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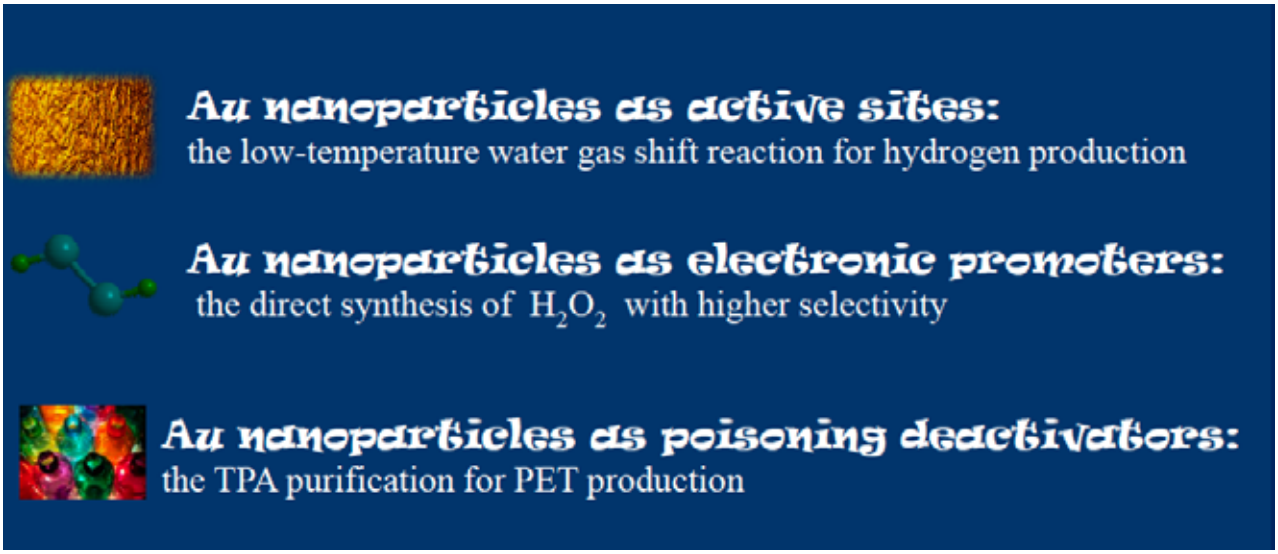
A golden perspective for catalysis

F. Menegazzo, M. Signoretto, T. Fantinel, V. Trevisan, F. Pinna



In the present paper we discuss the importance of gold nanoparticles in heterogeneous catalysis and show their different roles as active phases, electronic promoters and poisoning deactivators.

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A golden perspective for catalysis

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Abstract: In the present paper we discuss the importance of gold nanoparticles in heterogeneous catalysis and show their different roles as active phases, electronic promoters and poisoning deactivators. In particular, some examples of our recent experience are presented:

i) Gold nanoparticles as active sites: the LT-WGSR. In this example gold acts as the active phase, and catalytic performances are strongly related to gold nanosizes.

ii) Gold nanoparticles as electronic promoters: the H_2O_2 direct synthesis. In this example gold nanoparticles are inactive for the reaction, while they are able to increase selectivity since they act as electronic promoters.

iii) Gold nanoparticles as poisoning deactivators: the TPA purification. In this example gold nanoparticles are not active for the reaction but have an important role in delaying deactivation by sulphur poisoning.

Keywords: gold, catalyst, nanoparticles, Au/ZrO_2, Au/CeO_2, Au/C.DOI: 10.1002/elan.

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1. Introduction

Gold has always been able to fascinate humanity and it plays a central role in the modern society. However, unlike other noble metals (such as Pd, Pt, Cu, Ag, …), gold had never been considered for catalysis. In fact, due to its chemical inertness towards reactive molecules such as oxygen and hydrogen, for many years it was generally regarded as a poor catalyst. Only since the pioneering work of Professor Haruta and co-workers [1], gold has been shown to be highly active if deposited as nanoparticles over oxidic supports. In particular, the first studies have demonstrated that surface adsorption and reactivity of gold could be enhanced by creating defective surface structures through downsizing of gold nanoparticles. When gold nanoparticles, with sizes of less than about 5 nm, are supported on oxides, very active catalysts are produced. Nanoparticulated gold catalysts are active under mild conditions, even at ambient temperature or below, and this feature makes them quite unique.

Therefore gold nanoparticles are now firmly established as effective catalysts and the catalogue of reactions that they can catalyze is really wide [2-6]. As a matter of fact, catalysis by gold nanoparticles is a topic of current interest, as proved by the exponential growth of the papers on this subject, as schematized in Figure 1.

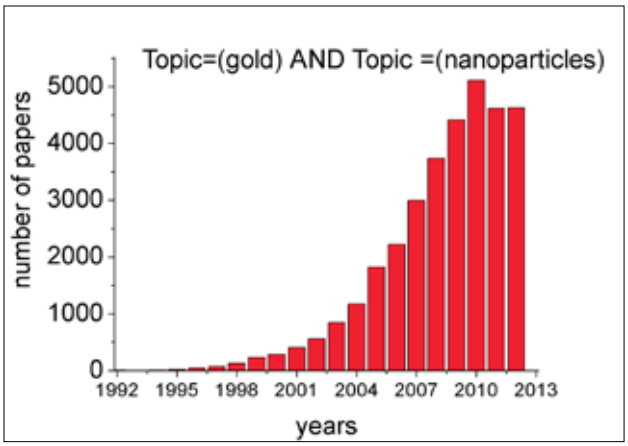

Figure 1. Papers on gold nanoparticles.

The reasons for small gold particles activity are still a matter of debate. It has been shown that the catalytic activity of gold critically depends on the gold size, on the support type, on the preparation method 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 gold low coordination sites. Several methods have been tested for making suitably small sized gold particles, the method known as deposition-precipitation (DP) qualifying as the best so far. In this method [7] the pH of a solution of $HAuCl_4$ is raised by addition of a base to the point where the adsorption of the species in solution can react with or be deposited on the support. The choice of support is essential for a good catalytic performance too.

Although gold nanoparticles show activity in many reactions, it is not true that they can act as an effective catalyst for every reaction they are applied to. For example, we'll see that gold nanoparticles are not active neither in the hydrogen peroxide direct synthesis under our reaction conditions, nor in the hydrogenation of aromatic aldehydes. Nevertheless the presence of gold, in a bimetallic system, deserves an appropriate investigation since it can affect activity, selectivity and stability. Owing to synergistic effects between two metals, bimetallic nanocrystalline catalysts often display superior catalytic performance compared to their single metal counterparts. Bimetallic systems are a promising new class of materials to meet increasing industrial demand for optimized catalysts. Presently, the basic research in this field addresses preparation of bimetallic systems with enhanced properties in terms of selectivity and activity as well as resistance to poisoning and/or metal sintering.

In the present paper we will discuss the importance of gold nanoparticles in heterogeneous catalysis; we will show their different roles as active phases, electronic promoters and poisoning deactivators. In particular, some examples of our recent experience will be presented:

i) Gold nanoparticles as active sites: the LT-WGSR. In this example gold acts as the active phase, and catalytic performances are strongly related to gold nanosizes.
ii) Gold nanoparticles as electronic promoters: the H_2O_2 direct synthesis. In this example gold nanoparticles are inactive for the reaction, while they are able to increase selectivity since they act as electronic promoters.
iii) Gold nanoparticles as poisoning deactivators: the TPA purification. In this example gold nanoparticles are not active for the reaction but have an important role in delaying deactivation by sulphur poisoning.

i) Gold nanoparticles as active sites: the LT-WGSR

The water-gas shift (WGS) reaction

$CO + H_2O = CO_2 + H_2$

is one of the oldest catalytic processes employed in the chemical industry, since it provides an economical route to hydrogen production. It usually proceeds in two distinct steps with two types of catalyst: a high temperature (HT) stage over an iron oxide promoted with chromium oxide catalyst, and a low temperature (LT) stage, on a catalyst composed of copper, zinc oxide and alumina. Recently, there has been a renewed interest in this reaction because it is one of the key steps in important applications such as pure H_2 production for fuel-cell power systems and in the automobile exhaust processes. However, in these applications heterogeneous catalysts with high activity as well as good structural stability in air and in cyclic operation are required, but this target is not met by the commercially available LT-WGS catalysts [8].

We have investigated [9] the LT-WGS reaction on gold-loaded zirconia (Au-Z) and sulphated zirconia (Au-SZ). The activity of these catalysts has been compared to the Au/TiO_2 reference catalyst obtained from the World Gold Council and to a commercial and industrially used $30\%Cu/ZnO/Al_2O_3$ sample (Figure 2).

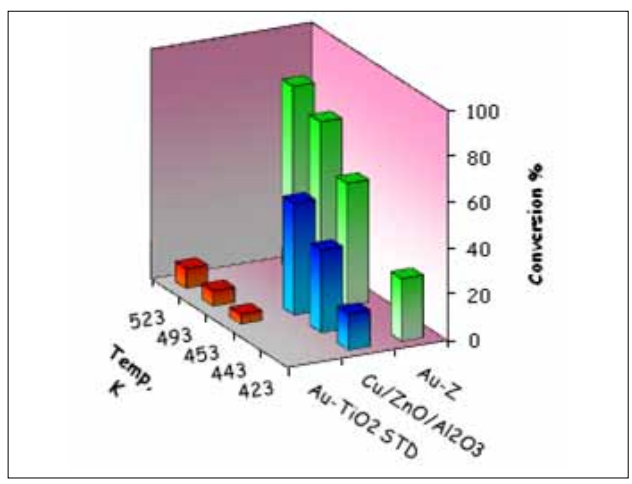

Figure 2. Catalytic performances in the LT-WGS reaction.

At low temperatures both Au-Z and Au-SZ samples are more active than the commercial cupper based catalyst, pointing out the good efficiency of gold as active phase for this reaction. Moreover, gold on zirconia catalysts have an activity of about

one order of magnitude higher than the Au-Ti reference catalyst [9]. This result has been related to the presence in the gold on zirconia samples of a much higher number of sites capable of adsorbing CO, as indicated by the results of the CO chemisorption [9]. Therefore we have investigated for different Au/ZrO_2 samples the possible correlation between chemisorbed CO and catalytic activity in the LT-WGSR [10] (Figure 3). It was pointed out that the samples with higher CO/Au molar ratio were the most active in the water-gas shift reaction, evidencing a strong correlation between catalytic activity and gold particles dispersion [10].

Therefore this example evidences that gold nanoparticles are suitable to catalyze the LT-WGSR and that their activity is closely connected to the Au nanosize.

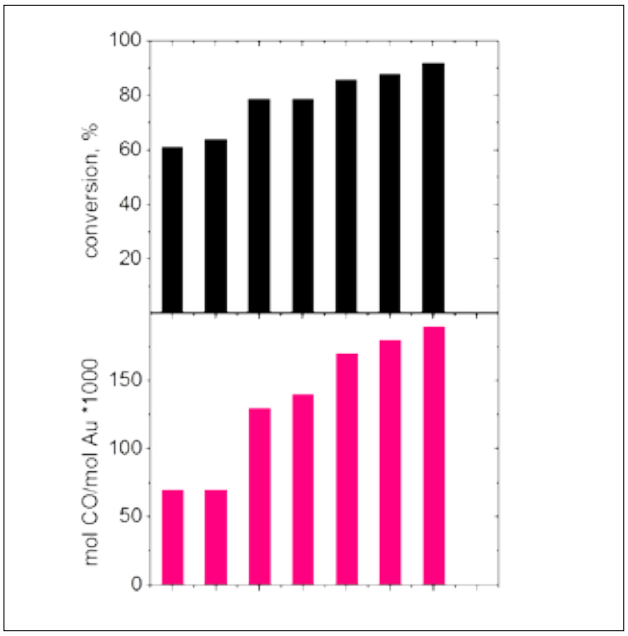

Figure 3. Correlation between chemisorbed CO and catalytic activity in the LT-WGSR.

Experimental

$Zr(OH)_4$ was prepared by precipitation from $ZrOCl_2 \cdot 8H_2O$ at constant pH= 8.6, aged for 20 hours at 363 K, washed with warm water free of chloride, dried at 383 K overnight. Part of the $Zr(OH)_4$ was sulphated with $(NH_4)_2SO_4$ (Merck) by incipient wetness impregnation in order to obtain a 2 wt % amount of sulphates on the final support. Sulphated zirconium hydroxides was then calcined in flowing air at 923 K.

Gold was added by deposition-precipitation (DP) at pH=8.6: the oxide support (5 g) was suspended in 200 mL of aqueous solution of $HAuCl_4 \cdot 3H_2O$ for 3 hours and the pH was controlled by the addition of NaOH (0,5 M).

After filtration the samples were dried at 308 K overnight and finally calcined in air for 1 hour at different temperatures (423 K, 573 K, 773 K, 873 K, 923 K).

The residual sulphate content of all samples was determined by ion chromatography.

The gold amount was determined by atomic adsorption spectroscopy.

CO pulse chemisorption measurements were performed at 157 K in a lab-made equipment. Before the analysis the following pretreatment was applied: the sample (200 mg) was reduced in a H_2 flow (40 mL/min) at 423 K for 60 min, cooled in H_2 to room temperature, purged in He flow and finally hydrated at room temperature. The hydration treatment was performed by contacting the sample with a He flow (10 mL/min) saturated with a proper amount of water. The sample was then cooled in He flow to the temperature chosen for CO chemisorption (157 K).

WGSR was performed in a fixed-bed flow reactor at atmospheric pressure and in the temperature range from 523 to 423 K. The following conditions were applied: space velocity = 9400 h^{-1}; catalyst volume = 0.5 cm^3 (35-50 mesh) diluted to 1.5 cm^3 with quartz sand (Carlo Erba; 35-50 mesh); the feed mixture contained 1.9%vol. CO, 39.7% vol. H_2, 9.5% vol. CO_2, 11.4% vol. N_2, 37.5% vol. H_2O. Samples were previously subjected to a slow (50 K/h) thermal activation in nitrogen (50 mL/min) up to 523 K and kept at this temperature for 17 hours in the same N_2 flow. The progress of the reaction was followed by gas-chromatographic analysis of the converted mixture at the reactor outlet.

ii) Gold nanoparticles as electronic promoters: the H_2O_2 direct synthesis

Hydrogen peroxide is widely accepted as a green alternative to conventional chlorinated oxidants, as it is easy to handle, is relatively non-toxic, and breaks down readily to water in the environment [11]. The so called anthraquinone process covers over 95% of the world's H_2O_2 production, but it cannot be considered a sustainable one, and suffers from several limitations: (i) it produces a significant amount of organic waste due to the over-reduction of

anthraquinone, (ii) it needs several costly separation and concentration steps and (iii) it is economically feasible only on large scale plants.

The direct reaction of H_2+O_2 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_2O_2 vs. H_2O that can be achieved with known catalysts. In fact, as shown in Figure 4, the same catalysts used to produce H_2O_2 are also active for its decomposition and its hydrogenation to water as well as for water direct synthesis.

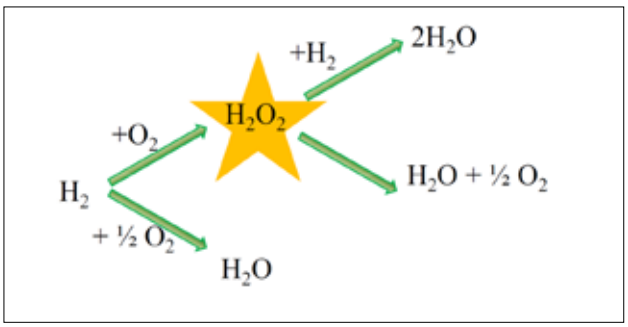

Figure 4. Reactions involved in the direct synthesis of hydrogen peroxide.

Another serious problem that has limited the implementation for this process is the significant risk of handling the explosive hydrogen/oxygen gas mixture. Therefore, despite several patents [12-18] and recent literature [19-35], the direct synthesis of hydrogen peroxide has not yet found the way to commercialization.

Until very recently, the catalysts used in these investigations were based predominantly on palladium. In the past years, Hutchings and co-workers have reported that catalysts based on Au-Pd alloys supported on alumina, iron oxide, titanium oxide, or carbon [26, 29] can improve the hydrogen peroxide yield when compared with the Pd only catalyst. However all these investigations were performed using moderately high pressures (37 bar).

We have investigated bimetallic palladium-gold catalysts for the direct synthesis of hydrogen peroxide under very mild conditions (Room temperature and 1 bar) and outside the explosion range [36-38]. Zirconia and ceria, both plain and sulphated, were chosen as supports.

First of all we have verified that the monometallic gold catalysts show neither hydrogen peroxide nor water production under the mild experimental conditions used [36-38]. On the contrary, the addition a 1:1 amount of gold to a monometallic Pd sample improves the productivity and in particular the selectivity of the process (Figure 5) [36].

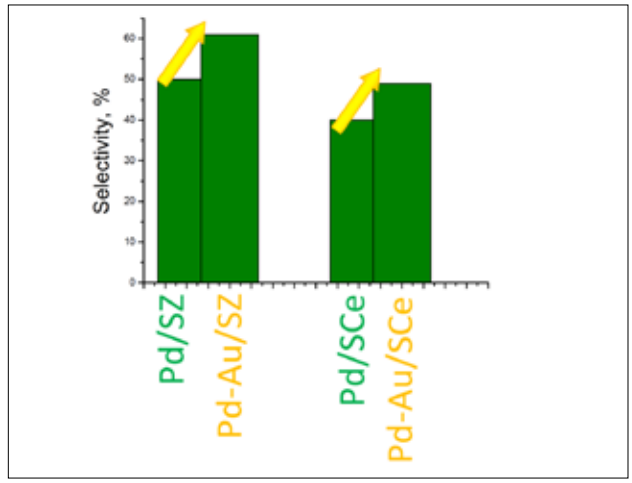

Figure 5. Catalytic performances in the direct synthesis of hydrogen peroxide.

Characterization data have shown [36] that a Au-rich core/Pd-rich shell morphology is induced in the Pd-Au bimetallic catalysts (Figure 6).

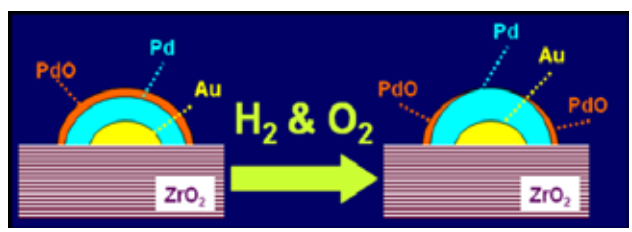

Figure 6. Hypothesis for the morphology of PdAu bimetallic samples.

It can be suggested that the Au core would exert an electron donation effect on the Pd shell. This would make Pd more "noble", less reactive towards oxygen, decreasing dissociative chemisorption on more energetic sites. As a consequence, the addition of Au allows maintaining a high proportion of low energy sites, increasing selectivity [36].

Therefore PdAu bimetallic catalysts improved productivity and selectivity, producing already at room temperature and atmospheric pressure a hydrogen peroxide concentration useful for some industrial applications and maintaining a stable selectivity after several hours.

This example evidences that gold nanoparticles are inactive for the reaction, while are able to increase selectivity since they act as electronic promoters.

Experimental

Zirconia support was prepared by precipitation from $ZrOCl_2$ $8H_2O$ at constant pH (pH=10), aged under reflux conditions [39, 40], washed free from chloride ($AgNO_3$ test) and dried at 383 K overnight. Ceria support was synthesized by precipitation from $(NH_4)_2Ce(NO_3)_6$ by urea at 373 K in aqueous solution [41]. The solution was continuously mixed and boiled for 6 h at 373 K, the precipitate was washed twice in boiling deionized water and dried at 383 K overnight. These materials were impregnated by an incipient wetness method with $(NH_4)_2SO_4$ in amounts necessary to yield an 8 wt% anion loading. Impregnated supports were then calcined in flowing air (50 ml/min) at 923 K for 3 hours. Calcined supports were impregnated by incipient wetness with H_2PdCl_4 and/or $HAuCl_4$ aqueous solutions to give a nominal 2.5 wt% metal loaded catalyst and finally calcined again at 723 K in flowing air for 3 hours.

Catalytic tests were carried out at atmospheric pressure in a 293 K thermostatted glass reactor [42] 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: H_2:O_2 4:96 (nonexplosive and lower limit for nonflammable mixture) [43].

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. Samples were pretreated in situ first by H_2 (15 min - 30ml/min) and then by O_2 (15 min - 30 ml/min) flow. During catalytic tests small aliquots of the liquid phase were sampled 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:

$$S_{H_2O_2} = \frac{[H_2O_2]}{[H_2O_2]+[H_2O]}$$

iii) Gold nanoparticles as poisoning deactivators: the TPA purification

Deactivation by sulphur poisoning of noble metal supported catalysts is a serious industrial problem [44]. As it is well known, sulphur compounds are the most effective poisons for palladium catalysts, which are extensively used in both petrochemical and fine chemical industries for many chemical reactions. For example palladium samples supported on active carbon are typically used in the important reaction of hydrogenation of 4-carboxybenzaldehyde for the purification of crude terephtalic acid. It has been shown that in such aqueous systems the formation of bulk Pd_4S occurs [45].

We have therefore investigated bimetallic palladium-gold catalysts supported on active carbon, in order to verify possible effects of gold addition on Pd/C samples for the resistance to deactivation by sulphur compounds [46]. Bimetallic catalysts are in fact very interesting and promising as they feature interesting catalytic behaviour with respect to monometallic systems [44]. An expedited deactivation test was tuned: catalysts were conveniently poisoned in an autoclave with an aqueous Na_2S solution. We employed Wide Angle X-ray Diffraction (WAXS) in order to check for the crystallographic nature of the formed phases and for the presence of Pd_4S. A schematization of Pd_4S unitary cell is reported in Figure 7.

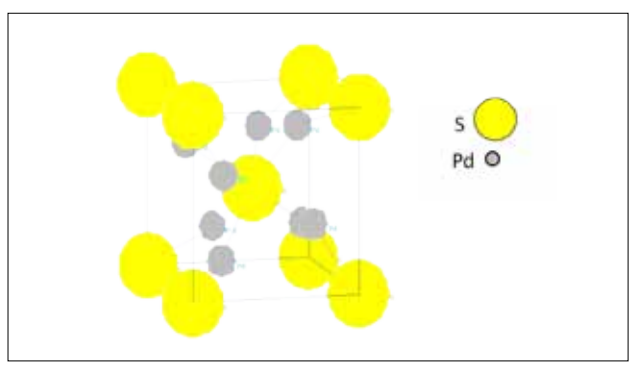

Figure 7. Schematization of Pd_4S unitary cell.

Figure 8 reports WAXS patterns for samples Pd/C and Pd-Au/C before (dashed line) and after poisoning (solid line) [46]. In the figure the Bragg positions relative to the reflection of Pd_4S are reported (*). The pattern of monometallic sample shows a peak at 2θ=40.1°, the position of the most intense peak of Pd. From the XRD pattern of the bimetallic sample it is possible to see that Pd-Au/C consists of

a palladium/gold alloy and of pure gold. With the addition of S in the monometallic sample the main Pd peak completely disappears, and the formation of Pd_4S occurs (*).

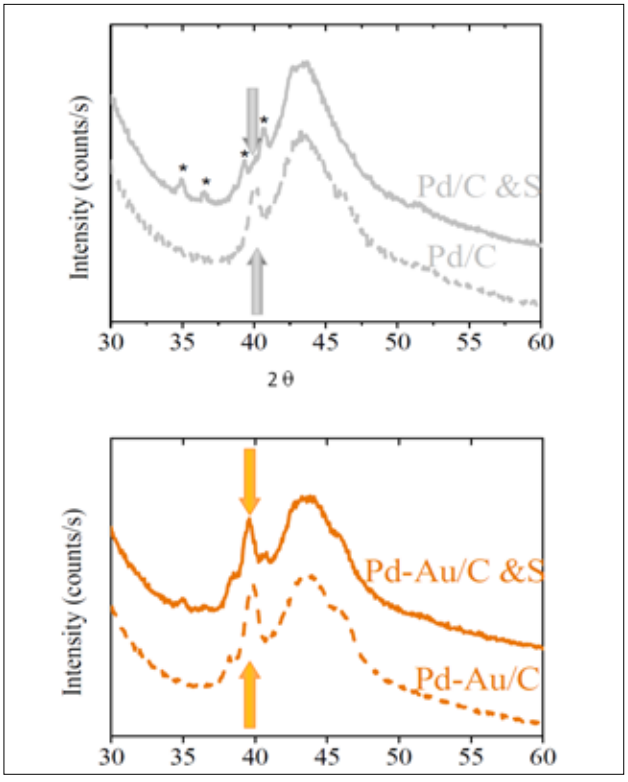

Figure 8. WAXS patterns for samples Pd/C and Pd-Au/C before (dashed line) and after poisoning (solid line).

On the contrary, in the poisoned Pd-Au/C catalyst, the presence of Pd_4S is recordable, but in a much smaller amount with respect to the monometallic Pd sample, and the main peak of the metallic phase is almost intact. This can be explained considering that after the formation of a Pd-Au solid solution, palladium atoms are not in a suitable geometry for assisting the Pd_4S formation. In fact, in the solid solution it is really unlikely to find four Pd atoms in close contact in order to interact and form the structure of Pd_4S [46, 47].

Therefore gold addition in this sample prevents the Pd_4S formation and the disappearance of the metallic phase in the presence of S [46].

Subsequently we studied the effects on catalytic activity using as probe reaction the selective hydrogenation of benzaldehyde to benzyl alcohol. The specific activity data before and after sulphur poisoning are shown in Figure 9.

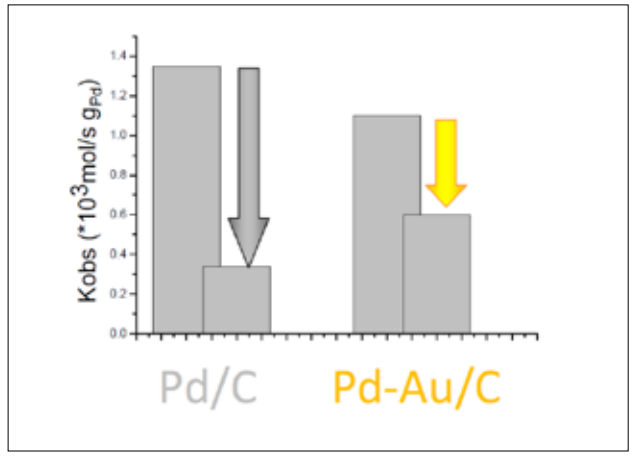

Figure 9. Catalytic activity for the selective hydrogenation of benzaldehyde to benzyl alcohol.

Pd-Au/C sample evidences a slightly lower activity if compared to the monometallic one [46]. However, gold addition improves catalyst resistance to sulphur poisoning. In fact, a decrease of about 70% activity occurs for the monometallic Pd/C sample after poisoning, while the activity is only approximately halved for the poisoned bimetallic catalyst [46].

These results agree with characterization data, the decrease in the catalytic activity being correlated with the formation of Pd_4S phase. From a practical point of view, gold addition to Pd in carbon-supported catalysts does not give any advantage as to activity in hydrogenation of aromatic aldehydes, while imparting a positive effect on resistance to deactivation. In conclusion [46], gold addition to monometallic Pd/C improves catalyst resistance to sulphur poisoning, preventing Pd_4S formation and showing higher catalytic activity for benzaldehyde hydrogenation after poisoning with Na_2S. As no activity increase results in the absence of sulphur poisoning, gold seems to act only as an inert diluent that prevents Pd_4S formation. In fact, palladium atoms are averagely more spaced in the bimetallic samples than in the compact fcc structure of the monometallic Pd. In this way, structural geometry is not suitable for assisting Pd_4S formation, since it is unlikely to find four Pd atoms in the correct position to interact with sulphur atoms and form the structure of Pd_4S [46].

The importance of gold nanoparticles is therefore due to their role as poisoning deactivators.

Experimental

Pd/C and Pd-Au/C catalyst were prepared by wet impregnation of a commercial coconut ac-

tive carbon (1200 m^2/g) by (co-)impregnation of Na_2PdCl_4 and $HAuCl_4$ aqueous solution. Reduction was performed by sodium formate. Catalysts were poisoned in an autoclave with an aqueous Na_2S solution at 473 K for 3 h under H_2 atmosphere (S/Pd=0.33 atomic).

WAXS measurements were done in Bragg-Brentano geometry using an X'Pert diffractometer equipped with a focusing graphite monochromator on the diffracted beam and a proportional counter with electronic pulse height discrimination [46].

The catalytic hydrogenation of benzaldehyde to benzyl alcohol was carried out at 293 K [48] in a glass batch reactor fitted with a reflux condenser, a mechanical stirrer and an external jacket. The catalyst (corresponding to 4 mg Pd) was suspended in the solvent (100 ml ethanol) and pre-treated in H_2 flow (30 ml/min) at 80 °C for 1 h. A mixture of benzaldehyde (1.0 ml) and n-octane (0.3 ml), used as internal standard, was added. The reactor was stirred at 1500 rpm and operated at atmospheric pressure in H_2 flow. The progress of the reaction was followed by gas-chromatographic analysis of samples withdrawn from the reaction mixture.

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