Catalytic behavior and active sites structure of PtAu/Al$_2$O$_3$ bimetallic catalysts prepared by surface redox reactions

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Abstract

Alumina supported Pt–Au bimetallic catalysts, in which Au was deposited onto Pt by reduction of AuCl$_4^-$ with adsorbed hydrogen, were studied using hydrogen TPD and X-ray diffraction. Their catalytic behavior was tested in methylcyclopentane reaction. The gold inhibits the hydrogen adsorption indicating that gold atoms are deposited on platinum sites. In methylcyclopentane reaction, the catalysts containing the largest amounts of Au, promoted the formation of dehydrogenation products although in conversions very low. However, the environmental conditions or oxidation treatments irreversibly affect the catalytic behavior in these systems, suggesting a rearrangement of the metallic sites created by the redox reaction. This rearrangement effect was investigated by X-ray diffraction and by high resolution electron microscopy (HREM) studies. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

In recent years, many studies concerning bimetallic or multimetallic catalysts for hydrocarbon reactions have been published [1]. Compared to monometallic catalysts, bimetallic or multimetallic catalysts show an increased selectivity or better resistance to deactivation. In a bimetallic alloy, as platinum–gold, the structure of the various platinum surface sites can be altered [2], and the surface composition of an alloy may differ from that of the bulk [3]. Segregation of a component (often the component with the lowest melting point) is known to decrease the surface energy, and is highly dependent on environmental conditions. However, others factors, such as the nature of the carrier, the preparation method, and the metal particle size, may be responsible, also, for the differences in the composition and structure of bimetallic surface sites that determine the catalytic behavior.

Concerning the preparation method of supported bimetallic catalysts; the main problem is to bring the two metals into close contact. The classical coimpregnation method is often unsatisfactory and new techniques are being used. One strategy is to modify a supported monometallic catalyst by the addition of a second metal in order to create metal–metal interactions. The second metal is deposited via a selective reaction occurring on the monometallic particles initially present on the support [4,5]. Such modification can be

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achieved by surface redox reactions in the liquid phase between the chemically prereduced monometallic catalyst or a preadsorbed reducing agent, i.e. adsorbed hydrogen, and the oxidized form of the modifier.

To determine the role of the preparation method on the properties of the surface sites of the Pt–Au system, we have prepared a series of bimetallic catalysts with different amounts of gold on alumina supported platinum catalyst, and studied their catalytic behavior in methylcyclopentane reaction. This reaction has been often employed to indirectly elucidate the structure of the metallic particles [6]. The mechanisms of skeletal rearrangements of hydrocarbons on metals, the cyclization and bond shift mechanisms are now well characterized [7]. Extensive work on supported platinum catalysts and platinum films has shown that in methylcyclopentane reaction, the isomerization of hexanes and aromatization are very sensitive to the surface structure and especially to the metal particle size, in contrast to the reactions involving only carbon–hydrogen bonds [8].

The catalysts were characterized by hydrogen TPD, in order to obtain the exposure of platinum in the bimetallic catalysts. We have determined the cell parameters by X-ray diffraction, and obtained HREM images for selected catalysts, to determine their microstructures. Moreover, we have explored the effect of oxidation/reduction treatment on the behavior of these Pt–Au bimetallic catalysts, and compared these results with the stabilization effect attributable to environmental conditions (air at temperature close to 25°C).

2. Experimental

2.1. Catalyst preparation

2.1.1. Monometallic catalyst

The support was a low area alumina (Rhone-Poulenc, $60\,m^2\,g^{-1}$) crushed and sieved to 0.1–0.25 mm. The monometallic catalyst was prepared by impregnation with a $H_2PtCl_6\cdot6H_2O$ solution, whose concentration provided a Pt content of 1.0 wt.% in the catalyst. The catalyst was dried at 330 K for 6 h and oxidized in flowing air at 723 K for 4 h, then it was reduced in flowing hydrogen at 773 K for 6 h. The Pt catalyst showed a dispersion close to 60% determined by hydrogen adsorption/volumetric method. In order to increase the platinum particle size, the catalyst was treated by heating in flowing nitrogen mixed with oxygen (99:1 wt.% ratio) at 823 K for 3 h and reduced in flowing hydrogen at 773 K for 6 h. After this treatment the dispersion was found to be 44%.

2.1.2. Bimetallic catalysts

The bimetallic catalysts were prepared reducing $AuCl_4^-$ (from $HAuCl_4$) with hydrogen preadsorbed on the platinum surface. A slurry of the monometallic catalyst was prepared with a solution of HCl (pH = 1). The slurry was purged with flowing nitrogen for 30 min, in order to eliminate the air. Then, a hydrogen flow was passed through the slurry. After 2 h the hydrogen bubbling was stopped and the vessel was purged again with a nitrogen flow. The $HAuCl_4$ solution was purged in flowing nitrogen and, after 30 min, it was mixed with the slurry for 30 min. The catalysts with different amounts of gold were obtained by varying the solution $HAuCl_4$ concentration. The nominal Au loads were 0.06, 0.12, 0.24 and 0.48 wt.%. After the redox reaction, the catalysts were filtered, rinsed with distillate water, dried at 393 K overnight and reduced in flowing hydrogen at 773 K for 6 h.

2.1.3. Reference catalyst

One alumina supported Pt monometallic catalyst was treated as mentioned above for the Pt–Au catalysts, except for reaction with the $AuCl_4$. The thermal treatments also were the same.

2.1.4. Measurements of hydrogen TPD

The TPD was carried out in a system (Zeton Altamira AMI-3). The catalyst sample, previously reduced, was first pretreated in flowing H_2 ($30\,cm^3\,min^{-1}$) at 773 K for 1 h, afterwards the temperature was decreased and the flow of H_2 is changed by Ar. At 373 K the adsorption of hydrogen is carried out passing a flow of H_2/Ar (H_2, 10%) for 30 min. After purging the system at this temperature with flowing pure Ar, the temperature was increased at a rate of 10 K/min with a sweep gas flow rate of $30\,cm^3/min$. Bottled gases of the highest commercial grade of purity were used.

2.1.5. Catalytic tests

Methylcyclopentane (Aldrich 98%) ring opening experiments were carried out at atmospheric pressure

in a fixed-bed continuous flow reactor. The internal diameter of the glass reactor was 6 mm. Typically 0.05 g of catalyst of particle size 0.1–0.25 mm was used. Reaction products were analyzed on-line using a Perkin-Elmer 8410 gas chromatograph, equipped with a FID detector and a 50 m fused silica capillary column with methyl-5%-phenyl-silicon coating. The reaction temperature was 623 K, and the molar ratio of reactants was $H_2/MCP = 14$. Partial pressure control of the MCP was achieved by using a saturator at 273 K. The total gas flow was 1 ml/s in all experiments. The conversion was calculated using the next equation.

$X_{MCP} =$ (moles of MCP in the feed-moles of MCP in the outlet stream)/moles of MCP in the feed.

The selectivity of any species i is given by the following relation.

$S_i =$ (moles of i species generated/moles of all products) $\times 100$.

2.1.6. X-ray diffraction and microscopy studies

X-ray diffraction patterns were obtained with a Siemens D-500 diffractometer coupled to a copper anode tube. The Kα radiation was selected with a diffracted beam monochromator. To estimate the cell parameters of the supported catalyst, the γ-Al$_2$O$_3$ peak (4 0 0) was used as an internal standard. An angular range 2θ from 45 to 47° was recorded using step scanning and long counting times to determine the position of the platinum peak (2 0 0).

Conventional and High Resolution Electron Microscopy (CTEM and HREM, respectively) observations were carried out in a JEOL 4000 EX electron microscope equipped with a pole piece with an aberration coefficient of $C_s = 1.00$ mm. Powder samples were softly ground in an agate mortar and then dispersed in isopropylic alcohol in an ultrasonic bath for several minutes. Some drops were deposited on 200 mesh copper grids covered with a holey carbon film and, after drying, samples were mounted inside the microscope column.

3. Results and discussion

The compositions of the mono- and bimetallic catalysts are summarized in Table 1 as estimated by atomic absorption and X-ray fluorescence analysis. The Pt

Table 1
Characteristics of the catalysts

Catalyst	Au (wt.%)[a]	Au atom (%)	Pt exposure (%)[b]	Cl (wt.%)[a]
Reference	0.00	–	34.4	0.45
R1	0.02	2.20	17.1	0.54
R2	0.10	10.13	14.9	0.42
R3	0.18	17.53	2.9	0.82
R4	0.35	33.47	6.5	0.77

[a] Estimated by X-ray fluorescence.
[b] Estimated from TPD profiles.

dispersions were calculated from the TPD profiles which are showed in Fig. 1. The content of gold has a clear effect on the amount of desorbed hydrogen at 373 K. The decrease of the adsorbed hydrogen on the bimetallic catalysts as Au content is increased, shows that gold is blocking the platinum surface sites.

The preparation method of bimetallic catalysts by means of redox reactions, as used in the present study, was chosen to deposit gold on the platinum surface and to achieve a close interaction between both metals, platinum and gold. The reduction treatment at 773 K in hydrogen flow for 6 h, which is performed after redox reaction, could possibly favor inter-diffusion between
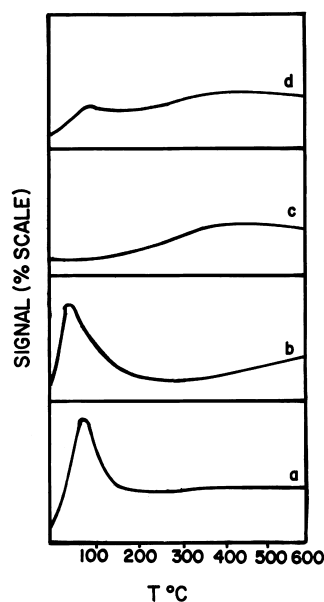

Fig. 1. TPD profiles of bimetallic catalysts: (a) reference; (b) R1, Au 0.02 wt.%; (c) R3, Au 0.18 wt.%; (d) R4, Au 0.35 wt.%.

both metals, forming a superficial alloy, however, no additional experiments were performed to verify alloy equilibrium. On the other hand, the nominal compositions of the bimetallic catalysts R3 and R4 are in the miscibility gap of the Pt–Au phase diagram [9], at reduction temperature and test reaction temperature (773 and 623 K). This means that if alloys were to be formed, these would correspond, one to an Au-rich phase and the other to the Pt-rich. As it is known, the Au-rich phase tends to cover the Pt-rich phase, according to the Cherry Model [10]. In both cases a decrease of the surface platinum sites is expected, and therefore, a decrease in hydrogen adsorption capacity, as in our catalysts.

4. Methylcyclopentane reaction

The specific rate for methylcyclopentane reaction varied, depending on the amount of gold (Table 2). Furthermore, the distribution of the products shows more dramatic changes. It has been claimed [11] that, on small Pt particles, MCP reaction occurs non-selectively leading to about 40% n-hexane (nH), 40% 2-methylpentane (2-MP), and 20% 3-methylpentane (3-MP), which corresponds to statistical ring opening. In contrast, on very large Pt particles, the branched hexanes 2-MP and 3-MP are formed almost selectively. In addition to these 'classical' products, we have obtained benzene (Bz) and, identified by mass spectroscopy (JEOL JMS AX505WA), 1-methylcyclopentene and 4-methylcyclopentene due to MCP dehydrogenation. We can observe that in those bimetallic catalysts with the highest amounts of gold, in which the specific rates are smaller, we obtain the higher selectivity to benzene. If we suppose that the platinum surface sites

are surrounded by gold atoms, we have in these catalysts single sites of platinum in which it is possible the enlargement of MCP ring. The presence of platinum sites isolated by gold atoms has been studied in alloys prepared with a compositions close to 90 at.% of gold [12]. It is noticeable in such study, the formation of methylcyclopentene or methylcyclopentadiene products in methylcyclopentane reaction tested on Pt–Au catalysts obtained from another preparation methods. So our results show relation with those obtained previously by other authors, which form intentionally Pt–Au alloys with a great amount of gold in order to isolate the platinum atoms.

The catalysts were deactivated during the catalytic runs. The catalysts showing the highest initial activities were deactivated more drastically. As the amount of gold was increased, the catalysts became relatively more stable, although the initial activities were lower (Fig. 2). On these catalysts the methylcyclopentene isomers were the main products.

A significant factor in this study is that self-poisoning can occur due to the accumulation of carbonaceous residues on the catalyst. Moreover it has been reported [13] that the methylcyclopentane molecule is very active for the formation of coke This process, which is described as polymerization of dienic compounds derived from methylcyclopentenes, plausibly involves a group of several atoms [14]. If this is true, it should decrease with alloying or formation of bimetallic sites. This, indeed, is the case, and we have already reported this effect on coke and sulfur deposition over the deactivation [15].

4.1. Oxidation/reduction treatment effect

We have omitted any oxidation treatment in air flow at high temperature, after the preparation of the

Table 2
Results of methylcyclopentane reaction

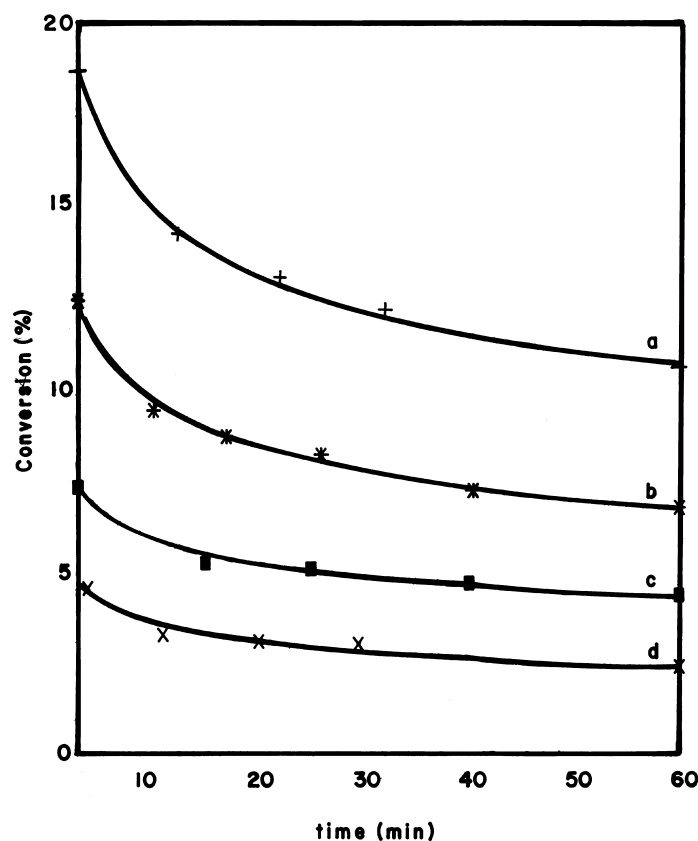| Catalyst	r_A mol g^{-1} s^{-1} (10^6)	Products distribution (mol%)				
		2-Methylpentane	3-Methylpentane	n-Hexane	Methylcyclopentenes	Benzene
Reference	3.11	53.97	24.94	12.52	7.60	0.97
R1	2.66	53.11	24.73	11.97	9.55	0.63
R2	0.25	47.93	15.13	4.81	32.36	0.0
R3	0.14	18.39	7.60	1.78	62.88	9.35
R4	0.16	8.00	2.92	0.0	82.43	6.65

Fig. 2. Conversion vs. time curves, in the methylcyclopentane reaction at 350°C: (a) reference catalyst; (b) R1; (c) R2; (d) R4.

bimetallic catalysts because the structure of the mentioned bimetallic sites created by the redox reactions could be modified by a temperature treatment in presence of oxidant atmosphere.

Nevertheless, our catalysts suffer an effect that alters their catalytic behavior. This effect results in increased activity and different product distribution for

the methylcyclopentane reaction as shown in Table 3, for catalysts with the highest contents of gold. These results were obtained under similar conditions to those mentioned above for the fresh catalyst samples, but such experiments were carried out after a period of nearly 6 months from the preparation date. The catalysts were stored in bottles during this time; so,

Table 3
Results of methylcyclopentane reaction for the stored catalysts

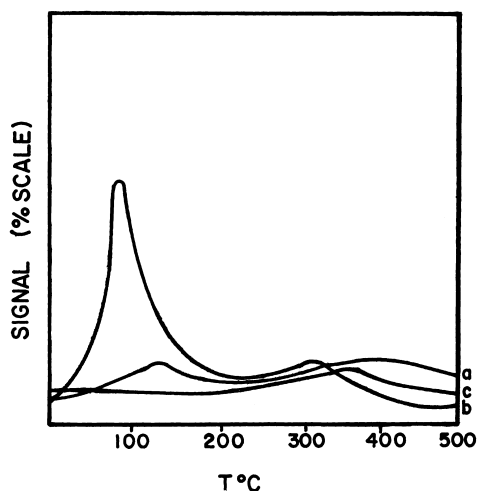| Catalyst	r_A mol g^{-1} s^{-1} (10^6)	Products distribution (mol%)				
		2-Methylpentane	3-Methylpentane	n-Hexane	Methylcyclopentenes	Benzene
Reference	3.45	50.11	21.74	19.98	2.42	5.74
R1	2.70	50.14	24.05	14.91	9.17	1.73
R2	0.57	47.15	17.76	7.30	27.78	0.0
R3	0.86	45.40	20.92	18.15	15.03	0.0
R4	0.46	42.83	20.06	11.45	24.39	1.28

Fig. 3. TPD profiles of the bimetallic catalysts: (a) R4 fresh; (b) R4 stored; (c) R4II fresh.

these samples were changed in air and atmospheric temperature.

Fig. 3 compares the TPD profiles of the freshly prepared and the stored R4 samples. The adsorption peak at about 90°C increased drastically in the saved R4 sample. In other words, the number of exposed platinum atoms has increased. In order to understand this phenomena, the preparation of one sample, similar to R4 catalyst, named R4II was repeated. In Fig. 3, we compare the TPD hydrogen profile of this new fresh catalyst, with those corresponding to the fresh and stored R4 samples. For this new sample the hydrogen desorption peak at 90°C is not observed as in the fresh R4 sample. Their catalytic behavior seems to the fresh R4 catalyst (Table 4).

Moreover, we carried out one oxidation/reduction treatment over the R4II fresh catalyst. This treatment consisted of oxidation in flowing air at 723 K for 10 h, and reduction in flowing hydrogen at 773 K for 6 h. The catalytic properties of this sample were similar to those shown by the stored R4 sample (Table 4). We

have also measured the corresponding X-ray diffraction patterns.

4.2. X-ray diffractograms

The X-ray diffraction patterns of the various samples showed broad peaks of typical γ-Al_2O_3 and small peaks due to the presence of supported metal. Fig. 4 compares the X-ray diffraction patterns of the carrier, the mono- and bimetallic catalysts in the 2θ interval 45.0–47.5°. The first peak at $2\theta = 45.8°$, used as reference, is an alumina peak, the second one ($d = 1.96\,\text{Å}$) is the (2 0 0) peak of Pt in the Pt/Al_2O_3 sample (reference catalyst), corresponding to the platinum cell parameter (3.92 Å).

The maximum of the metal peaks of the fresh and stored PtAu/Al_2O_3 (R4 catalyst) were also located at $2\theta = 46.8°$ ($d = 1.96\,\text{Å}$). Therefore the cell parameters were also 3.92 Å. This result indicates that the metal particles of the Pt–Au catalyst are constituted by metallic platinum and, hence, Pt–Au alloys are not present, since the peak for the alloy would be shifted towards small angles (following Vegard's law).

However, if the shape of the metal diffraction peaks corresponding to R4 fresh and stored or R4II stabilized by the oxidation treatment is compared (Fig. 5), it is found that the peaks for the stored and stabilized samples are more symmetrical, whereas the diffraction peak of the fresh catalyst is not symmetric, i.e. broader towards small angles. The asymmetric peak can be interpreted as resulting from strain between crystallographic planes (2 0 0), or as the convolution of small peaks shifted to smaller angles, as a result of the presence of particles whose composition is bimetallic. The last hypothesis is not probable due to the preparation method, hence it is concluded that the asymmetry of the fresh catalyst peak, is a result from strains between planes; and after the storing or oxidation/reduction treatment these strains present in the metallic particles disappear.

Table 4
Results of methylcyclopentane reaction for the R4II sample, fresh and treated by oxidation/reduction cycle

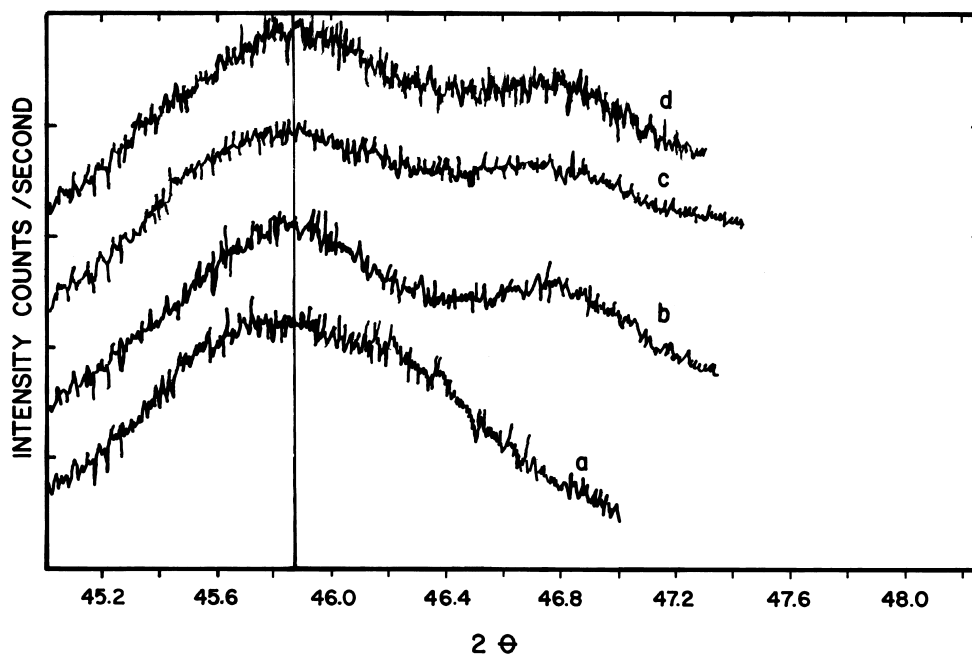| Catalyst	r_A mol g^{-1} s^{-1} (10^6)	2-Methylpentane	3-Methylpentane	n-Hexane	Methylcyclopentenes	Benzene
Fresh	0.10	0.00	0.0	11.95	80.06	7.99
Treated	1.14	42.90	19.93	13.68	23.50	0.00

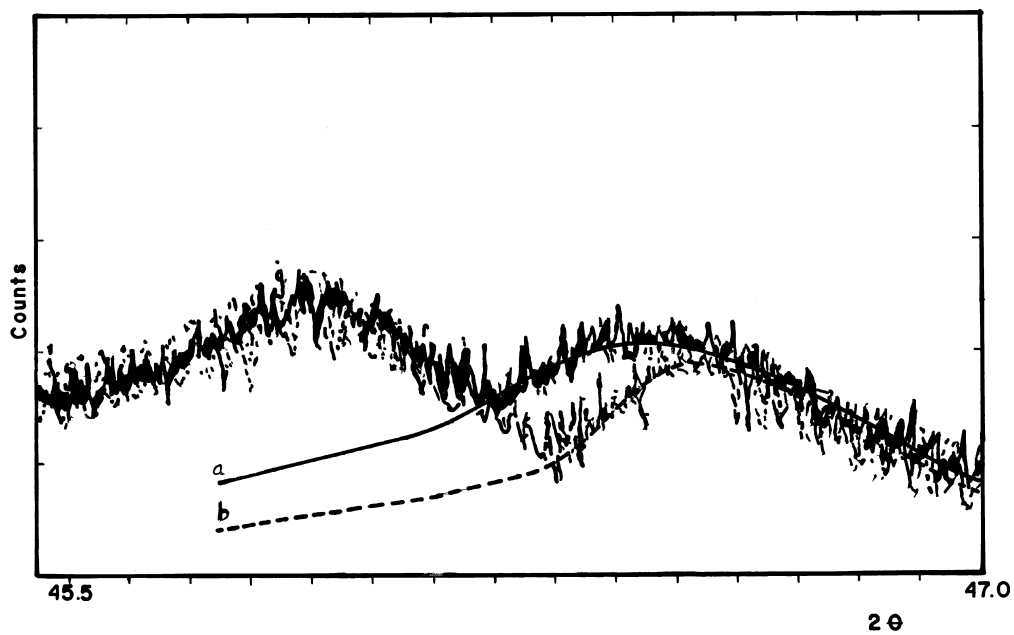Fig. 4. XRD patterns of the samples: (a) γ-alumina; (b) reference; (c) R4 fresh; (d) R4 stored.

Fig. 5. Comparison between the XRD patterns of (a) R4 fresh; (b) R4 stored.

4.3. Microscopy results

From bright field images and selected area electron diffraction patterns, the particle dispersion and structural information were derived. Particle sizes found runs from 3.5 up to 20.6 nm but small particles (less than 8 nm) were the most frequent.

Lattice interplanar distances were derived from diffraction patterns corresponding to metallic platinum and gold. Lattice interplanar distances corresponding to Pt–Au alloy or to any metallic oxide were not found. From HREM images, dispersed platinum and gold particles were found over the alumina support and in very few cases cluster or aggregates were observed. Fig. 6 comes from sample R1 and corresponds to a HREM image where atomic resolution of Au and Pt is observed.

Fig. 7 comes from a different zone of the same sample with a low number of supported particles. An Au particle with hexagonal profile, arrowhead, is presented with a higher magnification in the inset at the right upper corner; in this image two details are clear. In the upper left side of the particle a loss of flatness can be observed and in the lower right side of the particle, a line of atomic columns with different contrast can be observed. The distance between atomic columns is very close to 0.224 nm and suggests the presence of an oxide layer on some specific place of the particle surface. These facts might be a consequence of support metal interactions.

In Fig. 8, a very high magnification image of a cluster with three particles showing lattice and atomic resolution is presented; the particle at the right side corresponds to a gold particle with hexagonal profile and it shows some kind of erosion. In the other two apparently coalesced particles, structural defects with multiple twinning can be detected. From the image presented in Fig. 8, the irregularities on particle borders suggest again the interaction of particles with the Al_2O_3 support.

In previous studies [16], the $PtAu/Al_2O_3$ system has been shown to segregate or rearrange the components in contrast to the same system supported over silica. This phenomenon could be attributed to the higher interaction between the metals with the oxygen basic sites of the alumina, compared to the interaction between both metals.
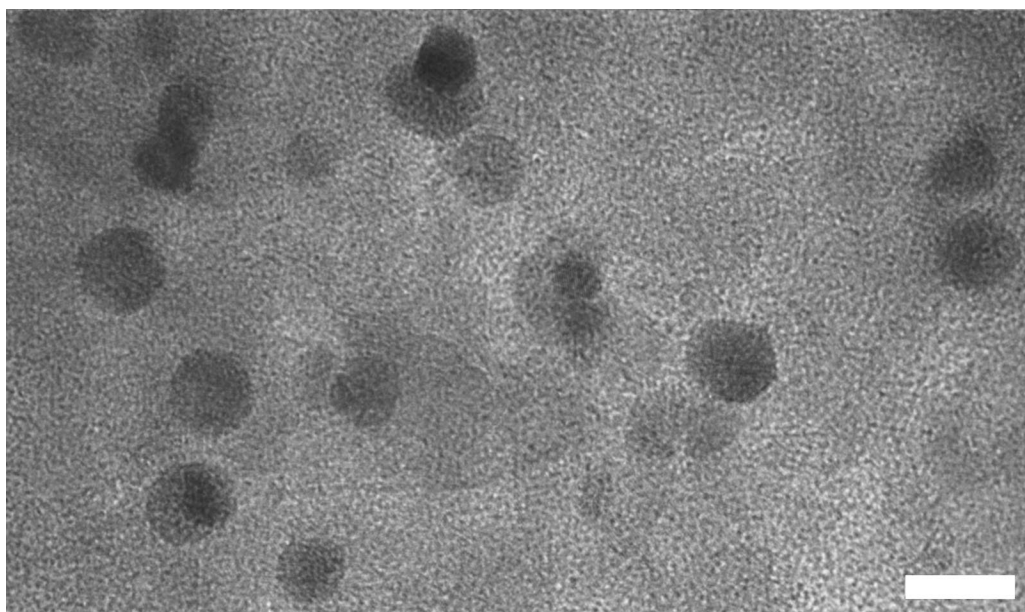

Fig. 6. Platinum and gold particles showing lattice and atomic resolution. The bar means 11.5 nm.
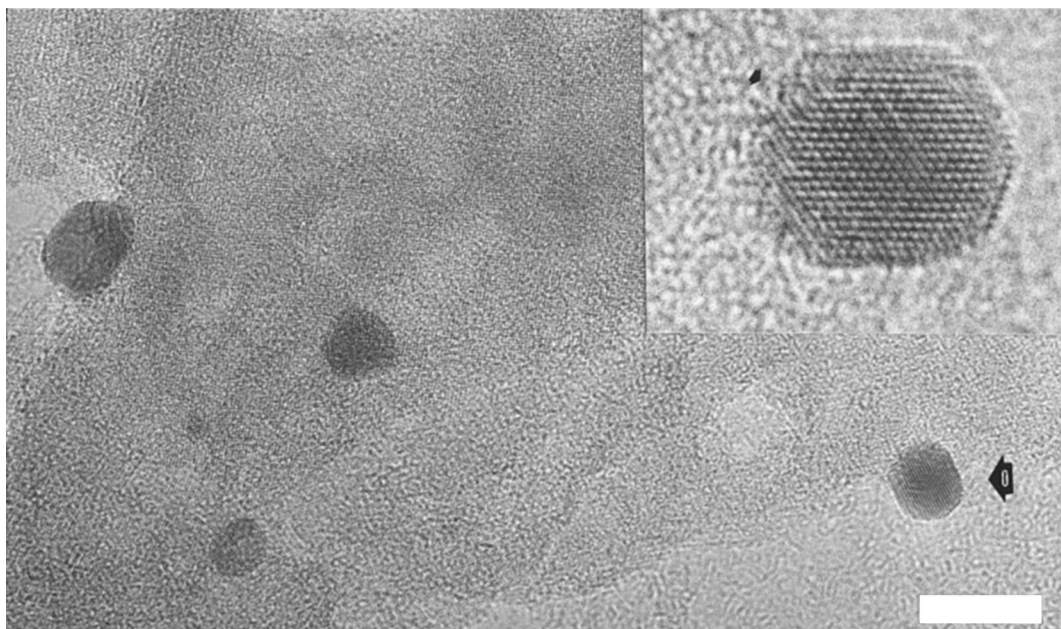
Fig. 7. R2 sample showing particles dispersion. The arrowed particle is presented in the inset; eroded borders and a border with different contrast can be observed. The bar means 8.72 nm.
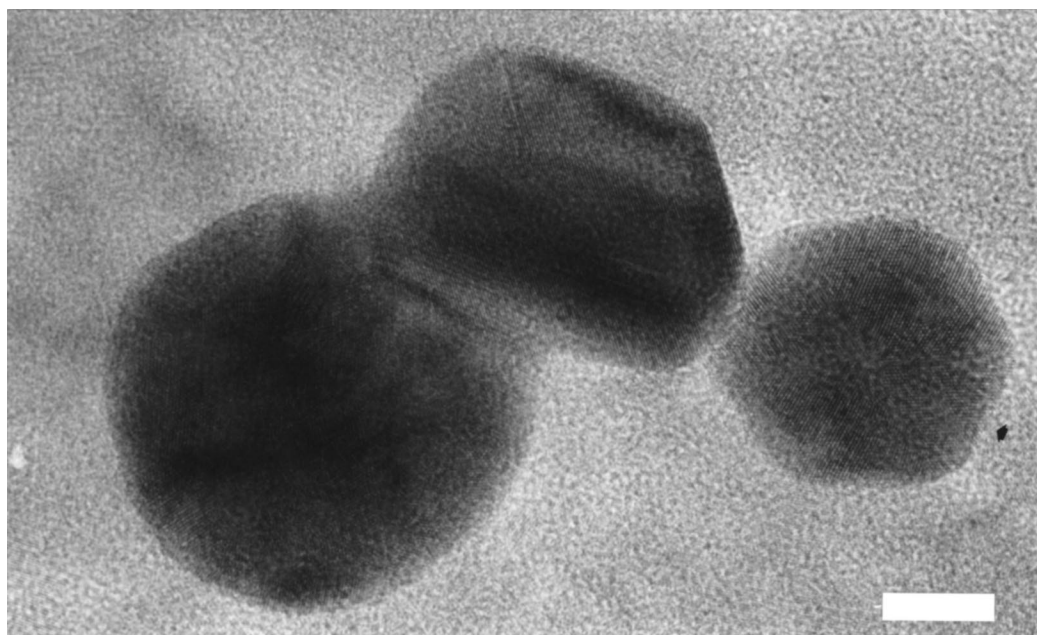

Fig. 8. Particles presenting lattice and atomic resolution are observed. In the right side in the hexagonal gold particle, an eroded border can be noticed. The bar means 79.7 nm.

The equilibrium of the components in alloys and the effect of gaseous atmosphere over surface composition have been discussed [17]. In this work, our purpose is to elucidate the role of the preparation method on the surface configuration of the Pt–Au bimetallic system and we have employed a surface redox reaction to do it. However, the ambient conditions may modify the surface interactions between platinum and gold at least in the catalysts with the highest contents of gold.

5. Conclusions

The results show that supported fresh metal particles constituted by platinum and gold in close interaction, are obtained by the redox interaction.

The platinum catalytic behavior is modified such that the olefin formation in methylcyclopentane reaction is increased with the content of gold.

After storing under ambient conditions or stabilizing by oxidation treatment, the platinum–gold interaction is modified, increasing the catalytic activity and producing the typical selectivity attributed to platinum in methylcyclopentane reaction.

The XRD patterns indicate that bimetallic particles reach a more stable structure after the stabilization.

The microscopy images suggest interaction of metal particles with the alumina, which could be responsible for the rearrangement effect.

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