e c_{\text{H}_2}^f$$

$$\frac{dc_{\text{O}_2}}{dt} = -k_1 c_{\text{H}_2}^a c_{\text{O}_2}^b - k_2 c_{\text{H}_2}^c c_{\text{O}_2}^d$$

$$\frac{dc_{\text{H}_2\text{O}_2}}{dt} = k_1 c_{\text{H}_2}^a c_{\text{O}_2}^b - k_3 c_{\text{H}_2\text{O}_2} e c_{\text{H}_2}^f$$

$$\frac{dc_{\text{H}_2\text{O}}}{dt} = k_2 c_{\text{H}_2}^c c_{\text{O}_2}^d + 2 k_3 c_{\text{H}_2\text{O}_2} e c_{\text{H}_2}^f$$

The results of the hydrogen peroxide decomposition tests clearly indicate that H_2O_2 is stable in contact with the catalyst in the absence of H_2 . On the contrary, there is a clear indication that H_2O_2 is poorly stable in presence of H_2 only. Hence it can be concluded that the most likely decomposition mechanism under our mild experimental conditions is H_2O_2 reduction caused by H_2 , while H_2O_2 dismutation is negligible. Therefore, as already discussed [23,33], we accounted only for H_2O_2 decomposition by H_2 reduction, while H_2O_2 disproportionation reaction was not considered. In the system of differential equations coming from mass balance the concentrations of H_2 and O_2 into the liquid phase can be considered constant, since these reagents are continuously fed into the semi-batch reactor [14,23]. Their concentrations can be incorporated into the kinetic constants k_n to give apparent kinetic constants k'_n , and the resulting system of differential equations can be solved for the H_2O_2 and H_2O concentrations to give:

$$c_{\text{H}_2\text{O}_2} - c_{\text{H}_2\text{O}_2}^0 = \frac{k'_1}{k'_3} (1 - e^{-k'_3 \cdot t}) \quad \text{and}$$

$$c_{\text{H}_2\text{O}} - c_{\text{H}_2\text{O}}^0 = (k'_2 + 2k'_1 + 2k'_3 c_{\text{H}_2\text{O}_2}^0) \cdot t - 2 \frac{k'_1}{k'_3} (1 - e^{-k'_3 \cdot t})$$

Catalytic tests data fitting was carried out with a computer program (OriginLab OriginPro7.5[®]), equipped with a special fitting tool (based on the Levenberg–Marquardt (LM) algorithm) performing non-linear regression analysis.

3. Results and discussion

3.1. Sulfated zirconia

Zirconia sulfation [34] has been the subject of extensive research due to its characteristics. In fact, it causes not only modifications of the acid properties of the material, but it affects also surface features, since sulfates retard crystallization, stabilize ZrO_2 tetragonal phase and improve the surface area and the pore size. These properties make sulfated zirconia interesting both as catalyst and as catalyst support. In the present work sulfated zirconia was used as support and was characterized by N_2 physisorption and sulfur content measurements. The use of a mesoporous material is very important in this investigation, since the presence of micropores could bear mass transfer problems, while a low surface area would not allow a good dispersion of the active phase. The N_2 physisorption analysis of the support after calcination (reported in Fig. 2) shows a type IV isotherm with a hysteresis loop typical of mesoporous materials. Surface area of the calcined material is about $142 \text{ m}^2/\text{g}$ and the mean pore size around 9.8 nm, similarly to previous works [35].

Since H_2O_2 is more stable under acidic conditions, a strongly acidic catalyst support can prove useful, in principle, for the direct synthesis of H_2O_2 . We have already demonstrated [14,23] that sulfated zirconia is an excellent support for this reaction with Pd-based catalysts, performing better than plain zirconia. In the present work the support was impregnated before calcination with amounts necessary to yield 8% wt anion loading. In calcined (923 K) sulfated zirconia samples the final amount of sulfates is about 4% wt, a typical value for these catalysts [35].

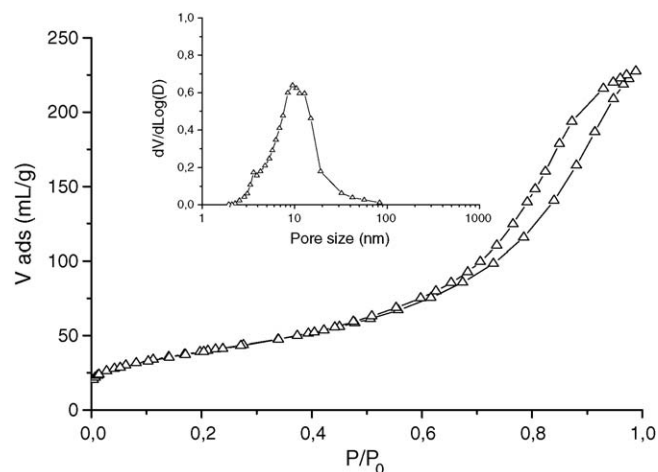


Fig. 2. N_2 physisorption isotherms of calcined support and (insert) its BJH pore size distribution.

3.2. Pd–Pt bimetallic catalysts

Some papers [26,27,36–38] about Pd–Pt bimetallic systems have found that an optimum Pt concentration is required for achieving high H_2O_2 yields. Besides, some of us have recently studied the synthesis of H_2O_2 on Pd–Pt catalytic membranes [25,33] and found that with carbon-coated membranes, both productivity and selectivity increased with an optimum Pd/Pt molar ratio = 18 with respect to pure Pd. In this work we have prepared three bimetallic Pd–Pt samples with different platinum amounts and the same Pd content (1.3%). Two catalysts have a Pd/Pt molar ratio of 20 (Pd0.1Pt) and 10 (Pd0.2Pt) respectively (the notation refers to the wt% of Pt), close to that already indicated as optimum in several patents [26,27,36–38], while a third sample (Pd1.2Pt) has a much lower Pd/Pt molar ratio (2.0).

Metal dispersion, namely the ratio between surface and total metal atoms, is a critical factor for several catalytic reactions and generally has to be as high as possible. In this work we have chosen to perform pulse flow CO chemisorption measurements [39–41] on mildly reduced catalysts, in order to mimic the same reductive pretreatment of the catalytic reaction and determine in such a way the amount of active sites that are actually present during the reaction. The chemisorption results, reported in Table 1, show that CO adsorbed in bimetallic Pd0.1Pt and Pd0.2Pt catalysts is very similar and higher than the monometallic sample or the sample with the higher Pt concentration (Pd1.2Pt) indicating that in the latter samples the total adsorbing sites are less abundant and metal dispersion is lower.

After metal deposition and calcination, a TPR analysis was performed in order to investigate the metal oxidation state and in the case of bimetallic samples identify possible interactions between palladium and platinum. Fig. 3 shows the TPR analyses for Pd–Pt catalysts over sulfated zirconia. The TPR profile of the support, not reported for sake of simplicity, shows only a peak at about 920 K due to sulfate reduction mainly to SO_2 and in part to H_2S [23]. The same peak becomes broad and shifted to lower

Table 1
Pd loading on final Pd–Pt catalysts, chemisorption values and productivity after 5 h of reaction.

Sample	% Pd (wt%)	% Pt (wt%)	Sample	$\text{ml}_{\text{CO}_{273\text{K}}}/\text{g}_{\text{Me}}$	Productivity $\text{mmol}_{\text{H}_2\text{O}_2}/\text{g}_{\text{Pd}}\text{h}$	Productivity $\text{mmol}_{\text{H}_2\text{O}_2}/\text{g}_{\text{metal}}\text{h}$
Pd	1.3	–		44	915	915
Pd0.1Pt	1.3	0.1		45	1168	1083
Pd0.2Pt	1.3	0.2		49	1236	1046
Pd1.2Pt	1.3	1.2		14	937	480

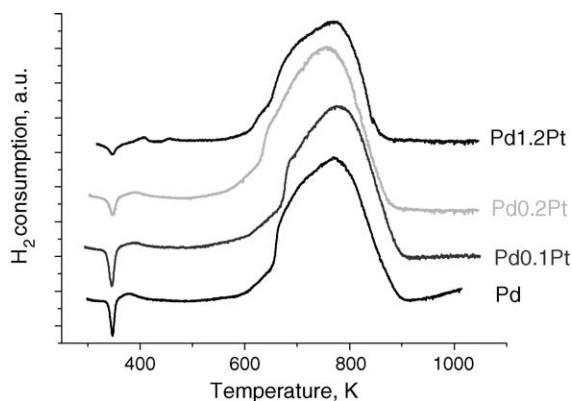


Fig. 3. TPR patterns of Pd–Pt bimetallic samples.

temperature (around 770 K) in Pd and Pd–Pt containing samples. Mass spectroscopy shows that it is almost completely due to H_2S evolution, meaning that the presence of the noble metals catalyzes sulfate reduction. In addition to the peak ascribed to sulfate reduction, the TPR profiles of the catalysts show a negative peak at about 340 K, which corresponds to hydrogen evolution, as identified by mass spectrometry. It must be remembered that the TPR testing set up requires the reducing mixture pass through the samples to be analyzed to clean the apparatus, prior to starting the temperature ramp. This procedure can cause PdO reduction already at room temperature. If the Pd metal particles are large enough, they can lead to the formation of Pd β -hydride [42,43], which decomposes at about 340 K. A broad peak at 370 K, reasonably due to PdO species, is present in the TPR profiles of the two bimetallic samples with low Pt content and is similar both in shape and in position to that of the Pd sample. This is important from a catalytic point of view, since we have recently suggested [14,23] that surface oxidized Pd⁰ catalysts perform better than Pd⁰ or completely oxidized palladium. No peaks that could be assigned to Pt reduction have been noticed in Pd0.1Pt and Pd0.2Pt samples, probably because of the low platinum content. On the contrary the TPR profile of the bimetallic Pd1.2Pt catalyst shows two broad peaks at 410 and 450 K, indicating Pt reduction and presence of platinum oxychlorides.

Fig. 4 shows the comparison of XRD patterns for the Pd–Pt bimetallic and the single Pd monometallic catalysts. The 2θ positions of the Pd and Pt characteristic lines are also shown in the expanded 2θ region. The pattern of monometallic sample shows a

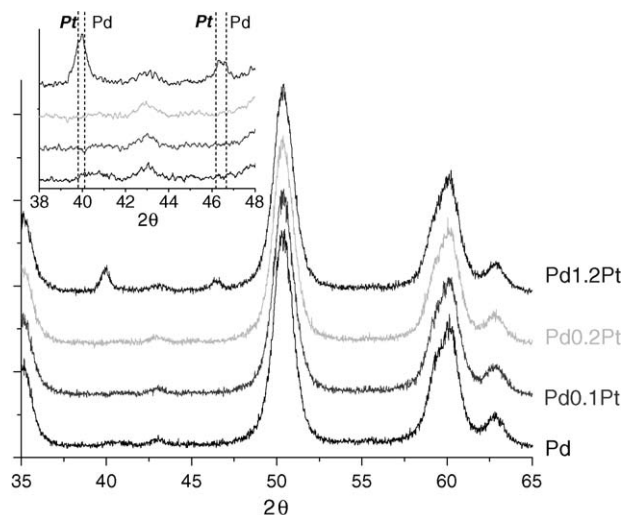


Fig. 4. XRD patterns of Pd–Pt bimetallic samples.

weak and poorly defined feature of scattered intensity above the background at $2\theta \approx 40.1^\circ$, the position of the most intense peak of Pd. It is worth noting that such a weak intensity is nevertheless consistent with the nominal amount of Pd added, as confirmed by both RIR and Rietveld methods. The broad scattered intensity which can be ascribed to Pd particles or clusters almost disappears in the XRD pattern of the two bimetallic catalyst with low platinum amount, suggesting that Pd dispersion increases after Pt addition. On the contrary, in the Pd1.2Pt pattern a well defined and relatively narrow peak is evident at $2\theta = 39.97^\circ$ which can be associated to the occurrence of an alloy between platinum and palladium. This is further confirmed by the refined cell parameter, $a = 3.9066 \text{ \AA}$, in excellent agreement to what previously reported for (Pd0.5Pt0.5). The crystal size of Pd in the monometallic sample is estimated below 2 nm while the larger size of about 16 nm, as obtained from the Rietveld fit of the PdPt alloy in the bimetallic sample, is in perfect agreement with the chemisorption results.

Fig. 5 reports the comparison of the catalytic performance in H_2O_2 formation between the Pd and Pd–Pt bimetallic samples. All catalytic tests were carried out in methanol, the best solvent according to previous work [14] and also the solvent of many oxidation reactions involving H_2O_2 . Tests were carried out under very mild conditions (1 bar and 293 K) and outside the explosive regime. All samples have been pretreated before activity tests in order to obtain a surface oxidized Pd⁰ catalyst: samples were reduced in situ by passing a pure hydrogen flow into the reaction medium, leading to a completely reduced catalyst. Then, pure oxygen was fed. Excess oxygen was then removed by passing pure nitrogen. The undiluted hydrogen/oxygen mixture used for catalytic tests allows to maintain the sample surface oxidized [14,23]. As expected, the monometallic palladium sample shows a linear increase in hydrogen peroxide and a constant selectivity during the reaction (Fig. 5). All three bimetallic Pd–Pt catalysts display higher hydrogen peroxide production, the best ones being Pd0.1Pt and Pd0.2Pt with almost superimposable profiles, while Pd1.2Pt lies above the monometallic Pd sample. In Table 1 the values of productivity calculated after 5 h of time on stream are collected: with respect to the monometallic Pd sample, productivity increases for the Pd0.1Pt and Pd0.2Pt catalysts (from 915 to 1083 – 1046 $\text{mol}_{\text{H}_2\text{O}_2}/\text{g}_{\text{metal}} \text{ h}$), while it is significantly lowered for the sample with the higher platinum amount (from 915 to 480 $\text{mol}_{\text{H}_2\text{O}_2}/\text{g}_{\text{metal}} \text{ h}$).

After 2 h of reaction the selectivities of Pd0.1Pt and Pd0.2Pt are very high, 68% and 70% respectively, as reported in Fig. 5. These values are remarkable [14,23] and are higher than the value obtained with the monometallic Pd sample (55%) throughout the experiment, but they are not constant. Again, addition of larger platinum amount is detrimental for hydrogen peroxide selectivity, which is firmly below the value of the monometallic Pd catalyst.

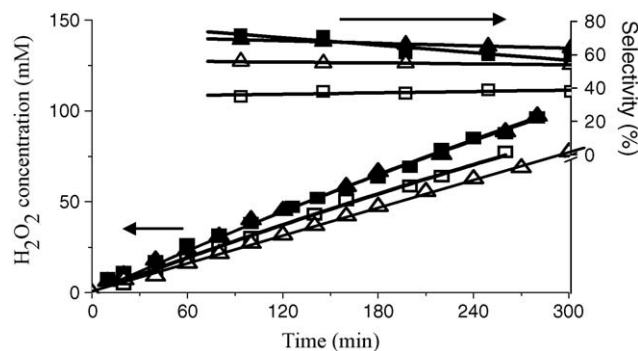


Fig. 5. H_2O_2 production and selectivity with Pd (Δ), Pd0.1Pt (\blacktriangle), Pd0.2Pt (\blacksquare), Pd1.2Pt (\square) catalysts.

Table 2
Kinetic constants for samples tested after the reductive–oxidative pretreatment.

Sample	k_1 ($\times 10^4 \text{ mol l}^{-1} \text{ min}^{-1}$)	k_2 ($\times 10^4 \text{ mol l}^{-1} \text{ min}^{-1}$)	k_3 ($\times 10^3 \text{ min}^{-1}$)
Pd	3.3	1.6	1.7
Pd0.1Pt	4.2	0.4	1.6
Pd0.2Pt	4.1	0.3	1.4
Pd1.2Pt	4.4	0.3	2.9
Pd0.2Au	3.5	1.7	1.8
Pd1.2Au	4.2	0.3	2.5
Pd2Au	4.2	0.4	2.6

Fitting the catalytic curves for Pd–Pt samples allows to calculate the kinetic constants as indicated in Section 2 [14,23]. The values are collected in Table 2 and confirm that low Pt bimetallic catalysts have higher k_1 and lower k_2 than the Pd only sample, explaining respectively their higher productivity and selectivity. On the contrary, the Pd1.2Pt sample shows a much higher constant for H_2O_2 hydrogenation (k_3), giving rise to low selectivity.

In summary, a comparison between the results of the bimetallic PdPt samples and the monometallic Pd catalyst reveals that the effect of the addition of Pt to Pd in enhancing the yield of hydrogen peroxide is sensitive to Pt amount. The addition of a low Pt content to a Pd sample allows to improve both H_2O_2 selectivity and productivity with respect to the monometallic catalyst.

Platinum metal in this reaction is known to be active, albeit much less than Pd, but poorly selective towards hydrogen peroxide formation. This implies that the residual reactivity of pure Pt in addition to Pd reactivity is virtually negligible at such low amounts of Pt, as is evidenced by the observation that the performance of the bimetallic catalysts is better (and not worse) than the monometallic one. The positive effect of Pt addition on the activity has been assigned to a Pd particle morphology change (evidenced even in the present case) and also to a stabilization of the oxidized Pd surface [33]. On the other hand, the higher selectivity in H_2O_2 formation requires non-dissociative chemisorption of oxygen on the catalyst surface that is favored on low energy sites and by an electron rich Pd surface. In this respect close contact with a more “noble” metal such as Pt would result in a sort of ligand effect increasing the electronegativity of Pd and justifying the better selectivity.

3.3. Pd–Au bimetallic catalysts

We have recently reported [23] that gold by itself is not active in H_2O_2 direct synthesis at room temperature and atmospheric pressure. On the contrary, the addition of Au to a Pd-based catalyst decreases Pd particle size increasing productivity, while at the same time increasing selectivity maintaining a high proportion of low energy sites [23]. In order to further improve H_2O_2 productivity and selectivity, the present work was undertaken to investigate the effect of the amount of gold in three bimetallic Pd–Au samples with different gold amount and the same Pd content. Similarly to Pd–Pt samples, we have chosen to synthesize a catalyst with a very low gold content (Pd0.2Au), another sample with a Pd/Au 1/1 ratio based on weight (Pd1.2Au) and a third sample with a higher gold amount (Pd2Au). Data reported in Table 3.

Table 3
Metal loading on final Pd–Au catalysts, chemisorption values and productivity after 5 h of reaction.

Sample	% Pd (wt%)	% Pd found (wt%)	% Au (wt%)	% Au found (wt%)	$\text{ml}_{\text{CO}_{273\text{K}}}/\text{g}_{\text{Pd}}$	Productivity $\text{mmol}_{\text{H}_2\text{O}_2}/\text{g}_{\text{Pd}}\text{h}$
Pd0.2Au	1.3	1.28	0.2	0.16	42	946
Pd1.2Au	1.3	1.22	1.2	0.92	61	1190
Pd2Au	1.3	1.29	2	1.94	56	1054

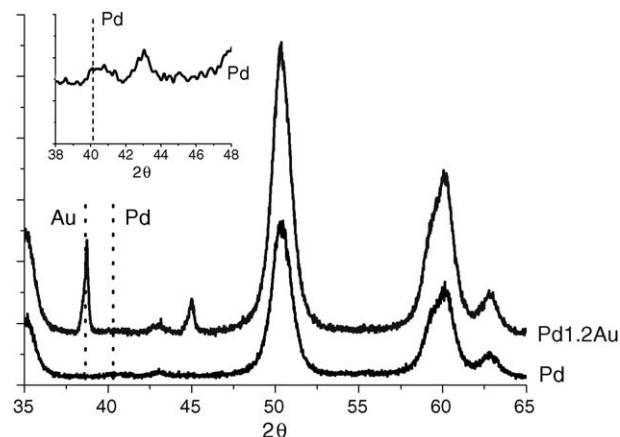


Fig. 6. XRD patterns of Pd and Pd1.2Au catalysts.

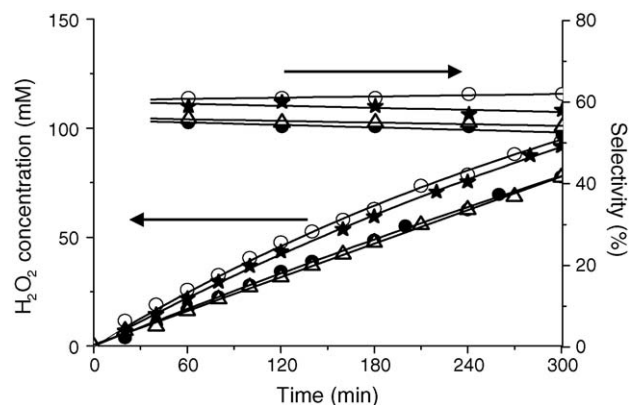


Fig. 7. H_2O_2 production and selectivity with Pd (Δ), Pd0.2Au (\bullet), Pd1.2Au (\circ), Pd2Au (\star) catalysts.

Also for bimetallic palladium–gold samples we have performed pulse flow CO chemisorption measurements [40], in order to determine the amount of active sites that are present during the reaction. We have previously proved [44,45] that under the experimental conditions used gold does not chemisorb CO. In the absence of any information about a possible influence of Au on Pd/CO chemisorption stoichiometry in bimetallic samples, only the experimental CO/Pd values have been reported in Table 3 [46]. No evident role on Pd dispersion seems to be played by low gold amount: the catalyst Pd0.2Au, unlike Pd0.2Pt sample, presents the same CO chemisorption capacity as the monometallic Pd sample. On the contrary, the addition of higher gold amounts (Pd1.2Au and Pd2Au catalysts) shows an increase of even 50% with respect to monometallic Pd sample. These chemisorption data confirm our previous findings on Au addition to a Pd catalyst decreasing Pd particle size [23].

Fig. 6 reports XRD patterns of Pd1.2 Au and Pd samples, the 2θ positions corresponding to characteristic lines for Pd and Au being indicated. In the pattern of the monometallic sample the peak at $2\theta \approx 40.1^\circ$ is clearly detectable. Such main Pd peak disappears in the XRD pattern of the bimetallic catalyst,

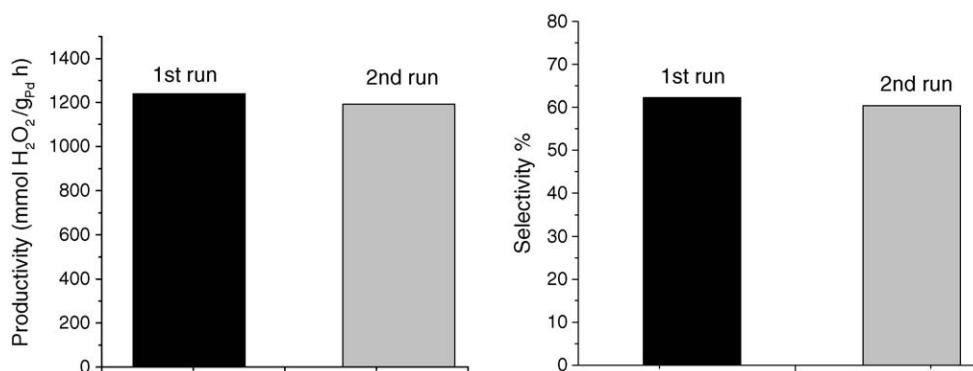


Fig. 8. Test of reusability: H₂O₂ productivity and selectivity after 3 h of reaction with Pd1.2Au catalyst.

indicating that Pd dispersion changes after gold addition. Besides in the Pd1.2Au diffractogram a narrow peak ascribed to pure Au is evident, showing that gold particles in this sample are large (~44 nm as estimated by the Rietveld profile fit). The refined unit cell parameter for gold, $a = 4.024 \text{ \AA}$, is appreciably shorter than what reported for pure gold ($a = 4.06\text{--}4.07 \text{ \AA}$). This can be due to the incorporation of smaller Pd atoms in the Au lattice or the formation of an alloy between gold and palladium in this sample.

The comparison of the catalytic performance in H₂O₂ formation between the pure Pd and Pd–Au bimetallic samples supported on sulfated zirconia are reported in Fig. 7. All catalytic tests were carried out in methanol, under very mild conditions (1 bar and 293 K) on surface oxidized Pd⁰ catalysts [23]. The profiles of the H₂O₂ concentration for Pd and Pd0.2Au catalysts, i.e. the two samples with the same dispersion, are almost superimposable, pointing out the close connection between catalytic activity and palladium particle size. Selectivities for these catalysts are also very similar, as shown in Fig. 7. We can therefore conclude that, unlike Pt addition, loading a low gold amount is not significant at all. Conversely, both bimetallic Pd1.2Au and Pd2Au samples show a higher hydrogen peroxide production (Fig. 7), although in terms of productivity (Table 2) the best sample is Pd1.2Au, i.e. the catalyst with a 1/1 Pd/Au ratio, as the result of the best the H₂O₂ selectivity (62%) that is constant over the 5 h catalytic test. Even in these samples there is a close connection between H₂O₂ yield and Pd dispersion. Nevertheless, as previously demonstrated [23], we think that the role of gold in the catalytic reaction is a complex one, improving the performance of Pd particles changing their size, morphology and electron density and making them more suited to the reaction requirements.

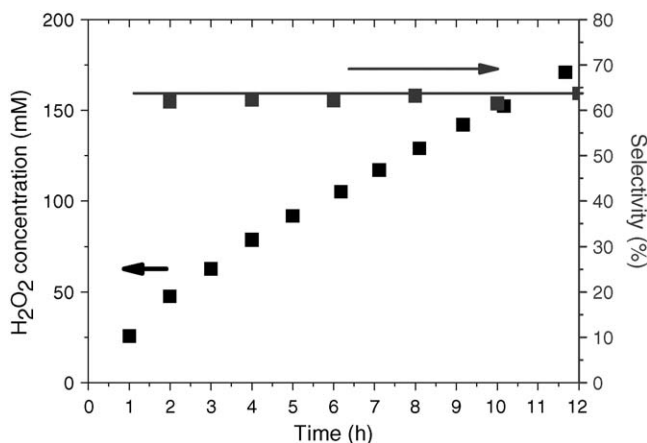


Fig. 9. Catalytic activity for 12 h of reaction with Pd1.2Au catalyst.

Table 2 reports the values calculated for the kinetic constants related to the reaction network indicated in Fig. 1. It is interesting to notice that: (i) as expected, the kinetic constants of the Pd0.2Au sample are the same as those of the monometallic Pd sample; (ii) in both Pd1.2Au and Pd2Au catalysts k_1' is higher than in the monometallic Pd sample explaining the improvement in catalytic performance; (iii) k_2' , the constant associated with direct water formation, decreases remarkably for both Pd1.2Au and Pd2Au samples, explaining the increase in selectivity with respect to the monometallic Pd catalyst.

The Pd1.2Au catalyst, our best sample according to the above results, was tested for stability and reusability. First of all, a sample already used in a previous reaction, after filtration and drying was recycled in a second run. As shown in Fig. 8, both productivity and selectivity remained unchanged. Additionally the same catalyst was checked in a day long test (12 h time on stream). As reported in Fig. 9, H₂O₂ production increases linearly over the whole duration of the test while selectivity remains stable. The result is very promising, since at the end of the test a hydrogen peroxide concentration of almost 0.8 wt% was obtained. Such H₂O₂ concentration, that can be already useful for some industrial applications, has been obtained working under mild and safe conditions, i.e. at room temperature, at atmospheric pressure, and outside the explosive region.

4. Conclusions

Bimetallic Pd–Au and Pd–Pt samples supported on sulfated zirconia were successfully tested for the direct synthesis of hydrogen peroxide under very mild conditions (1 bar and 293 K) and outside the explosion range. The effect of the addition of Pt to Pd in enhancing the yield of hydrogen peroxide is sensitive to Pt amount: only using a low Pt content it is possible to improve H₂O₂ productivity and selectivity with respect to the monometallic sample, reaching a selectivity of 70%. On the other hand, the addition of gold in a relatively high amount (1/1 wt) to the monometallic palladium sample improved the productivity and the selectivity of the process, producing a hydrogen peroxide concentration already useful for industrial applications and maintaining a stable activity and selectivity even after 12 h of time on stream.

Acknowledgement

We thank MIUR (Rome) for financial support through PRIN national projects.

References

- [1] G. Centi, S. Perathoner, in: I.T. Horvath (Ed.), Encyclopedia of Catalysis, vol. 6, J. Wiley&Sons Pub, New York, 2003, pp. 239–299.
- [2] S. Abate, G. Centi, S. Perathoner, S. Melada, F. Pinna, G. Strukul, Top. Catal. 38 (2006) 181.

- [3] H.-J. Riedl, G. Pfeleiderer, US Patent 2,215,883 (1940).
- [4] L.W. Gosser, US Patent 4,681,751 (1987).
- [5] L.W. Gosser, J.T. Schwartz, US Patent 4,772,485 (1988).
- [6] J. Van Weynbergh, J.-P. Schoebrechts, US Patent 5,447,706 (1995).
- [7] B. Bertsch-Frank, I. Hemme, S. Katusic, J. Rollmann, US Patent 6,387,364 (2002).
- [8] G. Paparatto, R. D'Aloisio, G. De Alberti, R. Buzzoni, US Patent 6,630,118 (2003).
- [9] K.M. Vanden Bussche, S.F. Abdo, A.R. Oroskar, US Patent 6,713,036 (2004).
- [10] R. Burch, P.R. Ellis, Appl. Catal. B: Environ. 42 (2003) 203.
- [11] C. Samanta, V.R. Choudhary, Catal. Commun. 8 (2007) 2222.
- [12] J.K. Edwards, A. Thomas, B. Solsona, P. Landon, A.F. Carley, G. Hutchings, Catal. Today 122 (2007) 397.
- [13] D. Hancu, E.J. Beckman, Green Chem. 3 (2001) 80.
- [14] S. Melada, R. Rioda, F. Menegazzo, F. Pinna, G. Strukul, J. Catal. 239 (2006) 422.
- [15] Q. Liu, J.H. Lunsford, J. Catal. 239 (2006) 237.
- [16] T.A. Pospelova, N.I. Kobozev, Russ. J. Phys. Chem. 35 (1961) 262.
- [17] J.H. Lunsford, J. Catal. 216 (2003) 445.
- [18] J.M. Campos-Martin, G. Blanco-Brieva, J.L.G. Fierro, Angew. Chem. 118 (2006) 7116.
- [19] C. Samanta, Appl. Catal. A 350 (2008) 133.
- [20] J.A. Rodriguez, Prog. Surf. Sci. 81 (2006) 141.
- [21] G. Li, J.K. Edwards, A.F. Carley, G.J. Hutchings, Catal. Commun. 8 (2007) 247.
- [22] P. Landon, P.J. Collier, A.J. Papworth, C.J. Kiely, G.J. Hutchings, Chem. Commun. (2002) 2058.
- [23] F. Menegazzo, P. Burti, M. Signoretto, M. Manzoli, S. Vankova, F. Boccuzzi, F. Pinna, G. Strukul, J. Catal. 257 (2008) 369.
- [24] G. Luft, U. Luckhoff, Chem. Eng. Technol. 66 (1994) 187.
- [25] S. Abate, S. Melada, G. Centi, S. Perathoner, F. Pinna, G. Strukul, Catal. Today 117 (2006) 193.
- [26] V.R. Choudhary, C. Samanta, T.V. Choudhary, Appl. Catal. A: Gen. 308 (2006) 128.
- [27] Q. Liu, J.C. Bauer, R.E. Schaak, J.H. Lunsford, Appl. Catal. A: Gen. 339 (2008) 130.
- [28] S. Melada, M. Signoretto, F. Somma, F. Pinna, G. Cerrato, G. Meligrana, C. Morterra, Catal. Lett. 94 (2004) 193.
- [29] M. Signoretto, S. Melada, F. Pinna, S. Polizzi, G. Cerrato, C. Morterra, Micropor. Mesopor. Mater. 81 (2005) 19.
- [30] S.J. Gregg, K.S.W. Sing, Adsorption, Surface Area and Porosity, 2nd ed., Academic Press, 1982, p. 111.
- [31] C. Sarzanini, G. Sacchero, F. Pinna, M. Signoretto, G. Cerrato, C. Morterra, J. Mater. Chem. 5 (1995) 353.
- [32] B. Lewis, G. von Elbe, Combustion, Flames and Explosion of Gases, Academic Press, New York/London, 1961.
- [33] S. Melada, F. Pinna, G. Strukul, S. Perathoner, G. Centi, J. Catal. 237 (2006) 213.
- [34] X. Song, A. Sayari, Catal. Rev. Sci. Eng. 38 (1996) 329.
- [35] C. Morterra, G. Cerrato, F. Pinna, M. Signoretto, J. Catal. 157 (1995) 109.
- [36] L.W. Gosser, J.T. Schwartz, US Patent 4,832,938 (1989).
- [37] J.T. Schwartz, US Patent 5,128,114 (1992).
- [38] G. Paparatto, F. Rivetti, P. Andrigo, G. De Alberti Eur. Pat. Appl. 1 (160) (2001) 195.
- [39] P. Canton, G. Fagherazzi, M. Battagliarin, F. Menegazzo, F. Pinna, N. Pernicone, Langmuir 18 (2002) 6530.
- [40] G. Fagherazzi, P. Canton, P. Riello, N. Pernicone, F. Pinna, M. Battagliarin, Langmuir 16 (2000) 4539.
- [41] P. Canton, F. Menegazzo, S. Polizzi, F. Pinna, N. Pernicone, P. Riello, G. Fagherazzi, Catal. Lett. 88 (2003) 141.
- [42] W. Palczewska, in: Z. Paal, P.G. Menon (Eds.), Hydrogen Effects in Catalysis, Dekker, New York, 1988, p. 373.
- [43] Z. Karpinski, Adv. Catal. 37 (1990) 45.
- [44] F. Menegazzo, M. Manzoli, A. Chiorino, F. Boccuzzi, T. Tabakova, M. Signoretto, F. Pinna, N. Pernicone, J. Catal. 237 (2006) 431.
- [45] F. Menegazzo, F. Pinna, M. Signoretto, V. Trevisan, F. Boccuzzi, A. Chiorino, M. Manzoli, ChemSusChem 1 (2008) 320.
- [46] P. Canton, F. Menegazzo, M. Signoretto, F. Pinna, P. Riello, A. Benedetti, N. Pernicone, Stud. Surf. Sci. Catal. 143 (2002) 1011.