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Preparation, characterization and catalytic activity of gold-based nanoparticles on HY zeolites

G. Riahi [a], D. Guillemot [a], M. Polisset-Thfoin [a], A.A. Khodadadi [b], J. Fraissard [a,*]

[a] *SIEN-FRE 2312, Chimie des Surfaces, Université Paris VI, 4 place Jussieu, 75252 Paris Cedex 05, France*
[b] *Department of Chemical Engineering, Faculty of Engineering, University of Teheran, Teheran, Iran*

Abstract

An original method is used to obtain stable nanoparticles of gold-based mono- and bimetallic systems supported on an acidic zeolite. This approach has been applied to Au/Y, and to bimetallic Pd–Au/Y and Pt–Au/Y systems containing between 1 and 3% of metal.

Metal clusters of gold or alloy are formed inside the supercages of the zeolite framework by the thermal reduction of cations by the ligands (en = $H_2N–CH_2–CH_2–NH_2$) under inert gas flow at a temperature depending on the metal.

The use of acidic zeolites favours the dispersion of the metal and the thermal stability of the particles. This stability is explained by chemical anchoring of metal clusters by the Brønsted sites of the support.

The different mono- and bimetallic catalysts tested on the methylcyclopentane hydroconversion reaction reveal that the addition of gold to the metal (platinum or palladium) leads to an increase in the activity and an improvement in the selectivity for isomerization of the skeleton (cyclohexane and benzene) to the detriment of hydrogenolysis. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Gold-based nanoparticles; Zeolite; Mixed metal catalysts

1. Introduction

For a long time gold was not being employed industrially because it was perceived to have poor catalytic properties, resulting from an inability to chemisorb molecules such as dioxygen and dihydrogen at ambient temperature. To the inertness of gold was added the absence of techniques for the dispersion of the metal comparable to those which exist for other metals traditionally used for heterogeneous catalysis. The work of Haruta [1] shows that a strong interaction between the support and the gold particles is necessary to avoid their coalescence.

A known means for dispersing and stabilizing metal particles is to use zeolites. While Au^{3+} is a metal cation which is very easy to reduce, gold is certainly the most difficult metal to disperse and to anchor in zeolites, because the steric constraint is insufficient [2]. For this reason we have chosen to employ acid faujasites (denoted HY) in the work reported here in order to increase the stability of the metallic particles by interaction with the acidic sites of the zeolite.

The interest in supported bimetallic catalysts in heterogeneous catalysis has been very adequately demonstrated. The addition of a second metal can favour the reduction of the first [3,4], increase the dispersion of a metal which has a tendency to form large particles [5] or decrease its fritting [6]. Sometimes the second metal allows an improvement in the resistance to poisoning by coke, by sulphur and nitrogen compounds,

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[*] Corresponding author. Tel.: +33-1-44-27-60-13;
fax: +33-1-44-27-55-36.
E-mail address: jfr@ccr.jussieu.fr (J. Fraissard).

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by metals such as Pb or V, etc. [7]. The presence of this other metal can also modify the selectivity for a reaction or increase the activity of the first [7,8]. A well known example is that of the Pd–Au system used for the reaction of H_2 and O_2 where the addition of gold to the palladium increases the reaction rate by a factor of 50 [9].

In general, gold has a tendency to reduce hydrogenolysis reactions catalysed by group 10 metals in favour of dehydrogenation and isomerization [10–12]. This behaviour can be exploited in the catalytic processes of reforming and hydrocracking [13]. We report here a new method for the synthesis of gold and bimetallic Pd–Au and Pt–Au nanoparticles on acidic Y zeolite, some characterizations and a catalysis test. It should be recalled that all previous attempts to stabilize gold particles in zeolites had failed.

2. Experimental

Samples were prepared with 1% of gold by weight of the anhydrous sample and for the bimetallic samples with a constant amount, 3% of palladium and 1% of platinum, to which is added the amount of gold required to give Pt/Au and Pd/Au molar ratios of 20, 40, 60 and 80%. The support is a $Na_{0.1}H_{0.9}Y$ zeolite (denoted HY) obtained by calcining an industrial zeolite NH_4Y (Union Carbide) at 300 °C for 48 h.

Two methods for preparing the catalysts were compared. The first route (route 1) involves introducing the metal by cation exchange and reducing the two cations $[Pt(en)]^{2+}$ or $[Pd(en)]^{2+}$ and $[Au(en)_2]^{3+}$ complexed with ethylenediamine (en $= H_2N–CH_2–CH_2–NH_2$) simultaneously. The platinum and/or palladium chloride complexes $[Pt(en)]Cl_2$ and $[Pd(en)]Cl_2$ are commercial products (Aldrich Chemicals) and the gold chloride complex $[Au(en)_2]Cl_3$ was synthesized in the laboratory by the method of Block and Bailar [14]. The cations are autoreduced in a stream of inert gas (helium or argon, 1.5 l/h); after a slow increase in temperature (24 °C/h) they are held for 1 h at 150 °C for monometallic gold, at 250 °C for the bimetallic Pd–Au and at 300 °C for the platinum-based samples.

The second method (route 2) includes several stages. The $[Pt(en)]^{2+}$ or $[Pt(NH_3)_4]^{2+}$, $Pd(en)]^{2+}$ or $Pd(NH_3)_4]^{2+}$ cations are introduced first. They are decomplexed by heating at 300 °C in dioxygen (6 l/h). The $[Au(en)_2]^{3+}$ cation is then introduced by exchange and all the cations are then reduced by the ethylenediamine ligands of the $[Au(en)_2]^{3+}$ cation in an inert atmosphere at 250 °C (Pd–Au) or 300 °C (Pt–Au).

Study of the autoreduced samples by ^{129}Xe NMR (Bruker MSL-400 spectrometer, frequency 110.6 MHz) shows that the “en” ligands or their residues remain at the surface of the metallic particles after reduction [15]. Consequently, all the metallic samples, whatever the synthesis procedure, were treated in a stream of dioxygen (6 l/h) at 300 °C for 48 h in order to eliminate these organic compounds. The metals are then retreated in a stream of dihydrogen for 1 h (1.5 l/h) at the same temperature.

Temperature-programmed reduction (TPR) studies were performed with a Thermoquest TPDRO 1000 apparatus operating in the automatic mode with Noxal (Ar/H_2 mixture with 5% of H_2). The surface accessible to the reactants was estimated from the metal dispersion and the particle size. The dispersion is determined by dihydrogen chemisorption at ambient temperature (26.5 °C) from two successive isotherms and calculated from the difference between the amounts of dihydrogen adsorbed in these two isotherms, extrapolated to zero pressure. The particle size was determined from the histograms drawn by counting the particles on electron microscopic photos of microtomed samples obtained with a JEOL JEM 100 CXII microscope (3 Å resolution).

The mono- and bimetallic catalysts were tested in the hydroconversion reaction of methylcyclopentane. Reactivity experiments were performed at atmospheric pressure, between 250 and 350 °C, with 150 mg of catalyst in the presence of a 16/1 H_2/methylcyclopentane gas mixture.

3. Results and discussion

3.1. Characterization

Recently published studies [16,17] show that by heating it is possible to reduce cations such as Pt, Pd or Au by their ethylenediamine ligands in monometallic systems of nanometric size supported on zeolites. This method of reduction has now been successfully applied to bimetallic Pt–Au and Pd–Au systems. In

Table 1
Diameters ($d_{\mathrm{TEM}} \pm 0.3\,\mathrm{nm}$) of metallic particles determined by electron microscopy for monometallic and bimetallic samples on HY zeolite[a]

Samples	Au	Pd	Pt	Pd–Au		Pt–Au	
				80/20	60/40	80/20	60/40
Just reduced	3.4	1.9	1.6	2.6	2.7	2.9	3.3
Treated in O_2	3.9	1.8	1.6	2.6	2.7	3.2	2.5

[a] “Just reduced” samples were not thermally treated after reduction and samples “treated in O_2” were treated at 573 K after reduction.

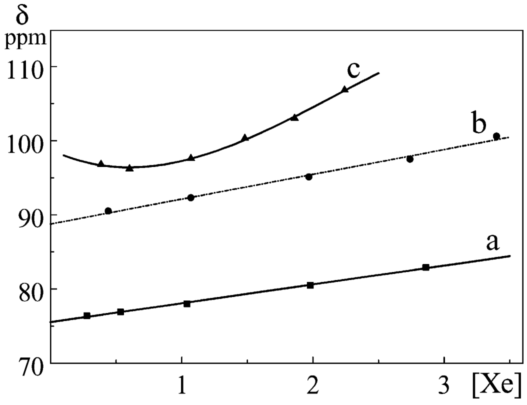

Fig. 1. Chemical shift δ of xenon against the number of Xe atoms per gram of zeolite ($\times 10^{-20}$). Samples: (a) HY without metal, (b) Au/HY (just reduced) and (c) Au/HY (after calcination and second reduction).

these cases, it is observed that the gold facilitates the reduction of the other metal, which is more difficult to reduce than gold. It can, therefore, be assumed that there is an interaction between the two metals at the moment of their reduction, as a consequence of the formation of mixed particles [18]. Comparison of the results of electron microscopy shows the usefulness of the acidic support. If a non-acidic zeolite (NaY) is used as support, the particles are never smaller than 10 nm in the case of gold and 5 nm in the case of palladium. If the zeolite is acidic (HY), the mean particle size remains always less than 4 nm even after several hours of thermal treatment at 300 °C in dihydrogen or dioxygen (Table 1). The complexed ions can only be located in the supercages since, in view of their size, they cannot enter the other cages (β cages and hexagonal prisms) which are smaller. Since the particle size is not affected by the method of preparation (simultaneous or successive exchange and reduction), it seems likely that the decomplexed ions are located, as are the complexes, in the supercages, since a more random distribution would lead to the formation of smaller particles due to strong environmental constraint. Thus, when they are reduced in an inert atmosphere, all the cationic species involved in the formation of metallic particles are in the same cavities. The result is that the particles formed stay in the supercages, as is shown by the NMR spectra of adsorbed xenon. Curve c in Fig. 1 (for the Pd–Au catalyst free of organic residues) has the characteristic shape of a sample with strong adsorption sites. These sites are those of the metal situated inside the supercages, the only cavities accessible to xenon. These sites cannot be observed on a sample which has been reduced but not calcined, where the organic residues remain adsorbed on the metal, as is shown by curve b whose shape is similar to that of the zeolite without metal (curve a). The chemical shift (88 ppm at zero xenon pressure) and the slope of the straight line “b” ($\delta = f[\mathrm{Xe}]$) are greater than those of line “a” because of crowding of the supercages. That the particles are exclusively in the supercages does not seem to hold true after reoxidation. If the TPR profiles of Pt–Au samples simply exchanged and reoxidized after reduction are compared, a new reduction peak at about 370 °C is seen for the reoxidized sample (Fig. 2), corresponding to a different location of certain particles. When a metal is oxidized, the size of the unit cell increases [19] which must lead to an increase in the particle size. It is well known that metallic particles

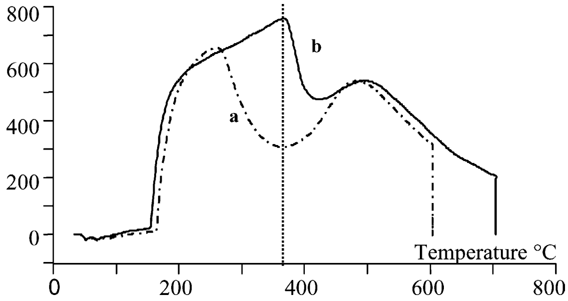

Fig. 2. TPR profiles of samples of gold on HY zeolite. (a) First TPR* performed by reduction of $[\mathrm{Au(en)_2}]^{3+}$ cations. (b) Second TPR* performed on the sample used for the first TPR and reoxidized TPR* are performed in a stream of Noxal, a mixture of dihydrogen (5%) and argon.

greater than the cage dimensions can remain in the zeolite lattice by dilating the cages or even by breaking the walls and/or the windows [20]. A particle can then "overflow" from its supercage and partly enter an adjacent cage. During a TPR performed on the oxidized sample these parts of such particles become less readily accessible, whence the need for a greater energy for their reduction, which explains this extra signal.

The small size of the gold particles and the stability of all the nanoparticles is explained by the anchoring of the metal on the Brønsted acid sites of the support. Metal–support interaction by the intermediary of proton bridges (O···H···M_n bonds) has been demonstrated by diffuse reflectance IR spectroscopy. The characterization of CO adsorbed on a monometallic Au–HY sample (Fig. 3) shows that the metal is mainly in the form of electron-deficient particles (denoted $Au_n^{\sigma+}$) and, to a lesser extent, in the form of neutral particles and oxidized species [15]. The presence of electron-deficient gold particles results from their contact with the protons of the zeolite (for the HY zeolite there are 5 H^+ per supercage, i.e. 40 H^+ per gold atom), which confirms that the latter are the cause of the anchoring of the metal in the cavities.

In contrast to the results reported by certain other authors [21], we observe that the particle size does not increase with the gold content. The preparative methods (1 and 2), which differ in the nature of the complex (of platinum or of palladium) and the order of introduction of the metals, have little effect upon the particle size. The mean diameters of the bimetallic particles lie between those of monometallic platinum or palladium and gold. If the two metals were totally segregated, particle formation should follow the same process as for the preparation of monometallic particles and the particle size should vary linearly between those of the two monometallic samples (dotted or dashed curve in Fig. 4). This was not observed, either for the platinum–gold system or for palladium–gold, for which there is a maximum size for a gold content of about 20% (full curves in Fig. 4). Since the apparent anomaly in the variation of the particle sizes for the bimetallic samples is not related to the increase in the metal loading or to a segregation of the two metals, one can here again suggest that mixed particles are formed.

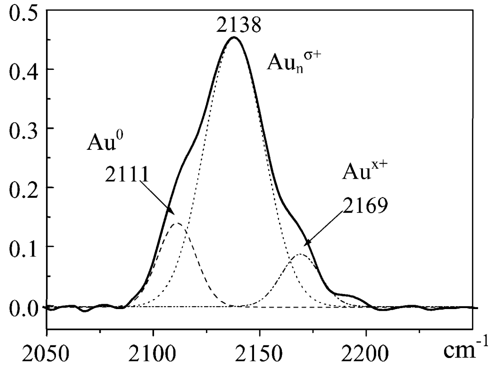

Fig. 3. IR diffuse reflection absorption spectra of CO adsorbed on a sample of HY zeolite-supported gold. Ambient temperature, equilibrium pressure of CO: 6.7 × 10^3 Pa. Dashed lines: mathematical decomposition of the full spectrum.

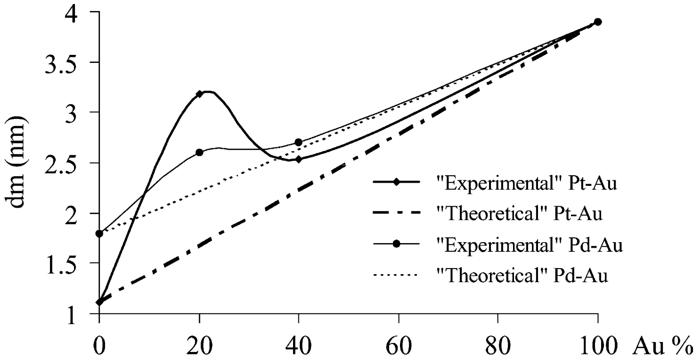

Fig. 4. Evolution of particle size of bimetallic. Pt–Au/HY and Pd–Au/HY samples, depending on the gold content. The dotted and dashed curves are the "theoretical" evolution curves assuming total segregation of the two metals and identical dispersion in the mono- and bimetallic samples.

The chemisorption of small gaseous molecules, such as H_2, O_2 or CO, on bimetallic systems is a simple but efficient method for demonstrating the formation of mixed particles when one of the two metals is incapable of dissociating and/or bonding the gaseous molecule in question. When the metals are totally segregated, the variation of the concentration of the metal which cannot chemisorb the molecule does not modify the total chemisorption capacity of the sample, if the particle size remains the same.

For the same quantity of platinum or palladium, the larger particles of the bimetallic samples should adsorb less dihydrogen. In fact, the relative amounts of dihydrogen adsorbed on the bimetallic samples (reduced to values taking into account the particle size and a random distribution of the two atoms types on the surface) are, except for the $Pt_{80}Au_{20}$ sample, equal to or greater than those for the monometallic samples (Table 2). This result is surprising, since it means that the addition of gold, a metal which is reputed to be incapable of dissociating dihydrogen at ambient temperature, increases the chemisorption capacity of the other metal, and that this effect increases with the amount of gold.

There are two possible explanations, both involving bimetallic particles:

- The formation of mixed particles following a model where the gold is partially covered by the other metal. The increase in the relative amount of dihydrogen chemisorbed would then be related to the increase in the number of atoms of the other metal exposed.
- The phenomenon of migration of dihydrogen dissociated on the platinum or palladium atoms towards the neighbouring gold atoms ("spillover"). This assumes also that there are two types of atoms at the surface of the particles and, therefore, that the particles are mixed.

However, this second idea is unlikely, since a stable form of Au–H association only exists at very low temperature. The first explanation is supported by some UV spectroscopic experiments on the platinum system. These analyses show that there is little difference between the spectra for supported platinum and a bimetallic Pt–Au sample with 20% of gold.

Table 2
Comparison of the dispersion of palladium and/or platinum in metallic catalysts determined by dihydrogen chemisorption at 26.5 °C and by electron microscopy

Catalysts	MET, d_{MET} (nm)	Hydrogen chemisorption, exposed Pt or Pd (%)
Pd/HY	1.9	20
$Pd_{80}Au_{20}$/HY	2.6	22
$Pd_{60}Au_{40}$/HY	2.7	38
Pt/HY	1.6	20
$Pt_{80}Au_{20}$/HY	3.2	16
$Pt_{60}Au_{40}$/HY	2.5	28
Au/HY	3.9	–

3.2. Catalytic activity

The hydroconversion of methylcyclopentane was performed with different mono- and bimetallic catalysts. Gold is practically inactive in this transformation, in contrast to platinum and palladium whose activity rises markedly with the temperature up to 300 °C and much less thereafter. For this reason most reactions were studied between 300 and 315 °C. The addition of gold to Pt or Pd has a spectacular effect on their activity, which becomes greater than that of the pure metal, provided this remains the major component. Moreover, this activity goes through a maximum, as noted by other authors [9,12,13,22,23], for both platinum and palladium with a gold content of about 20% (Table 3), for which the particle size is the greatest. Such an effect of gold on an active metal (palladium) has been patented in the field of catalytic reforming and hydrocracking [24].

As for the selectivity, the proportion of products resulting from ring expansion (RE, cyclohexane and benzene) increases with the Au/M ratio whereas that of cracking products ($C_{1\to5}$ hydrocarbons) decreases. The results are presented in Fig. 5. Moreover, with the improvement in the selectivity for ring expansion products, there is also an increase in the selectivity for

Table 3
Degree of methylcyclopentane conversion at 300 °C after 15 min reaction for different catalysts supported on HY

	Catalysts					
	Pd	$Pd_{80}Au_{20}$	$Pd_{60}Au_{40}$	Pt	$Pt_{80}Au_{20}$	$Pt_{60}Au_{40}$
Conversion (%)	4.4	22.4	14.1	5.6	12.4	11.4

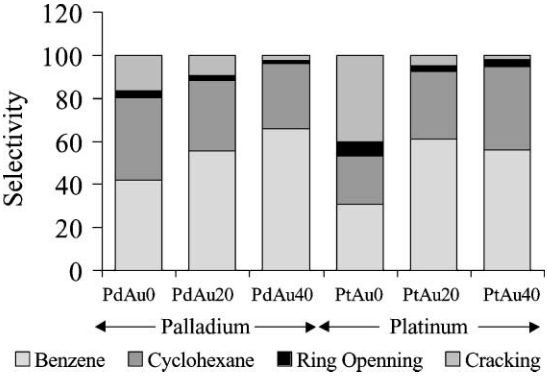

Fig. 5. Comparison of mono- and bimetallic catalyst selectivity in the hydroconversion of methylcyclopentane, at a conversion of about 10%, at 300 °C.

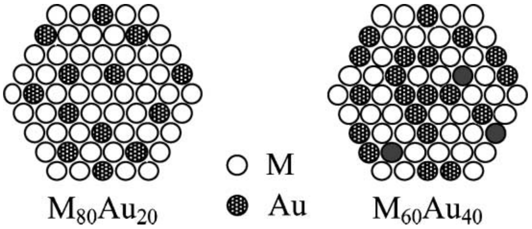

Fig. 6. Proposed model for mixed particles (M = Pt or Pd).

benzene with respect to cyclohexane, at least up to a gold content of 20% (Fig. 5). Ring-opening reactions (leading to three hexane isomers depending on where the C–C bond is broken) are always unimportant and the presence of gold never favours them.

The catalysts studied here can be considered as bifunctional in that there are both protons and metal on the support [25,26], since the chosen reaction implies steps catalysed by both metallic and acidic sites. The reaction leading mainly to ring expansion, by the formation of a 6-carbon ring desorbed from the catalyst either as cyclohexane or as benzene, is bifunctional. The idea that only metals can catalyse ring expansion by a sequence of ring-opening and ring closure has been rejected by some authors [27] who have shown that benzene and cyclohexane are not formed with Pd/NaY and Pt/NaY catalysts. Sachtler and Stakheev [28] and Mills et al. [29] observed that the initial rate of RE reaction is 20 times greater on the Pd/HY catalyst than on a mechanical mixture of Pd/NaY and HY. They propose a reaction mechanism implying a model where the acidic and metallic sites are close to each other or bonded, which avoids the migration of the molecule from the metallic site to the acidic site and vice versa. Since there are two indications that particles are formed in interaction with the protons of the HY zeolite (anchoring of the particles and reduction of the chemisorption capacity) this model of bifunctional sites can be used to explain the conversion of methylcyclopentane. The presence of increasing amounts of gold favours the RE reactions at the expense of hydrogenolysis which requires the breaking of a C–C bond on the metallic sites. This occurs if:

- enough metal atoms are close to each other to achieve dissociative adsorption and to constitute a reserve of hydrogen atoms;
- the metal–carbon bond is strong enough to make the reaction thermodynamically possible and avoid migration towards the acidic sites.

In the case of mixed particles these two conditions are not satisfied, since the presence of gold at the surface of the particles reduces the number of groups of palladium or platinum atoms. Ring expansion reactions, which occur at the acidic sites, are therefore favoured. The increase in the amount of benzene relative to cyclohexane when the Au/M ratio is increased can be attributed to the remarkable dehydrogenating power of gold, which has been known for a long time [30,31].

From the results obtained by the various physicochemical techniques, and by the conversion of methylcyclopentane, we can propose a structure for the M–Au particles which underlines:

- formation of mixed particles by autoreduction of the two precursors,
- the simultaneous increase in the fraction of palladium or platinum exposed and of the number of these atoms surrounded by gold at the surface as the Au/M ratio increases (Fig. 6).

4. Conclusion

The characterization by electron microscopy, dihydrogen chemisorption, ^{129}Xe NMR, EXAFS [16] and a catalysis test of bimetallic systems based on palladium or platinum and gold supported on an HY zeolite, obtained by autoreduction of the exchanged precursors, shows that bimetallic particles are formed inside the zeolite supercages, and that they are anchored on the acidic sites of the support.

Characterization of the surface of the particles by dihydrogen chemisorption and methylcyclopentane conversion shows that atoms of palladium or platinum and gold are side by side. Dihydrogen chemisorption confirms that the fraction of palladium or platinum exposed increases with the gold content, whereas the selectivity of the test reaction tends to prove that the number of gold atoms around the other metal is greater. A mixed particle model accounts for the various results.

Acknowledgements

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