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## **Pd-Au catalysts: influence of preparation procedure on direct oxidation of H<sub>2</sub> to H<sub>2</sub>O<sub>2</sub>**

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### **Introduction**

Hydrogen peroxide is a clean and excellent oxidizing reagent for the production of both fine and bulk chemicals, that could find applications also in the area of wastewater treatment and paper-pulp bleaching. Over 95% of the world's H<sub>2</sub>O<sub>2</sub> is currently produced by the sequential hydrogenation and oxidation of an alkyl anthraquinone, a process that employs multiple unit operations, generates considerable waste and requires significant energy input, lowering the sustainability of the process and raising the production costs. For H<sub>2</sub>O<sub>2</sub> to successfully break into new markets, the production should become cheaper. The H<sub>2</sub>O<sub>2</sub> direct synthesis from H<sub>2</sub> and O<sub>2</sub> is a promising alternative to the anthraquinone technology, but the contact between H<sub>2</sub> and O<sub>2</sub> is a significant safety hazard and, at present, no commercial processes have been developed. In addition, the other major problem associated with the H<sub>2</sub>O<sub>2</sub> direct synthesis is the low selectivity, since water is the termodinamically favoured product.

Until very recently, the catalysts used in these investigations have been based predominantly on Pd, but in the last years it has been reported that catalysts based on Pd-Au alloys supported on Al<sub>2</sub>O<sub>3</sub>, Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub> can significantly improve the rate of H<sub>2</sub>O<sub>2</sub> formation when compared with the Pd only catalyst [1].

### **Experimental**

ZrO<sub>2</sub> was used as support for preparing three bimetallic Pd-Au samples with the same Pd and Au loading (1.2wt%), but prepared with three different procedures: a catalyst (AuPdCl) was prepared by incipient wetness coimpregnation of H<sub>2</sub>PdCl<sub>4</sub> and HAuCl<sub>4</sub> aqueous solutions. Another sample (1Pd2Au) was prepared depositing separately the two metals by different techniques: first Pd was deposited on the support by an incipient wetness method; in a second step, after drying and calcination, Au was deposited by DP (deposition-precipitation), and the sample was dried and calcined again. The third catalyst (1Au2Pd) differs from the latter for the metals deposition order: first Au by DP, then Pd by an incipient wetness method were introduced on the support. The samples have been characterized by N<sub>2</sub> physisorption, metal content analysis, TPR, CO chemisorption, XRD, FTIR and HRTEM.

H<sub>2</sub>O<sub>2</sub> direct synthesis has been investigated under very mild conditions (1 bar and 20°C) and outside the explosion range (H<sub>2</sub>:O<sub>2</sub>:4:96). Catalytic tests were carried out in methanol at 20°C. An activation process giving rise to a Pd particle surface oxidation was used [2]: samples were pretreated in situ first by H<sub>2</sub> and then by O<sub>2</sub> flow. H<sub>2</sub>O<sub>2</sub> concentration was measured by iodometric titration, whereas water was determined by volumetric Karl-Fischer method.



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## Results and discussion

We have recently demonstrated for sulfated zirconia and ceria samples [3] that while the monometallic gold catalysts are inactive under our experimental conditions, the addition of gold in amount 1:1 to the monometallic Pd sample improved the productivity and especially the selectivity of the process. Therefore, in this work, in order to more fully understand the nature of Pd-Au interaction, various bimetallic Pd-Au samples supported on zirconia were prepared by different methods and then were tested for the H<sub>2</sub>O<sub>2</sub> direct synthesis.

The effect of the addition of Au to Pd in enhancing the yield of H<sub>2</sub>O<sub>2</sub> is sensitive to the preparation methods: the best catalytic results were obtained using the 1Au2Pd sample, that allows to achieve (already at atmospheric pressure) a productivity of 1429mmolH<sub>2</sub>O<sub>2</sub>/gPdh and a 52% selectivity stable even after 5 hours. Also the coimpregnated sample presents a stable, even if lower, selectivity (40%). It's very important to remark that these catalysts are recyclable without loss of activity and selectivity. On the 1Pd2Au sample, on the contrary, the selectivity is very high after 2 hours of time on stream (60%), but it decreases rapidly and after 5 hours is approximately 30%.

FTIR spectroscopy revealed the presence of differently coordinated palladium sites. No evidence of gold at the surface was found. CO adsorption at 90 K evidenced that only Pd<sup>2+</sup> species are present on the as prepared samples and that different Pd<sup>0</sup> sites are produced after interaction with H<sub>2</sub> at r.t.. The ratio between the integrated area of the band of CO adsorbed on the remaining Pd<sup>2+</sup> species and the CO bands due to Pd<sup>0</sup> sites gave information on the relative abundance of these species at the surface of the catalysts. We found that the higher is this ratio, the higher is the catalytic activity. Moreover, the Pd<sup>0</sup> sites are reoxidized in different extent on the examined samples after O<sub>2</sub> interaction at r.t., particularly on the most active sample, 1Au2Pd, the Pd reoxidation is almost complete, while the lower extent of reoxidation was observed on the monometallic sample, which showed the lowest activity. The origin of these differences will be discussed together with HRTEM measurements.

The role of Au in the catalytic reaction seems to be a complex one, improving the performance of Pd particles changing their morphology and electron density, making them more suited to the reaction requirements.

## Conclusions

These new catalysts improved the productivity and the selectivity of the process, producing already at room temperature and atmospheric pressure a hydrogen peroxide concentration useful for industrial applications and maintaining a stable selectivity after 12 hours of time on stream.

## References

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