Hydrogenation of Tetralin in the Presence of Sulfur over γ-Al$_2$O$_3$-Supported Pt, Pd, and Pd–Pt Model Catalysts

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γ-**Al$_2$O$_3$-supported Pd, Pt, and bimetallic Pd–Pt catalysts have been produced by laser vaporization of the respective bulk metals and alloys. Transmission electron microscopy and energy-dispersive X-ray analysis experiments show that these bimetallic clusters have a perfectly well defined stoichioemetry. Moreover, pure or bimetallic clusters have similar size distributions. One has taken benefit of these features to study in detail the resistance to sulfur poisoning as a function of the composition and to verify to what extent what is claimed in the literature, i.e., an improved resistance to sulfur poisoning of Pd–Pt catalysts as compared to pure metals, is verified. The catalytic properties of Pd, Pt, Pd$_{17}$Pt$_{83}$, and Pd$_{65}$Pt$_{35}$ in the hydrogenation of tetralin in the presence of varied amounts of H$_2$S have been compared. Contrary to what is claimed, the coexistence of Pd with Pt in the same particle has no influence on the hydrogenation activity nor on the sulfur tolerance of the catalysts. Hence, it has been shown that Pt has no electronic influence on the reactivity of Pd atoms.** © 2001 Academic Press

Key Words: **bimetallic Pd–Pt; laser vaporization; model catalysts; tetralin hydrogenation; surface segregation.**

INTRODUCTION

The need for relatively low aromatic contents in liquid fuels or solvents is continuously increasing. After a desulfurization and denitrogenation treatment, these products usually still contain relatively high percentages of olefins and monocyclic or polycyclic aromatics, so that further hydrogenation is required to produce acceptable products. Indeed, aromatics in diesel fuel not only generate undesired emissions of particles in exhaust gases but also lower the cetane number. The presence of sulfur compounds in the products to be hydrogenated complicates the process since sulfur constitutes a poison of the metal catalysts used for hydrogenation.

Thus, great efforts have been devoted to develop sulfur tolerant noble metal (generally Pt or Pd) catalysts with a high hydrogenation activity for the two-stage hydrogenation process. The resistance to sulfur poisoning is considered to come from the small bonding energy of the electron-acceptor sulfur atoms with the electron-deficient metal clusters. Modifications of the electron-deficient nature of the metal clusters would be induced by changing the geometry of the particles or the acid–base nature of the support or also by alloying with another metal.

In particular, studies have been focused on the sulfur tolerance of Pd–Pt alloy deposited on various supports such as Al$_2$O$_3$ (1, 2), SiO$_2$–Al$_2$O$_3$ (3–5), Al$_2$O$_3$–B$_2$O$_3$ (6), or HY zeolite (7) and industrial applications for hydrogenating aromatics and olefins in hydrocarbon feedstocks on Pd–Pt alloys were proposed and actually used in plants (8–10).

But the reasons for the high sulfur resistance of Pd–Pt-supported catalysts invoked in the literature are still controversial. On the one hand, Lin *et al.* (11) found that the addition of Pd to the supported Pt catalysts inhibits the agglomeration of Pt particles which could explain in part the better sulfur tolerance of the alloy even if this group has also invoked electronic interactions between Pd and Pt. On the other hand, Yasuda *et al.* (4) claimed that the high sulfur tolerance of the alloys is due to structural and electronic effects rather than maintaining the metal dispersion. Moreover, the situation is not really cleared up by the recent results reported by Fujikawa *et al.* (12) in their study of the hydrogenation aromatics in hydrotreated light oil on Pd–Pt/SiO$_2$–Al$_2$O$_3$ catalysts. Indeed, they demonstrated that the catalytic activity of bimetallic Pd–Pt is significantly enhanced with respect to the monometallic catalysts but also that all of them, pure or alloyed, are similarly affected by the concentration of the sulfur in the feed.

Finally these ill-matched results could be explained by Cooper and Donnis (13), who revealed that the details of the preparation of a Pd–Pt bimetallic catalyst and hence the degree to which Pd and Pt form alloyed clusters together with the size of these clusters strongly influence the activity as well as the sulfur tolerance of these catalysts.

Since the size, the structure, and the composition of supported bimetallic particles are difficult to control for active phases obtained by chemical methods, the comparison of the catalytic properties of a bimetallic catalyst to those of a monometallic one is far from straightforward. To obtain valuable information on the bimetallic interactions, one needs to prepare monometallic and bimetallic systems having approximately the same size, morphology, and overall uniform and well-defined composition. We attempted to prepare such model supported catalysts by using the soft landing deposition clusters over low-acidity γ-Al$_2$O$_3$ and to study their sulfur tolerance and catalytic behavior in the vapor-phase hydrogenation of tetralin in the presence of H$_2$S.

EXPERIMENTAL

Catalysts Preparation by Using Laser Vaporization

The laser vaporization cluster source has been extensively described elsewhere (14). In brief, the second harmonic of a Nd:YAG pulsed laser is used to vaporize the metal from a rod to create a plasma. Cluster nucleation and growth occur when a continuous flux of inert gas (a mixture of He and Ar) is introduced in the chamber. Differential pumping extraction of the clusters through a skimmer yields a cluster beam which carries neutral and ionized species. After removal of the ionized clusters by electrostatic deflection, the neutral ones are deposited on the substrates. Typical deposition rates (equivalent thicknesses) of about 5 nm/min are obtained with neutral clusters. The deposition rates were monitored using a quartz microbalance. In order to deposit the clusters on the support, in the present case of a γ-alumina powder (Condea, Puralox SCFa-240 with a specific surface area of 240 m^2/g), a device has been developed which stirs the powder in front of the cluster beam. After deposition, the samples are air transferred, characterized, and used for catalytic reactions. For these experiments Pd and Pt rods of 99.99% and 99.95% purity respectively as well as Pd$_{17}$Pt$_{83}$ and Pd$_{65}$Pt$_{35}$ bimetallic rods obtained by melting Pd (99.99% purity) and Pt(99.95% purity) were used. About 3 g each of Pd, Pt, Pd$_{17}$Pt$_{83}$, and Pd$_{65}$Pt$_{35}$ γ-alumina-supported catalysts were prepared. The metal contents of each catalyst, determined by atomic absorption spectroscopy, are reported in Table 1.

Catalytic Activity Measurements: Tetralin Hydrogenation in the Presence of H$_2$S

The hydrogenation of tetralin (1,2,3,4-tetrahydronaphthalene) was performed in a fixed-bed gas-flow microreactor at 573 K, at a constant H$_2$ pressure of 4.6 MPa (45 atm). The total flow rate was 56 ml/min. The partial pressure of tetralin (Fluka, purity >99%) was kept constant at 6.1 kPa

TABLE 1

Metal Loading of the Catalysts and Mean Diameters and Dispersion of Supported Clusters As Deduced from TEM Experiments

Catalyst	Metal loading (wt%)	Mean diameter,[a] fresh sample (nm)	Mean diameter, used samples (nm)	Dispersion (%)
Pd$_{100}$	0.038	4.0	6.1	14.6
Pd$_{65}$Pt$_{35}$	0.032	3.6	5.5	15.2
Pd$_{17}$Pt$_{83}$	0.08	3.4	5.2	16.0
Pt$_{100}$	0.048	3.4	5.1	16.2

[a] Mean diameter for the fresh samples, from Ref. (16).

by using a gas-phase saturator system (corresponding flow of tetralin, 5.48×10^{-8} mol/s). In order to investigate the influence of H$_2$S on the activity of the catalysts, the H$_2$S concentration was varied between 50 and 500 ppm. In order to avoid any H$_2$S consumption due to the reactivity of this gas with the walls of the reactor (15), the heated inner part was protected by a quartz tube whose diameter has been adjusted to minimize the resulting dead volume. The products of tetralin hydrogenation were analyzed every 30 min by gas chromatography. *Cis* and *trans* decalins were always obtained together with small amounts of naphthalene, while no detectable amounts of isomerization or cracking products were observed. The amount of catalyst (about 500 mg) was chosen in order to obtain a conversion below 10%, ensuring the validity of a differential model for the determination of the specific rates. A rapid deactivation of the catalyst is observed during the first hour of the experiment. In order to check for further deactivation of the catalyst, the usual bracketing method was used: several experimental points were repeated after the complete collection of data for a given set of reaction conditions. The deactivation of the catalyst appeared always to be negligible, within the experimental errors. The activation energy of the catalysts was also determined by measuring the activity for 500 ppm of H$_2$S at several temperatures between 550 K and 610 K, in order to ascertain that the reaction was carried out in the chemical regime.

RESULTS

Transmission Electron Microscopy Experiments

TEM experiments have been performed on each catalyst at three different stages: (1) fresh samples, (2) pretreated samples heated for 2 h at 573 K under hydrogen flow, and (3) after tetralin hydrogenation. The results for the fresh sample have been published in a recent paper reporting on the hydrogenation of toluene (16) on identical catalysts.
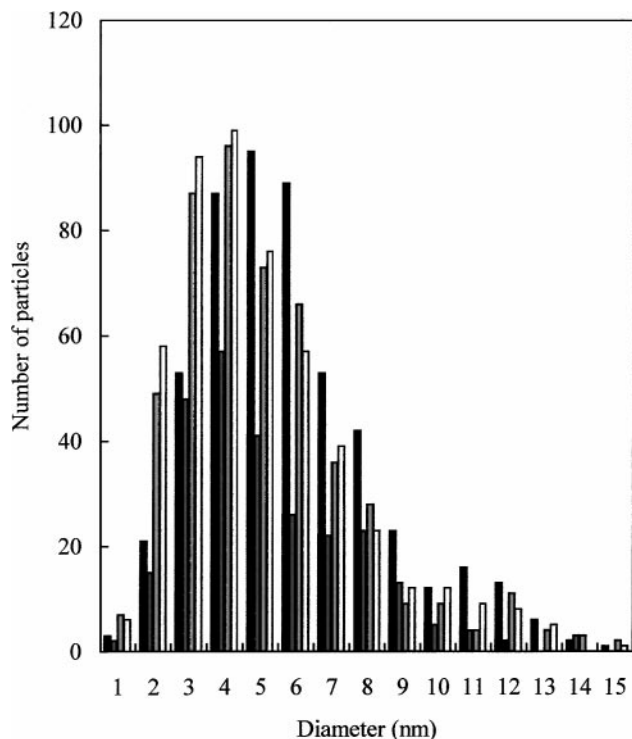
FIG. 1. Size distribution histograms of Pd–Pt clusters after reaction. Pure Pd (black), Pd$_{65}$Pt$_{35}$ (dark gray), Pd$_{17}$Pt$_{83}$ (light gray), and pure Pt (white).

The size histograms of the different catalysts after reaction are presented in Fig. 1. The mean sizes of the four fresh samples (16) are reported for comparison in Table 1. After reaction, analysis of the size histograms (Fig. 1) shows that the mean diameter of the particles is larger than that of the fresh catalysts (Table 1), remaining however similar to those of the preheated samples before reaction. The catalytic properties of the catalysts do not vary appreciably during the catalytic test, indicating that the observed increase of the mean particle size has already occurred during the annealing treatment and not during the reaction. This sintering, occurring at rather low temperature, is at first sight surprising for these low-loaded samples, compared to catalysts prepared by conventional methods. Actually, the clusters deposited by the so-called "soft landing mode" have a weak chemical interaction with the support and are thus able to diffuse easily at the surface. The composition of individual particles for both Pd$_{17}$Pt$_{83}$ and Pd$_{65}$Pt$_{35}$ bimetallic samples was determined by EDX-S analysis with 1-nm^2 electron probes which were defocused to the size of each analyzed cluster. The homogeneity of composition has been checked for both systems and found equal to that of the vaporized rod. Identical results obtained on the same kind of catalysts have been published recently (14, 16) and, consequently, the corresponding figures will not be presented in the present paper.

Hydrogenation of Tetralin in the Presence of H$_2$S

The thio-resistance of the catalysts can be evaluated by measuring the reaction rate at different sulfur concentrations. The hydrogenation of tetralin over the four catalysts in the presence of sulfur was carried out in the 50 to 500 ppm H$_2$S range. Figure 2 shows the effects of the H$_2$S partial pressure on decalin formation. As expected, all reaction rates decrease with an increase in the partial pressure of H$_2$S. Assuming a pseudo order of reaction with respect to the pressure of H$_2$S, one can fit the reaction rates by the following equation,

$$TOF = k[P(H_2S)]^n, \qquad [1]$$

where k and n are respectively the rate constant and the pseudo order. The turnover frequencies (TOFs) of pure Pt and pure Pd samples as well as the corresponding fitting curves are displayed in Fig. 3. The TOFs are based on surface metallic atoms deduced from TEM experiments and corresponding size histograms. The different k and n values corresponding to the four catalysts are reported in Table 2. The effects of temperature on the activity were also investigated and the corresponding Arrhenius plots and parameters are given in Fig. 4 and Table 2, respectively.

The activation energies obtained from the Arrhenius plots were found to be approximately 70 kJ/mol for all the systems, i.e., high enough to exclude the presence of a diffusion regime.
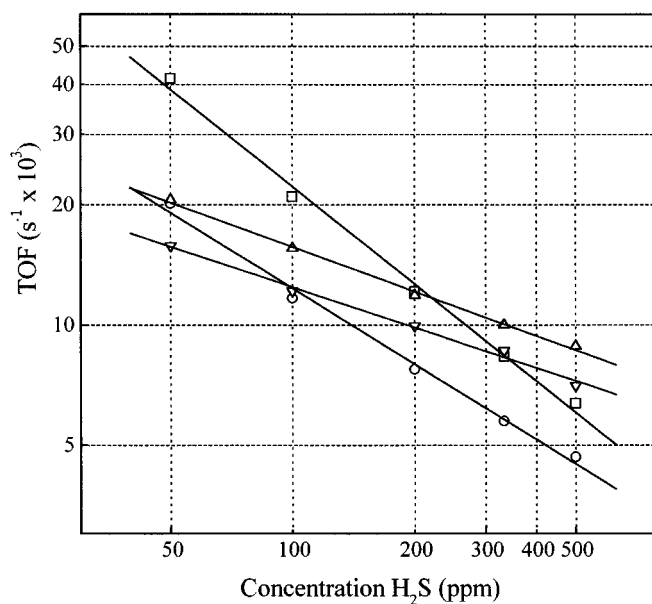

FIG. 2. Effects of H$_2$S partial pressure on reaction rate. Pure Pd ($\triangle$), Pd$_{65}$Pt$_{35}$ ($\triangledown$), Pd$_{17}$Pt$_{83}$ ($\bigcirc$), and pure Pt ($\square$).
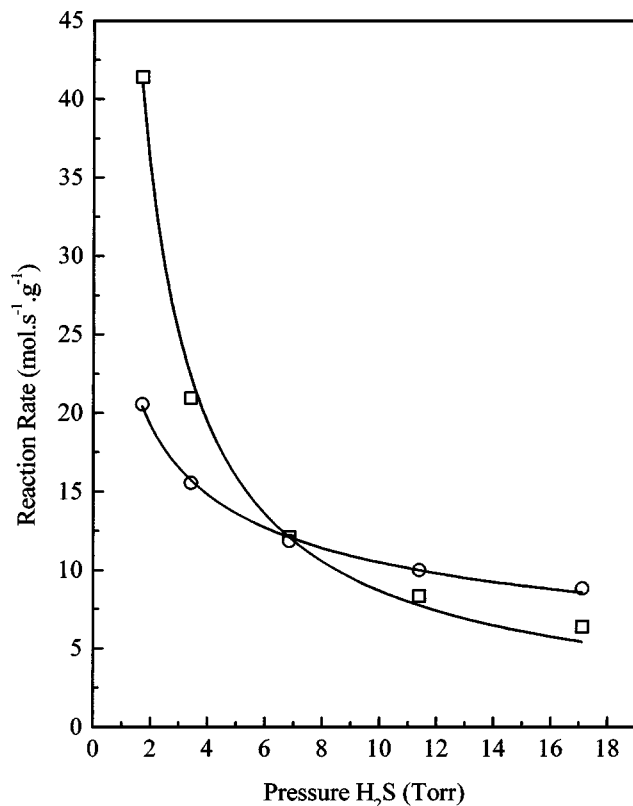
FIG. 3. Reaction rates of pure Pd (○) and pure Pt (□) catalysts in the presence of H_2S. The solid lines represent the best-fit data curves using Eq. [1] (see text).

DISCUSSION

Surface Composition of the Clusters

The surface composition of alloys and especially the composition of the topmost surface layer are generally different from that of the bulk one, due to segregation processes (17, 18). A first step in the understanding of the reactivity of alloys is the determination of the surface composition.

TABLE 2

Activation Energies and Pseudo Order Rate Constants for Tetralin Hydrogenation in the Presence of H_2S Derived Respectively from Arrhenius Plot (Fig. 4) and Best-Fit TOF Curves Using Eq. [1]

Catalyst	Activation energy (kJ/mol)	Rate constant k (s^{-1})	pseudo order n
Pd_{100}	70.1	25.0	−0.38
$Pd_{65}Pt_{35}$	71.2	18.6	−0.34
$Pd_{17}Pt_{83}$	73.1	28.4	−0.67
Pt_{100}	68.9	65.6	−0.88

In a recent work, low-energy ion scattering (LEIS) was employed to study Pd–Pt bimetallic clusters deposited on flat supports and a strong enrichment in Pd at the surface of the bimetallic particles was evidenced. In parallel with LEIS experiments, the modelling of the segregation process was performed using Monte-Carlo simulations (14) and the deduced surface concentrations were in good agreement with the experiments. In the present case, the metal loading is too low to measure the surface composition with a reasonable accuracy by LEIS. Thus, the surface compositions have been predicted on the basis of our theoretical model, thoroughly described elsewhere (17), since it has been shown to give reliable results. The present results have been obtained with the procedure described in a recent work (16). Following this procedure, one calculates the surface Pd concentration and, consequently, the number of Pd surface atoms for each cluster size. Taking into account the size histogram of the $Pd_{17}Pt_{83}$-supported catalyst (Fig. 1), a Pd surface concentration of 59% has been calculated. Concerning the $Pd_{65}Pt_{35}$ alloy, the calculations have shown that the surface is almost entirely covered by Pd atoms whatever the size of the clusters. Finally, one has to note that the large Pd surface segregation is associated with a Pd depletion in the second atomic layer (17).
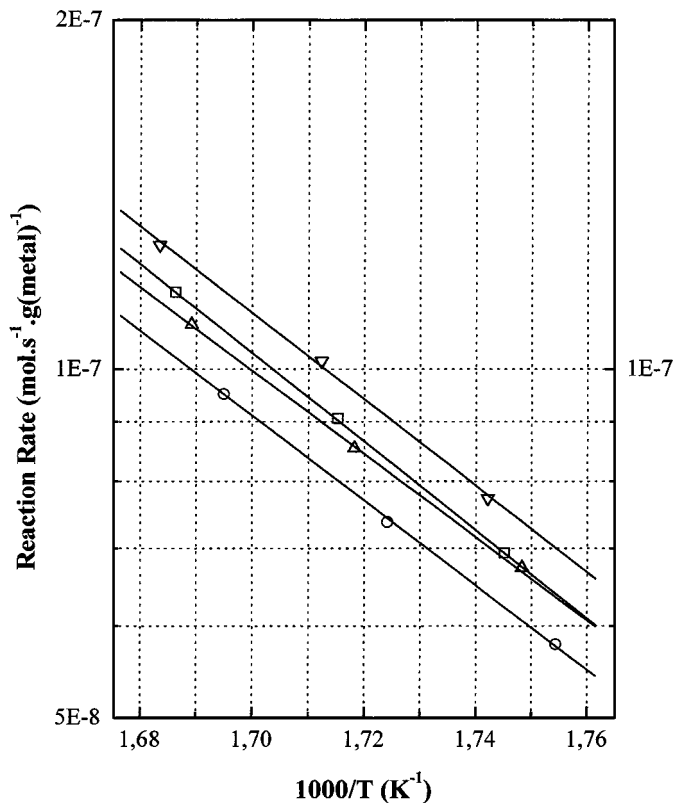

FIG. 4. Arrhenius plot for hydrogenation of tetralin on pure Pd (○), $Pd_{65}Pt_{35}$ (△), $Pd_{17}Pt_{83}$ (□), and pure Pt (▽). (Partial pressure of H_2S = 500 ppm.)

Tetralin Hydrogenation

To examine the sulfur tolerance of the noble metal catalysts, variable amounts of H$_2$S were added during the hydrogenation reaction. Comparing the TOF measured on the different samples, a first important result comes out: platinum is the most active catalyst at low sulfur concentration as shown in Fig. 2. In contrast, pure Pd becomes slightly more active than Pt for high sulfur contents. As a consequence of the observed pseudo order of reaction with respect to H$_2$S reported in Table 2, one notes that inhibition effects decrease in the following order: Pt$_{100}$ > Pd$_{17}$Pt$_{83}$ > Pd$_{65}$Pt$_{35}$ ≈ Pd$_{100}$. Additionally, one notes that the activity curve of the Pd$_{65}$Pt$_{35}$ alloy is almost superimposed with that of the pure Pd sample in the whole range of sulfur concentration. However, even if the surfaces of both systems are entirely covered by Pd atoms, the Pd surface atoms of the Pd$_{65}$Pt$_{35}$ catalyst are surrounded by Pt atoms lying in the layer underneath. These observations lead to the conclusion that neighboring Pt atoms have no influence on the reactivity of Pd atoms nor on their sulfur tolerance: the bimetallic catalyst behaves as a monometallic supported Pd catalyst. This is consistent with the results obtained with the same catalysts in the hydrogenation of toluene where no synergy between Pd and Pt was observed (16). For the Pd$_{17}$Pt$_{83}$ alloy, which is the only catalyst with a mixed Pd–Pt surface, the value of the pseudo order (Table 2) lies between those of pure Pt and pure Pd. To illustrate quantitatively its behavior, we have represented in Fig. 5 the TOF dependence on the H$_2$S concentration for this alloy and that obtained by adding the TOF of the pure metals weighted by the respective Pd (59%) and Pt (41%) surface concentrations. Fitting this predicted curve with Eq. [1] leads to a pseudo order value of −0.61, very close to −0.67, the value measured on the Pd$_{17}$Pt$_{83}$ catalyst. This indicates that the reactivity of the alloy in the presence of sulfur can be perfectly accounted for by an additivity of the catalytic properties of the pure metals. However, the activity of the alloys is not a simple weighted average of those of the two components. Indeed, one has to take into account an ensemble size effect of the active sites. More precisely, the nearly equal values of the pseudo orders derived above imply that the ratio of the measured TOF of the alloy to the simulated one is almost constant whatever the sulfur content. Actually, this ratio was found equal to 0.64 ± 0.05. A value smaller than 1 is not surprising and can be explained by a dilution effect of the Pt ensembles, constituting the active sites, by Pd atoms or vice versa, leading to a reactivity of mixed Pd–Pt sites lower than that resulting from a simple additivity of pure Pd and Pt activities. Indeed, it has been shown in several publications that the active site in the hydrogenation of aromatics is often composed of several atoms. For example, Cadenhead and Masse (19) and Leon y Leon and Vannice (20), who studied benzene hydrogenation, determined respectively an active site composed of two atoms over Pd–
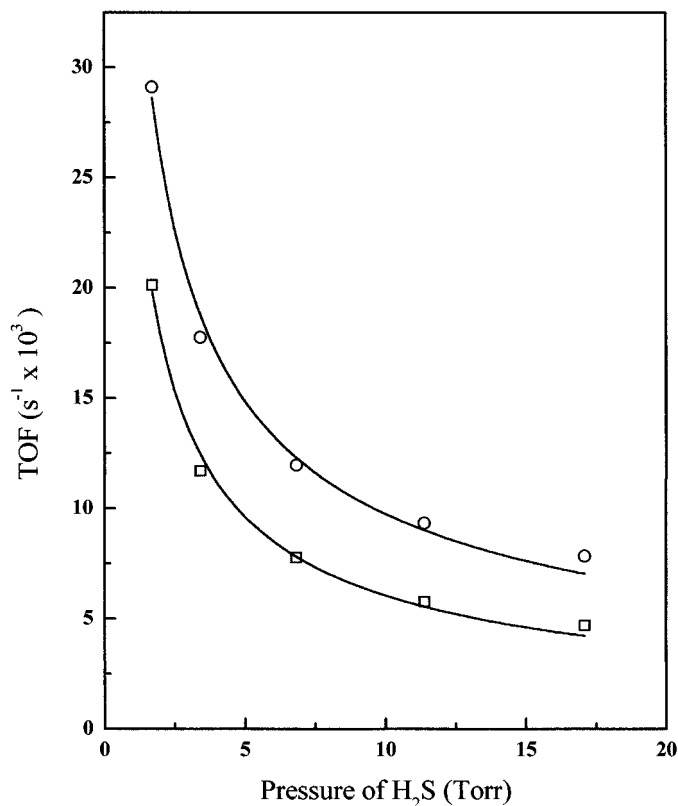

FIG. 5. Comparison of the reaction rate of Pd$_{17}$Pt$_{83}$ catalyst (□) with those obtained by adding the TOF of the pure Pd and Pt catalysts weighted by the respective Pd (59%) and Pt (41%) surface concentrations (○).

Au alloy and three atoms over Pd–Cu alloy. We have also found an active site composed of a pair of atoms in the case of toluene hydrogenation over Pd–Pt catalyst (16). Therefore, the results obtained in the present work can be summarized as follows: (i) The catalytic behavior of the Pd–Pt alloys in the presence of sulfur can be perfectly explained by an additivity of the properties of the two pure metals. (ii) The observed activities of the two alloys are smaller respectively than that of Pt for low H$_2$S concentration and than that of pure Pd for high sulfur content. This established lack of synergy between Pt and Pd seems in contradiction with many recent works devoted to Pd–Pt catalysts supported on acidic support prepared by chemical methods (3, 5–7, 21) excepted those of Qian *et al.*, who studied tetralin hydrogenation over Pd, Pt, and Pd–Pt supported on alumina (2). This could indicate that these new catalysts have a weaker interaction with the support, explaining their different catalytic properties.

CONCLUSION

If the results reported in the literature often do not agree among themselves, the reason, as outlined by Stanislaus and Cooper (22), is probably the simultaneous influence of many ill-defined parameters. According to these authors,

the resistance to poisoning of these catalysts should depend to a large extent on the nature of the support, and the size, the structure, and the location of the metal particles, which in turn are controlled by the preparation conditions. Therefore, the catalytic performances of these systems cannot be easily compared, especially if their structural characterizations have not been carefully performed. Thanks to the laser vaporization technique, the as-prepared pure Pd, pure Pt, and PdPt catalysts have the same structure and the bimetallic particles have a well-defined composition. This was indeed the key point which allowed us to easily compare their catalytic properties and to affirm that alloying Pd with Pt has no intrinsic influence on the activity and resistance to sulfur poisoning, compared to the pure metals, at least under the reaction conditions used in the present work.

To investigate to what extent an effect of the support is at the origin of the thio-resistance observed by many authors, these clusters obtained by using the laser vaporization technique will be, in the near future, deposited on supports of different acidic strengths.

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