

Pd-Au catalysts: influence of preparation procedure on direct oxidation of H₂ to H₂O₂

Federica Menegazzo^{1*}, Michela Signoretto¹, Elena Ghedini¹, Francesco Pinna¹, Giorgio Strukul¹, Maela Manzoli², Flora Boccuzzi²

¹*Department of Chemistry, Cà Foscari University and “Consorzio INSTM”, Venice (Italy)*

²*Department of Chemistry IFM and NIS Centre of Excellence, University of Torino (Italy)*

*corresponding author e-mail: fmenegaz@unive.it (F. Menegazzo)

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 H₂O₂ 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 H₂O₂ to successfully break into new markets, the production should become cheaper. The H₂O₂ direct synthesis from H₂ and O₂ is a promising alternative to the anthraquinone technology, but the contact between H₂ and O₂ is a significant safety hazard and, at present, no commercial processes have been developed. In addition, the other major problem associated with the H₂O₂ direct synthesis is the low selectivity, since water is the thermodynamically 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 Al₂O₃, Fe₂O₃, TiO₂ can significantly improve the rate of H₂O₂ formation when compared with the Pd only catalyst [1].

Experimental

ZrO₂ 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 H₂PdCl₄ and HAuCl₄ 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 N₂ physisorption, metal content analysis, TPR, CO chemisorption, XRD, FTIR and HRTEM.

H₂O₂ direct synthesis has been investigated under very mild conditions (1 bar and 20°C) and outside the explosion range (H₂:O₂:4:96). 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 H₂ and then by O₂ flow. H₂O₂ concentration was measured by iodometric titration, whereas water was determined by volumetric Karl-Fischer method.

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 H₂O₂ direct synthesis.

The effect of the addition of Au to Pd in enhancing the yield of H₂O₂ 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 1429mmolH₂O₂/gPd_h 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 Pd²⁺ species are present on the as prepared samples and that different Pd⁰ sites are produced after interaction with H₂ at r.t.. The ratio between the integrated area of the band of CO adsorbed on the remaining Pd²⁺ species and the CO bands due to Pd⁰ 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 Pd⁰ sites are reoxidized in different extent on the examined samples after O₂ 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

- [1] Edwards, J.K., Thomas, A., Solsona, B., Landon, P., Carley, A.F., Hutchings, G., *Catal. Today*, 122 (2007), 397.
- [2] Melada, S., Rioda, R., Menegazzo, F., Pinna, F., Strukul, G., *J. Catal.*, 239 (2006), 422.
- [3] Menegazzo, F., Burti, P., Signoretto, M., Manzoli, M., Vankova, S., Boccuzzi, F., Pinna, F., Strukul, G., *J. Catal.*, 257 (2008), 369.