

Palladium-gold catalysts for H₂O₂ direct synthesis at room temperature and atmospheric pressure

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Introduction

Hydrogen peroxide has always been considered a very interesting and environmentally friendly oxidant with applications confined mainly in unselective sectors such as the paper and textile industry and the treatment of waste waters. More recent applications, related to the discovery of TS-1 molecular sieve, are in the large scale selective oxidation processes for the chemical industry. The increasing demand for H₂O₂ and the general need for greener oxidants has revamped the interest for an alternative to its production by the oxidation of alkyl anthraquinone. Synthesis by direct reaction of hydrogen and oxygen has long been an attractive alternative, but it never found industrial application because of severe drawbacks due mainly to the hazardous nature of the gas mixtures and to the low yield and low selectivity to hydrogen peroxide rather than water that could be reached with known catalysts. Until very recently, the catalysts used in these investigations have been based predominantly on Pd. 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 catalyst¹. We have recently demonstrated² for sulfated zirconia and ceria samples, 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 improves the productivity and especially the selectivity of the process.

In this work, in order to better understand the nature of Pd-Au interaction, different bimetallic Pd-Au samples supported on zirconia were prepared by different methods and were tested for the direct synthesis of hydrogen peroxide under very mild conditions (1 bar and 20°C) and outside the explosion range.

Materials and Methods

Zirconia 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 a incipient wetness method; in a second step, after drying and calcination, Au was deposited by DP (deposition-precipitation). The obtained sample was then dried and calcined again. The third catalyst (1Au2Pd) differs from the latter for the metals deposition order: first gold by DP, then palladium by a 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 used³: samples were pretreated in situ first by H₂ and then by O₂ flow. Concentration was measured by iodometric titration, whereas water was determined by volumetric Karl-Fischer method.

Results and Discussion

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/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%. A FTIR characterisation by CO adsorption at low temperature has been performed on all samples pretreatment in H₂ and in H₂-O₂ at r.t.. Different ratios between the integrated intensity of the CO bands related to Pd²⁺ and Pd⁰ have been observed after both pre-treatments. The same experiments have been performed also on the Pd monometallic sample. In this case, a large fraction of residual Pd⁰ sites was present on this sample, also after H₂-O₂ interaction. These sites can be able to dissociate the oxygen molecules and therefore may have a detrimental effect on the overall reaction, as for activity and selectivity. A relation between the amount of oxidised and reduced palladium sites and the catalytic activity has been observed and will be fully discussed. The role of Au in the catalytic reaction seems to be a complex one, improving the performance of Pd particles by changing their morphology and behavior towards oxygen and hydrogen, making them more suited to the reaction requirements.

Significance

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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