



# Influence of the preparation method on the morphological and composition properties of Pd–Au/ZrO<sub>2</sub> catalysts and their effect on the direct synthesis of hydrogen peroxide from hydrogen and oxygen

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## ABSTRACT

Bimetallic Pd–Au samples supported on zirconia were prepared by different methods and tested for the direct synthesis of hydrogen peroxide under very mild conditions (room temperature and atmospheric pressure), outside the explosion range and without halides addition. Further catalytic tests were performed at higher pressure using solvents expanded with CO<sub>2</sub>.

Samples were characterized by N<sub>2</sub> physisorption, metal content analysis, XRD, HRTEM combined with X-ray EDS, TPR, and FTIR. The effect of the addition of gold to Pd in enhancing the yield of H<sub>2</sub>O<sub>2</sub> is sensitive to the preparation method: the best catalytic results were obtained by depositing gold by deposition–precipitation (DP) and by introducing in a second step Pd by incipient wetness impregnation. The origin of the differences between samples is discussed. The role of Au in the catalytic reaction seems to be a complex one, changing the chemical composition of the metallic particles, their morphology, and charge of the exposed Pd sites.

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## 1. Introduction

The direct reaction of H<sub>2</sub> + O<sub>2</sub> → H<sub>2</sub>O<sub>2</sub> is clearly the most atom-efficient method to form hydrogen peroxide, but none of the presently available processes has solved the productivity vs. safety dilemma. In fact, the major problem of the direct route to hydrogen peroxide is the poor selectivity to H<sub>2</sub>O<sub>2</sub> vs. H<sub>2</sub>O that can be achieved with known catalysts. As shown in Fig. 1, the process also involves the thermodynamically highly favoured but undesirable parallel and consecutive water-forming reactions. Another serious problem that has limited the implementation for this process is the significant risk of handling the explosive hydrogen/oxygen gas mixture over an active catalyst. Therefore, despite several patents [1–7] and recent literature [8–12], the direct synthesis of hydrogen peroxide has not yet found the way to commercialization.

For a long time it has been known that alloying or combination of two metals can lead to materials with special chemical properties due to an interplay of “ensemble” and “electronic” effects [13]. In particular for the direct synthesis H<sub>2</sub>O<sub>2</sub>, from its elements, for

which it is generally agreed that palladium is the most effective metal [8,9,14–16], it has been reported that the combination of Pd with Au [17–19], Ir [20], Ag [21], and Pt [17,21–23] improves the catalytic performance with respect to monometallic palladium samples. As far as gold is concerned, since the pioneering work of Haruta et al. [24], gold nanoparticles supported on metal oxides are known to be active in some important industrial reactions [25–28], the present reaction being not included. The reasons for the activity of small gold particles are still a matter of debate. It has been shown that the catalytic activity of gold critically depends on the preparation method, on the support type, and on the pre-treatment procedure. The most widely accepted explanation for the variability of gold catalytic properties focuses on the size of gold particles and on the amount of low coordination sites of gold. In addition, other factors have been considered in the literature: metal-support interface, and charge transfer from the support or metal cationic sites [29]. Several methods have been tested for making suitably small gold particles: the deposition–precipitation (DP) method has been qualified as the best so far. In this method [30] the pH of a solution of HAuCl<sub>4</sub> is raised by the addition of a base to the point where the adsorption of the species in solution can react with or be deposited on the support.

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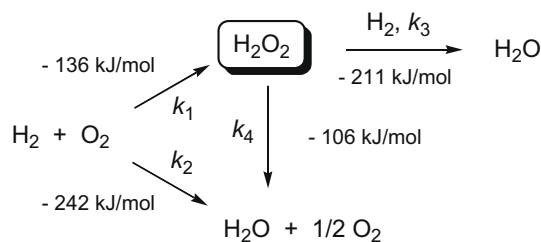


Fig. 1. Reactions involved in the direct production of  $\text{H}_2\text{O}_2$ .

We have already shown [31] that zirconia is a good support for Pd-based catalysts for the direct synthesis of hydrogen peroxide and that it is possible to prepare highly dispersed gold on zirconia by DP [32]. We have also recently demonstrated [33,34] for both plain and sulfated zirconia and ceria supports that while the monometallic gold catalysts are inactive under mild experimental conditions, the addition of a 1:1 amount of gold to a monometallic Pd sample improves the productivity and especially the selectivity of the process. In these samples gold must be in close contact with Pd, as its presence profoundly changes both Pd dispersion and its morphology and charge. However, no evidence for small Au particles was found, probably because of the preparation conditions. In the present work, we wish to report the preparation by different methods of a series of Pd–Au samples supported on zirconia in order to fully understand the nature of palladium–gold interactions. These catalysts were also tested for the direct synthesis of hydrogen peroxide both under very mild conditions (1 bar and 20 °C and outside the explosion range) and at higher pressure (10 bar) using solvents expanded with  $\text{CO}_2$  in order to increase productivity further.

## 2. Experimental

### 2.1. Materials

$\text{ZrOCl}_2$  (Fluka) was used as received for sample synthesis. All kinetic tests were performed in anhydrous methanol (SeccoSolv, Merck,  $[\text{H}_2\text{O}] < 0.005\%$ ). 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

Zirconia was prepared by precipitation from  $\text{ZrOCl}_2$  at pH 10, aged under reflux conditions for 20 h [35,36], washed free from chloride ( $\text{AgNO}_3$  test), and dried at 383 K overnight.  $\text{Zr}(\text{OH})_4$  was then calcined in flowing air (30 ml/min) at 923 K for 4 h. Calcined zirconia was used as a support for preparing three bimetallic Pd–Au samples with the same Pd (1.3 wt%) and Au (1.2 wt%) loading, but prepared with three different procedures:

- A catalyst (PdAu) was prepared by incipient wetness (IW) co-impregnation of  $\text{H}_2\text{PdCl}_4$  and  $\text{HAuCl}_4$  aqueous solutions, followed by calcination at 773 K in flowing air (30 ml/min) for 3 h.
- Another sample (1Pd2Au) was prepared by depositing the two metals separately by different techniques: palladium by IW and gold by DP. Pd was deposited first on the support from a  $\text{H}_2\text{PdCl}_4$  aqueous solution, then the material was dried at 383 K overnight and calcined at 773 K in flowing air (30 ml/min) for 3 h. In a second step, Au was deposited by DP by suspending the catalyst in a  $\text{HAuCl}_4$  aqueous solu-

tion at pH 8.6 (pH fixed by adding a 0.5 M sodium hydroxide solution). The sample obtained was then dried and calcined under the same conditions reported above.

- The third catalyst (1Au2Pd) was prepared as the second catalyst but by inverting the deposition order: first gold by DP, then palladium by an IW method. The sample was finally calcined at 773 K in flowing air (30 ml/min) for 3 h.

For the purpose of comparison a monometallic Pd catalyst (Pd) was prepared by IW impregnation of  $\text{H}_2\text{PdCl}_4$ , and two monometallic Au catalysts were synthesized both by IW impregnation and by DP. After drying, the samples were calcined under the same conditions reported for the bimetallic catalysts.

### 2.3. Methods

Surface areas and pore size distributions were obtained from  $\text{N}_2$  adsorption/desorption isotherms at 77 K (using a Micromeritics ASAP 2000 analyzer). Calcined samples (300 mg) were pre-treated at 573 K for 2 h under vacuum. Surface areas were calculated from the  $\text{N}_2$  adsorption isotherm by the BET equation, and pore size distributions were determined by the BJH method [37]. Total pore volumes were taken at  $p/p_0 = 0.99$ .

The actual metal loadings were determined by atomic absorption spectroscopy after microwave disgregation of the samples (100 mg).

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  $\text{Cu K}\alpha$  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  $2\theta$  range 20–80° with 0.02° stepsize and counting times of 10 s/step. The normalized reference intensity ratio (RIR) method and the Rietveld refinement method, 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 metal phases in the samples.

A careful analysis of the catalysts morphology, structure, and composition was performed by using a side entry stage high-resolution transmission electron microscopy (HRTEM) JEOL JEM 3010 UHR (300 kV) equipped with a  $\text{LaB}_6$  filament and fitted with X-ray EDS analysis by a Link ISIS 200 detector. The powdered samples were ultrasonically dispersed in isopropanol and a few droplets of the slurry were then deposited on a copper grid, coated with a porous carbon film.

TPR experiments were carried out in a home-made equipment: samples (100 mg) were heated with a 10 K/min ramp from 298 K to 1500 K in a 5%  $\text{H}_2/\text{Ar}$  reducing mixture (40 ml/min STP).

FTIR spectra were taken on a Perkin–Elmer 1760 spectrometer (equipped with a MCT detector) with the samples in self-supporting pellets introduced in a cell allowing thermal treatments under controlled atmosphere. All pre-treatments on the as-prepared samples were performed at room temperature (r.t.) before the spectroscopic experiments. The pre-treatments were (i) prolonged outgassing (1 h); (ii) 1-h outgassing and 1-h treatment under 50 mbar of  $\text{H}_2$ ; and (iii) 1-h outgassing at r.t., 1-h treatment under  $\text{H}_2$  (50 mbar), 30-min outgassing followed by 1-h treatment under 50 mbar of  $\text{O}_2$  and 30-min outgassing. After each pre-treatment, 7 mbar of CO was admitted at 90 K, in order to avoid possible Pd reduction by CO itself. Moreover, we chose to collect the spectra at 180 K to eliminate the physisorbed CO contribution. The spectrum of the sample before the CO inlet was subtracted from each spectrum. Finally, all spectra were normalized to the same palladium content. Band integration was carried out by “Curvefit”, in Spectra Calc (Galactic Industries Co.). The curvefits were performed

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