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In situ wide angle X-ray scattering (WAXS) study of bimetallic Au–Pd catalysts

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Aim of the paper is to apply a modified version of the Rietveld method to two Au–Pd/C catalysts prepared by successive impregnation and reduced *in situ* by a special holder in order to show that a suitable WAXS analysis, performed in routine lab and using an X-ray conventional generator, can be very detailed and rich of information especially when a bimetallic catalyst has to be considered.

Keywords: X-ray diffraction, gold, palladium, bimetallic catalysts, metal alloy, microstructure, Rietveld method

1. Introduction

The determination of the average particle size of a metallic active phase dispersed on a support can be very important in order to calculate the value of the metallic dispersion [1]. This can be considered as a crucial property of the system strongly related to its catalytic activity and it can be used to find a proper interpretation of heterogeneously catalyzed reaction kinetics.

In the study of metallic supported catalysts, usually, the X-ray diffraction at small and wide angle (SAXS and WAXS) is employed to support the microstructural features obtained by other techniques such as chemisorption, temperature-programmed reduction or electron microscopy micrographs. This second lead role is often due to the difficulty to study these systems by the analysis of the diffraction patterns. The total scattering, in fact, can be the result of different components partially amorphous or crystalline with size sometimes smaller than 2 nm very difficult to separate.

Recently [2,3], we have shown that by X-ray scattering measurements alone, it is possible to evidence very important features of the microstructure of Au and Pd metallic phase dispersed on an active carbon. In particular, the anomalous resonance effect in the diffraction experiments at small angle and the modified version of the Rietveld analysis at wide angle were used to show the presence of particles with size smaller than 2 nm and larger than 10 nm. The modified version of the Rietveld method was applied also to different Au–Pd systems [4]. However, the presence of oxidized phases, with size of about 2 nm, prevented us to describe correctly all the microstructural features.

Aim of the present study is to apply this method to two Au–Pd/C catalysts prepared by successive impregnation and reduced *in situ* and to show that a suitable WAXS analysis, performed in a normal laboratory and using an X-ray conventional generator, can be very detailed and rich of information especially when a bimetallic catalyst has to be considered [5].

2. Experimental

2.1. Sample preparation

A commercial active carbon with a specific surface area of 1200 m^2/g and a pore volume of 0.60 ml/g has been used as support. The two catalysts, Pd 0.40–Au 0.08 wt% (sample A) and Pd 0.91–Au 0.40 wt% (sample B) were obtained by successive impregnation of Na_2PdCl_4 and $HAuCl_4$ aqueous solution and reduced with $H_2NaO_2P\cdot H_2O$ at 298 K. The metal loading was determined by atomic absorption spectroscopy. The first of the two samples was also investigated after an ageing thermal treatment (in $H_2O/H_2 = 1$) at 673 K for 4 h (sample A673).

2.2. X-ray measurements

A Philips X'Pert vertical goniometer connected to a highly stabilized generator, Cu K_α Ni-filtered radiation, a graphite monochromator and a proportional counter with a pulse-height discriminator were used. The patterns of the samples were recorded at 295 K on a 10°–140° range with a step size of 0.05° (5 s/step). For each sample 12 runs were performed in order to have a final statistic of 60 s for each point. This high number of seconds was used in order to drop the noise of the data as much as possible [3].

Since previous XRD results [4] evidenced the possible presence of crystalline phases partially oxidized, before the X-ray measurements, the samples were subjected to a second *in situ* reduction process. For this reason the samples were left under a H_2 atmosphere for 1 h. Successively they were treated with N_2 for about 4 h until the peak of Pd-β hydride disappeared. Finally, the X-ray measurements were performed using a N_2 flux.

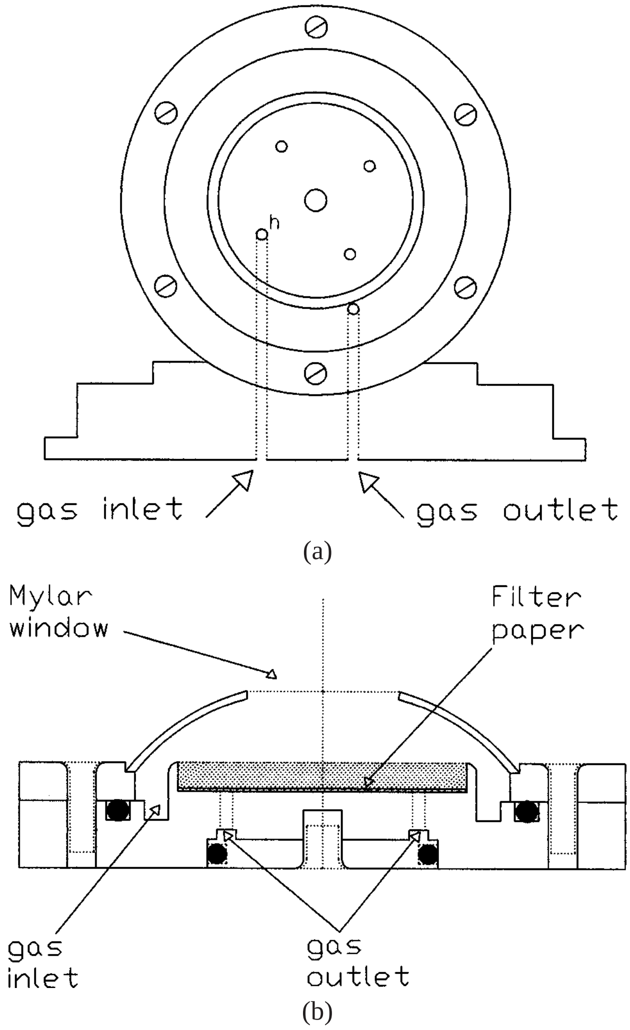

Figure 1. (a) Top view and (b) front view of the sample holder.

All these treatments have been done using the same sample holder opportunely tailored for diffraction experiments and shown in figure 1. It consists of a base of stainless steel with a gas inlet and outlet. The gas inlet is positioned in the upper part of the base and it can flow over the powder, so to avoid any movements of the sample. The gas is removed throughout the four holes indicated by the letter “h” and positioned at the bottom of the holder in contact with the lower part of the powder. The sample is sealed by a cup with a dome of polyethylene with a window of mylar. Both the sample holder scattering and the scattering due to the active carbon (support scattering) were measured under N_2 atmosphere after a 2 h drying pre-treatment.

2.3. Data analysis

Line broadening analysis was carried out according to a previously described procedure [6], which combines the results obtained by the Rietveld method and Fourier analysis: the optimized parameters concerning the peaks relevant to the $K_{\alpha 1}$ monochromatic radiation were analytically Fourier transformed and deconvoluted from the instrumental broadening.

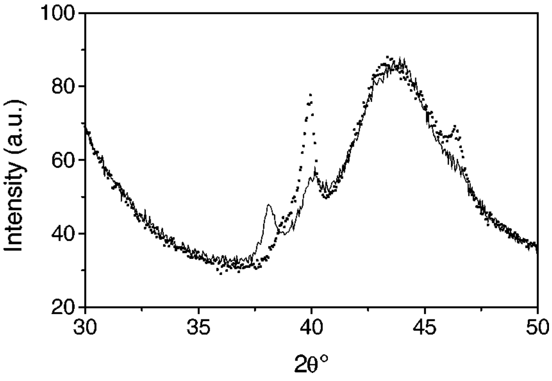

Figure 2. Comparison of the patterns of sample A (—) and sample A673 (···). The peaks at about 38°, 39° and 40° in 2θ correspond, respectively, to the 111 Au, the 111 Au–Pd alloy and 111 Pd profiles.

In order to apply the modified version of the Rietveld [3] analysis the theoretical intensity of a carbon-supported metal catalyst, in the fitting procedure, is written as

$$Y - Y_{\text{air}} = K_{\text{Cr}} Y_{\text{Cr}} + K_{\text{C}} Y_{\text{C}},$$

where $Y - Y_{\text{air}}$ is the air-corrected diffraction pattern and takes into account the following contributions: $Y_{\text{Cr}} =$ crystalline metal, $Y_{\text{C}} =$ carbon pattern measured separately, $K_{\text{Cr}}, K_{\text{C}} =$ refinable scale factors. By doing so the metal percentage can be calculated from the quantities of the crystalline phase obtained by the fitting procedure.

The carbon pattern used in the refinement has been firstly fitted by a polynomial function of fifth order and six pseudo-Voigt functions. This particular choice is not important since we want only to smooth the experimental pattern of the carbon used in Rietveld analysis.

In order to be sure of using the correct pattern we have processed the carbon as the catalyst and thermally treated it at 673 K. No changes were found among the different patterns [3].

3. Results and discussion

In order to give an easy and fast view of the problems related to the analysis, the figures will show only the range of the X-ray pattern between 30° and 50° in 2θ. The study of the 111 and 200 reflections, the most intense profiles for both the metals, are sufficient to give an immediate, but comprehensive idea about the microstructure of the crystalline phases.

The X-ray patterns of the samples A and A673 are shown in figure 2. The study of these systems evidenced the presence of two separated metallic crystalline phases: gold and palladium for the sample as prepared, while the thermal treatment transformed the gold in a solid solution of Au–Pd leaving the Pd unchanged. The composition of this alloy is very difficult to determine since the relative peak is just a shoulder to the 111 Pd profile.

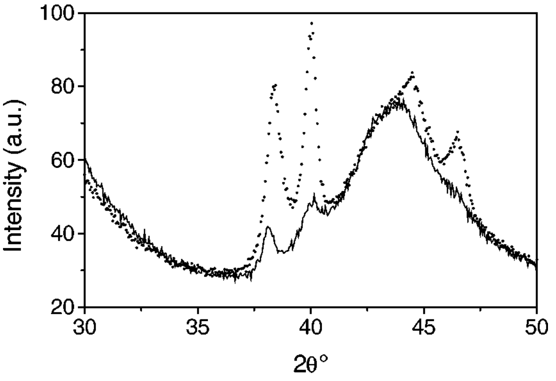

Figure 3. Comparison of the patterns of sample A (—) and sample B (· · ·). The 111 Au peak shifts to higher angles meanwhile the 111 Pd profile does not move.

Figure 3, shows the comparison of the patterns of samples A and B. The 111 Au profile of the sample B shows a small shift towards higher angles with respect to the A pattern where pure Au is present. This fact can be related to the formation of an alloy Au–Pd that was not found in the catalyst loaded with a smaller amount of metals.

These results refer to a qualitative analysis usually performed for this kind of studies. The X-ray line broadening analysis of the peaks could be performed, but it could be misleading [2–4] if part of the metal particles remains undetected by WAXS. Consequently further experimental evidence by other techniques should be requested in order to support the results and to obtain a comprehensive picture of the systems.

In contrast, if the modified version of the Rietveld analysis is performed on a semi-crystalline system it is possible to have information about

(i) the quantitative determination of the crystalline phases present in the sample also when an amorphous component is present;

(ii) the structure (cell parameters and thermal parameter);

(iii) the microstructure (crystallite size).

The use of this method in the study of metal supported catalysts can be very useful since from the quantitative analysis of the phases it is possible to know exactly the amount of detectable metal on which information about structure and microstructure can be obtained.

In a previous paper [4], the application of this approach had evidenced the presence of a component of very small crystallites (size ⩽2 nm) probably formed by an oxidized metal phase not describable with the profile functions used to fit the Au and Pd metallic phases. This fact prevented us to obtain the same amount of metal found by atomic absorption measurements with the consequent unreliability of the microstructural results.

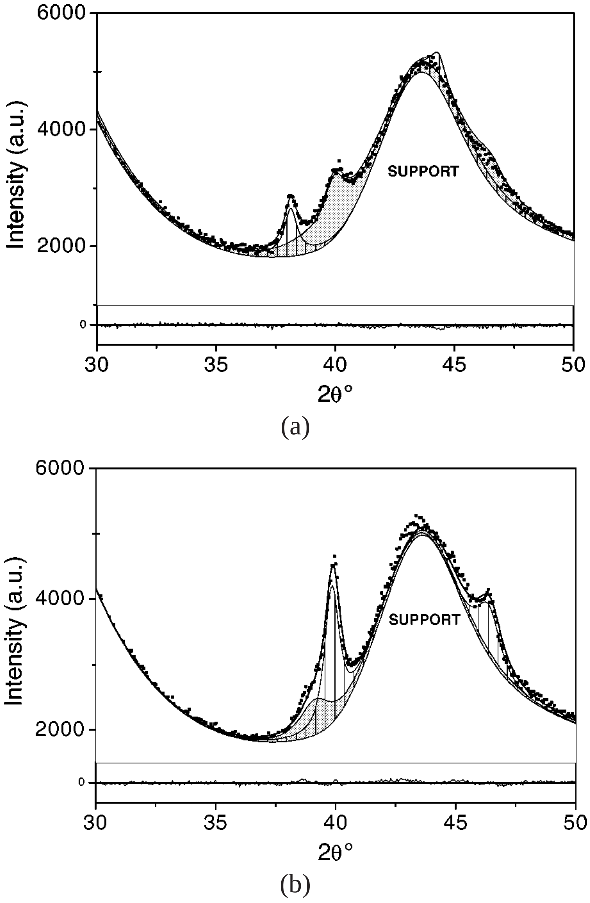

Figure 4. Results of the Rietveld analysis: (a) for sample A three different contributions can be evidenced: the scattering due to the carbon (white halo), the Au peaks (dashed region) and Pd peaks (light gray region); (b) for sample A673 also three different contributions can be evidenced: the scattering due to the carbon (white halo), the Au–Pd alloy peaks (light gray region) and Pd peaks (dashed region). At the bottom of the figures the plot of the weighted residuals is given.

Table 1
Metal loading of the catalysts calculated by the X-ray diffraction analysis and relative crystallite sizes.

Sample	Metal loading (wt%)		Average size (nm)			Alloy
	Pd	Au	Au	Au–Pd	Pd	(at% Au)
A	0.41(2)	0.08(1)	4.9		4.3	
A673	0.42(2)	0.09(1)		4.6	8.1	40
B	0.91(3)	0.42(2)		9.1	7.9	88

In figure 4 (a) and (b) the fits of the patterns of samples A and A673, in the range 30–50° 2θ, show that the second *in situ* reduction treatment and the subsequent measurements under N_2 atmosphere can be able to eliminate the oxidized component. All the scattering difference between the catalyst and the support can be described only by two metallic phases. In table 1 the wt% of the Au and Pd determined by this method that takes into account also the formation of a solid solution are reported. The results concerning samples A and A673 show that, with the modified Rietveld analysis, it is possible to determine all the metal loaded in the catalyst. This result is very important since, only in this way, we are sure that the analyzed peak refers to all the metal really loaded. Concerning sample A673 it is possible to separate the contribution of the alloy to the peaks envelope. The volume-weighted average crystallite

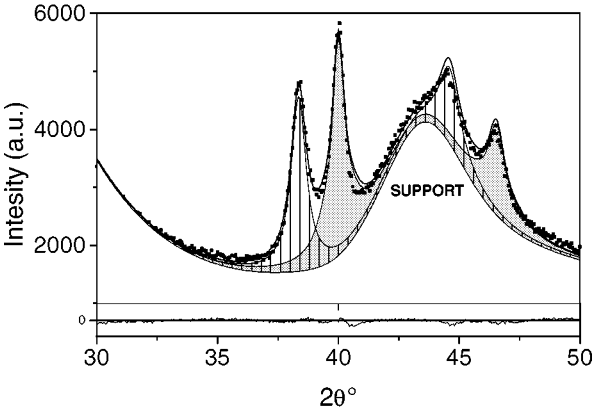

Figure 5. Results of the Rietveld analysis for sample B. Three different contributions can be evidenced. The scattering due to: the carbon (white halo), the Au–Pd alloy peaks (dashed region) and Pd peaks (light gray region). At the bottom of the figure the plot of the weighted residuals are reported.

sizes obtained by the line broadening analysis are, respectively, 4.6 nm for Au–Pd alloy and 8.1 nm for Pd and the composition of the alloy (40 at% Au) was calculated considering the variation of the cell parameter with respect to the literature data.

Also for sample B loaded with more metal, the quantitative results are in good agreement with the data of the atomic absorption. Figure 5 shows the experimental pattern and the optimized fit. The values of the sizes reported in table 1 show larger values if compared to results of A. Sample B presents already the formation of an alloy not found in sample A prepared in the same way. This is very interesting since the temperature used to prepare this sample is 298 K. In the presence of an activated carbon, the reactivity of the two metals seems to be very high and an alloying process seems to be controlled by the amount of the metal present. In addition, by using this approach it is possible to obtain some information about the possible presence of decorating phenomena of the metals [7]. In particular, since we are able to determine all the metal loaded in the catalysts, and since the X-ray diffraction measurements concern bulk properties of the phase we can conclude – within the error of our results – that pure metal or homogeneous Pd–Au alloys are formed. The presence of a still possible population of particles exhibiting a second metal surface enrichment has to be considered a minority one.

4. Conclusion

In this paper an *in situ* WAXS study on Pd–Au/C catalysts prepared by successive impregnation has been performed. The special sample holder and the method employed to analyze the data, that can be applied on patterns obtained by a conventional generator, are able to give information not only on the microstructural features, but also on the amount of the phase to which it is referring to. In this way it has been possible to show that the amount of the metal loading can be strongly related to the formation of alloy and that the quantitative analysis can give information about the decorating phenomena.

Finally, we would like to underline again that the goodness and the reliability of our microstructural analysis is strengthened by the capability of determining the true amount of loaded metal.

Acknowledgement

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