Catalysis Letters 34 (1995) 321–329

^{1}H NMR of hydrogen chemisorbed on Pt–Au/Al_2O_3 catalysts. Evidence for the formation of mixed particles

D. Rouabah and J. Fraissard

Laboratoire de Chimie des Surfaces, CNRS URA 1428, Université Pierre et Marie Curie, case 196, 4 place Jussieu, 75252 Paris Cedex 05, France

Received 25 October 1994; accepted 31 May 1995

The evolution of the Pt–Au/Al_2O_3 system with the reduction time can be followed by ^{1}H NMR of chemisorbed hydrogen. When the reduction time increases, the signal with the positive shift, due to hydrogen chemisorbed on pure gold, decreases and disappears completely. At the same time there is a large variation in the negative chemical shift of the hydrogen chemisorbed on the particles containing platinum. This evolution of the NMR spectra demonstrates that mixed Pt–Au particles are formed. Although it appears that after a very long reduction time the platinum covers the gold, the distribution of these two metals in the particles at the atomic scale cannot be determined by this technique.

Keywords: ^{1}H NMR; hydrogen chemisorption; Pt–Au bimetallic catalyst; metal dispersion

1. Introduction

In the context of studies on bimetallic catalysts much work has already been performed on Pt–Au catalysts in the form of films [1–6], mono- and polycrystals [7–9] and supported alloys [10–16]. This work has generally been concerned with hydrocarbon conversion. For example, we have shown that in Pt–Au/alumina catalysts, prepared as indicated below, mixed Pt–Au particles are formed, that in the dehydrogenation of methylcyclohexane to toluene the activity per superficial platinum site increases considerably with the gold concentration and that at the same time the amount of cracking decreases enormously [16].

By studying hydrogen chemisorbed on a metal by NMR it is possible to determine the nature of the hydrogen–metal bond, the average size of the metal particles and how the real degree of coverage (as opposed to the average) of the particles depends on the experimental adsorption conditions. Fraissard et al. were the first to show that the spectra of H_2 chemisorbed on Pt–SiO_2 [17] or Pt–Al_2O_3 [18] display a Knight shift upfield (therefore negative) relative to TMS, whose absolute magnitude increases with the size of the Pt particles and decrease in their coverage. These results were later confirmed by Gay et al. [19,20], then Haul et al. [21]. In the opinion of all these authors this shift corresponds to a partially covalent bond between the hydrogen and essentially the d electrons of the metal. In view of the interest of ^{1}H NMR of chemisorbed hydrogen in the study of supported monometallic catalysts, we wished to examine its potential for studying the formation of bimetallic particles and determining the relative distribution of the two metals in the particles.

2. Experimental conditions

The sample chosen for this study consists of 20% Pt and 80% Au supported on alumina. It is compared with a sample of pure supported Pt at the same w/w concentration (10%). These two catalysts are denoted Pt-20 and Pt-100, respectively.

2.1. CATALYST PREPARATION

The Pt-100 sample was prepared by impregnation of alumina (BET surface area: 100 ± 15 m^2 g^{-1}) with a solution of hexachloroplatinic acid at 90°C with constant shaking. Pt-20 was prepared under the same conditions by co-impregnation of the same support with a mixture of hexachloroplatinic and hexachloroauric acids. After drying, the samples were calcined in a stream of oxygen for 1 h at temperature $T_c = 400$°C (temperature gradient: 1°C/min). After cooling in helium, the metal was reduced in a stream of H_2–He at $T_r = 400$°C for 12, 56 or 120 h (temperature gradient from 25 to 400°C: 1°C/min).

Prior to any study of chemisorbed hydrogen, the samples were treated as follows: heated from 25 to 300°C at 10^{-5} Torr; held for 1 h at 300°C in oxygen at 300 Torr; heated for 1 h at 300°C and 10^{-5} Torr; reduced in hydrogen at 300 Torr for 1 h at 300°C; desorbed at 10^{-5} Torr for 12 h at 400°C.

2.2. DISPERSION

The dispersion was determined by chemisorption of hydrogen in a thermostated volumetric apparatus at 26.5°C and by electron microscopy on a Jeol 100 CX/II apparatus.

2.3. NUCLEAR MAGNETIC RESONANCE

^{1}H NMR studies were performed on a Bruker CXP-100 apparatus at 90 MHz and 26 ± 1°C. Chemical shifts are measured relative to gaseous TMS.

3. Experimental results

3.1. DISPERSION

3.1.1. Hydrogen chemisorption

The adsorption isotherm for Pt-100 is of the classical form for H_2 chemisorption, that is, there are two regions, AB and CD (fig. 1). The first large one corresponds to high H_2 chemisorption, the second both to the saturation of the monolayer of the metal surface and to hydrogen physisorption. There are two methods, (a) and (b), for determining the amount of hydrogen adsorbed at the monolayer:

(a) The linear section of the variation, CD, of the total adsorbed hydrogen, N_T, is extrapolated to zero pressure. The quantity defined in this way $N_{i,1}$(Pt-100), and equal to 11.1×10^{19} H_2 g^{-1} corresponds to the monolayer (table 1);

(b) After saturation the sample is desorbed at 26.5°C and 10^{-5} Torr for a few minutes, so as to eliminate the physisorbed hydrogen. To determine this latter, N_{phy}, one then readsorbs H_2 under the same conditions. In this case, the quantity of hydrogen chemisorbed at the monolayer, $N_{i,2}$(Pt-100), is given by the difference between the two isotherms, $N_T - N_{Phy} = N_{i,2}$(Pt-100) $= 8.2 \times 10^{19}$ H_2 g^{-1}. Dispersions deduced from $N_{i,1}$(Pt-100) and $N_{i,2}$(Pt-100) are $D_1 = 0.72$ and $D_2 = 0.55$, respectively. The corresponding mean diameters are $d_{m1} = 16$ Å and $d_{m2} = 23$ Å [22].

The isotherms for total and irreversible hydrogen adsorption on Pt-20 reduced for 12 h are of the same shape as for Pt-100. In the same way are deduced $N_{i,1}$(Pt-20) $= 4 \times 10^{19}$ H_2 g^{-1} and $N_{i,2}$(Pt-20) $= 3.1 \times 10^{19}$ H_2 g^{-1} (table 1). Comparison of the results for the two samples shows that the amounts of hydrogen, $N_{i,1}$ and $N_{i,2}$,

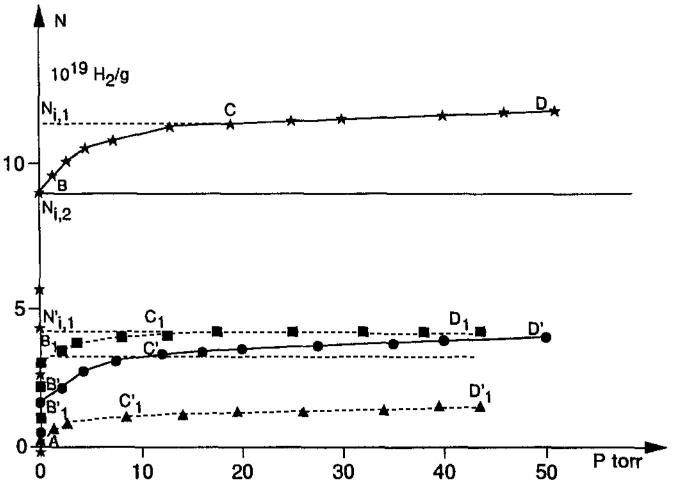

Fig. 1. Hydrogen chemisorption isotherms at 26.5°C. Pt-100 sample: (★) ABCD: total adsorption; (●) AB′C′D′: physical adsorption. Pt-20 sample: (■) $AB_1C_1D_1$: total adsorption; (▲) $AB'_1C'_1D'_1$: physical adsorption.

Table 1

Catalyst	Chemisorption of H_2					
	$N_{i,1}$ (H_2 g^{-1})	$N_{i,2}$ (H_2 g^{-1})	dispersion of Pt		mean diameter (Å)	
			D_1	D_2	d_{m1}	d_{m2}
Pt-100	11.1×10^{19}	8.2×10^{19}	0.72	0.55	16	23
Pt-20[b]	4×10^{19}	3.1×10^{19}	1.30[a]	1.00[a]	–	–

Catalyst	Electron microscopy; % particles of diameter d (Å)						
	<10	10–15	15–20	20–25	25–30	30–35	$d_{m,ME}$
Pt-100	16	26	35	0	17	5	20
Pt-20	72	28	0	0	0	0	<10

[a] Assuming that H_2 is only chemisorbed on Pt at 26.5 °C.

[b] Reduced for 12 h.

and the Pt concentration decrease by factors of 2.5 and 5, respectively. Referenced to the same amount of Pt there is therefore 2.5 times as much H_2 chemisorbed on the Pt-20 alloy as on pure platinum, Pt-100. It is clear that one cannot get back to the metal dispersion of Pt-20 and to the particle size from the amounts of hydrogen chemisorbed. At best, one can determine the Pt dispersion, assuming that the chemisorption of H_2 on the gold is negligible at 26.5°C. If this were the case one would find D_1(Pt-20) = 1.30 and D_2(Pt-20) = 1.00.

3.1.2. Electron microscopy

The particle size distribution and the mean diameters ($d_{m,ME}$) for the two samples are given in table 1. It can be seen that at the same metal concentration the metal particles of Pt-20 are much smaller than those of Pt-100: $d_{m,ME}$(Pt-100) = 20 Å and $d_{m,ME}$(Pt-20) < 10 Å.

3.2. PROTON NMR

Before hydrogen adsorption the NMR spectra of the two samples consist of a single symmetrical line, a, near 0 ppm and due to the proton resonance of the alumina OH groups. This line can be used as an internal reference.

3.2.1. Sample Pt-100

After chemisorption of a small amount of H_2 the NMR spectrum consists of two lines. The first, a, at about 0 ppm is due to the OH of the support. The second, b, with a negative chemical shift, is characteristic of hydrogen chemisorbed on the Pt particles. When the amount of chemisorbed hydrogen, N, increases line b grows but its shift, δ_b, stays the same at -29 ± 2 ppm up to $N = N_B = 5.1 \times 10^{19}$ H_2 g^{-1}

corresponding to a coverage θ_1 of about 0.5 or θ_2 about 0.65, depending on the value of N_i chosen (section AB, fig. 2). Beyond this concentration the chemical shift varies linearly from −29 to -4 ± 2 ppm when N goes from 5.1×10^{19} to 11.4×10^{19} H_2 g^{-1} (section BC, fig. 2). This variation is consistent with what is always found for Pt catalysts [17–20].

3.2.2. Sample Pt-20

After chemisorption of a small amount of hydrogen (0.31×10^{19} H_2 g^{-1}) on a Pt-20 sample reduced at 400°C for 12 h, the NMR spectrum consists, apart from line a, of a second line, c, whose chemical shift is positive. Line b, with a negative shift, as that observed with Pt-100, is only detected when the hydrogen concentration is at least 0.61×10^{19} H_2 g^{-1}. The variation of the chemical shifts δ_b and δ_c of lines b and c with increasing chemisorbed hydrogen concentration is as follows: δ_c decreases from 35 to 10 ppm when N goes from 0.31×10^{19} to 1.41×10^{19} H_2 g^{-1}; δ_b increases from −35 to −8 ppm when N goes from 0.61×10^{19} to 4.1×10^{19} H_2 g^{-1} (fig. 3). Above 1.41×10^{19} H_2 g^{-1} line c cannot be detected, either because the difference between δ_c and δ_b becomes too small compared to the width of line b, or because there is rapid exchange between the two species beyond this concentration.

The spectrum changes with the time of reduction at 400°C in hydrogen. After 56 h (fig. 4) line c can no longer be detected. The shift δ_b varies with N in much the same range of ppm as before, but the plot can be divided into two parts: the first, OP, is concave towards high δ when N is between 0.15×10^{19} and 2.06×10^{19} H_2 g^{-1}, almost levelling off at about this latter concentration; the other, PQ is linear for N between 2.06×10^{19} and 4×10^{19} H_2 g^{-1}. This trend continues with the reduction time. After 120 h the dependence of δ_b on N is similar to that of Pt (fig. 5). It shows a horizontal, AB, for the value of δ corresponding to that of point P in fig. 4, i.e. at -21 ± 2 ppm, when N is between zero and

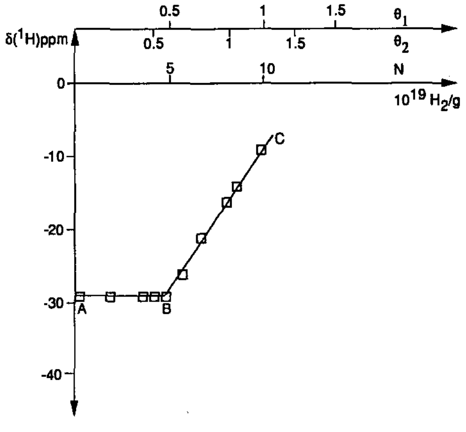

Fig. 2. Pt-100 sample: ^1H chemical shift (δ) versus the number of chemisorbed H_2 molecules (N) and the coverages θ_1 and θ_2 (see the text).

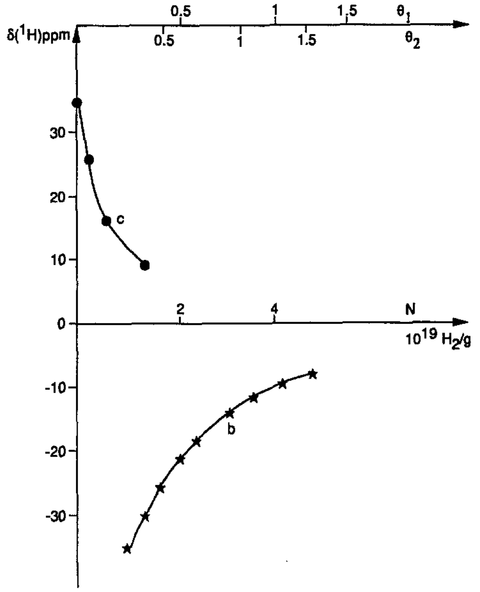

Fig. 3. Pt-20 sample reduced at 400°C for 12 h. ^{1}H chemical shift of lines b and c versus the number of chemisorbed H_2 molecules (N) and the coverages θ_1 and θ_2 (see the text).

1.57×10^{19} H_2 g^{-1}, then a linear decrease, BC, to -3 ± 2 ppm as N goes from 1.57×10^{19} to 3.9×10^{19} H_2 g^{-1} (fig. 5).

4. Discussion

Let us first consider the reference sample, Pt-100. We have already shown several times that the chemical shift of hydrogen chemisorbed on Pt depends on the size

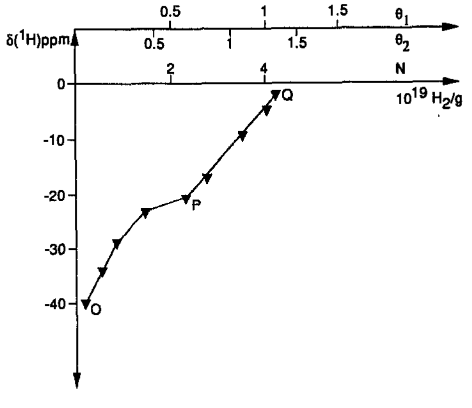

Fig. 4. Pt-20 sample reduced at 400°C for 56 h. ^{1}H chemical shift versus N, θ_1 and θ_2 (see the text).

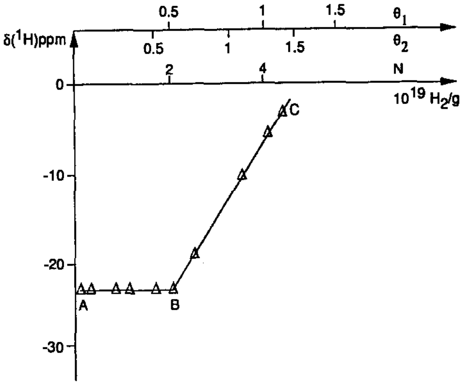

Fig. 5. Pt-20 sample reduced at 400°C for 120 h. ^1H chemical shift versus N, θ_1 and θ_2 (see the text).

of the particles and their coverage [17–21]. The constant value of δ_b in the first part of the δ_b vs. N plot proves that along the horizontal, AB, hydrogen is chemisorbed at 26.5°C with constant coverage, $\theta_{26.5}$, on the first particles encountered, creating two zones in the NMR tube, an upper one with the particles having this coverage and a lower one with only bare particles. The proportion of the former increases with the H_2 concentration at the expense of the latter. At point B all the particles have the same coverage, $\theta_{26.5}$, equal to $\theta_1 = 0.5$ or $\theta_2 = 0.65$ depending on the isotherm used to determine the dispersion. This is explained as follows [23,24]: when a small amount of H_2 enters the NMR tube the first particles encountered are more or less saturated, but partially desorb in favour of the next ones. The part which is retained corresponds to the coverage, $\theta_{26.5}$, for which the Pt–H attraction is at least equal to the repulsive interaction between the chemisorbed H atoms. Beyond this coverage the mean Pt–H interaction is weaker, diffusion of hydrogen from one particle to another easier and, therefore, δ_b then decreases linearly as the mean coverage of the particles increases.

The greater the Pt particles size, the more the chemical shift, δ_b, defining the position of the horizontal, AB, is negative. For Pt-100 this shift is −29 ppm, which corresponds to an average size of $d_{\delta_H} = 18$–21 Å, given the uncertainty on δ_b. This value is in very good agreement with the results obtained by electron microscopy ($d_{m,ME}$(Pt-100) = 20 Å). These values, $d_{m,ME}$ and d_{δ_H}, lie between the two values d_{m1}(Pt-100) = 16 and d_{m2}(Pt-100) = 23 Å, from the isotherms which again confirms, as we have often maintained, that $N_{i,1}$ and $N_{i,2}$ given by the isotherms are approximate values for the monolayer, the first an overestimate, the second an underestimate [24].

Let us consider now sample Pt-20 reduced at 400°C. We have shown previously that under the experimental conditions chosen we form alloy particles; the thermodesorption of chemisorbed hydrogen and the activity in methylcyclohexane dehydrogenation of these particles depend greatly on the reduction time [21]. In the present study, line b with negative chemical shift can only correspond to hydrogen chemisorbed on Pt particles. This does not exclude the possibility that they contain a little gold. The monotonic decrease in δ_b with increasing N may express a wide distribution of particle sizes and perhaps the existence of species which have not been completely reduced. Line c, whose shift is positive, corresponds to hydrogen chemisorbed on gold particles, this hydrogen having been perhaps previously dissociated on the Pt particles [25]. When the reduction time increases (56 h) signal c disappears, which proves that there are no longer any pure gold particles on the alumina and, therefore, indirectly that the gold is associated with the platinum, according to the results from TPD of chemisorbed hydrogen and catalysis of dehydrogenation [24]. The dependence of the $\delta_b = f(N)$ curve on reduction time is obviously associated with the rearrangement of Pt and Au in metal particules and the redistribution of particle sizes.

Finally, after 120 h, the particles obtained are very small. The $\delta_b = f(N)$ plot is similar to that for Pt-100. There are several possible explanations for this surprising variation of δ_b:

(1) The particles contain gold and platinum distributed heterogeneously on the surface and inside. Two situations are then possible: (i) hydrogen is chemisorbed on the Pt and does not diffuse onto gold at room temperature. But in this case one cannot understand why line c is detected after a short reduction (12 h); (ii) there is rapid exchange of H atoms located on the Pt and the gold, after dissociation of H_2 on the Pt. This exchange between the two metals is naturally much lower when the particles consist of pure Pt or Au metal and are far from each other.

(2) The Pt completely covers the gold. This spectrum is then characteristic of Pt alone, perturbed by its interaction with the gold.

Cases 1(ii) and 2 offer the best explanation, since, in particular, they explain the high chemisorption per platinum atom for this sample compared to the sample Pt-100 without gold.

5. Conclusion

Studying a sample supported pure platinum, taken as a reference, has first of all confirmed that the ^1H NMR of chemisorbed hydrogen can be used to determine the platinum dispersion. This first ^1H NMR study of hydrogen chemisorbed on a bimetallic Pt–Au catalyst has allowed us to follow the formation of mixed particles in terms of the reduction time: separate reduction of the gold and the platinum, then gradual formation of mixed particles when the reduction time is increased. However, when the reduction time is very long it is impossible to say whether the surface of the mixed particles contains both metals or simply platinum covering the gold.

References

[1] J.K.A. Clarke, A.F. Kane and T. Baird, J. Catal. 64 (1980) 200.
[2] F. Alan and J.K. Clarke, J. Chem. Soc. Faraday 76 (1980) 1640.
[3] J.J. Stephan and V. Ponec, J. Catal. 42 (1976) 1.
[4] F.J. Kuijers, R.P. Dessing and W.M.H. Sachtler, J. Catal. 33 (1974) 316.
[5] J.J. Stephan, V. Ponec and W.M.H. Sachtler, Surf. Sci. 47 (1975) 403.
[6] R. Bouwman and W.M.H. Sachtler, J. Catal. 19 (1970) 127.
[7] W.M.H. Sachtler and G.A. Somorjai, J. Catal. 89 (1984) 35.
[8] R.C. Yeates and G.A. Somorjai, J. Catal. 103 (1987) 208.
[9] P. Biloen, R. Bouwman, R.A. van Santen and H.H. Brongersma, *Proc. 7th Int. Vacuum Congr. and 3rd Int. Conf. on Solid Surfaces*, 1977, Vol. 2, p. 1401.
[10] J.R. Anderson, K. Foger and R.J. Breakspere, J. Catal. 57 (1973) 458.
[11] K. Foger and J.R. Anderson, J. Catal. 61 (1980) 140.
[12] J.K.A. Clarke, L. Manninger and T. Baird, J. Catal. 54 (1978) 230.
[13] J.R.H. van Schaik, R.P. Dessing and V. Ponec, J. Catal. 38 (1975) 273.
[14] S. Galvagno and G. Parravano, J. Catal. 57 (1979) 272.
[15] A. O'Cinneide and F.G. Gault, J. Catal. 37 (1975) 311.
[16] D. Rouabah and J. Fraissard, J. Catal. 144 (1993) 30.
[17] J.L. Bonardet, J. Fraissard and L.C. Menorval, *Proc. 6th Int. Congr. on Catalysis*, London, Vol. 2 (1977) 633.
[18] L.C. Menorval and J. Fraissard, Chem. Phys. Lett. 77 (1981) 309.
[19] T. Cheng and J.D. Gay, J. Catal. 71 (1981) 119.
[20] T. Cheng and J.D. Gay, J. Catal. 77 (1982) 53.
[21] N. Reinecke and R. Haul, Ber. Bunsenges. Phys. Chem. 88 (1984) 1232.
[22] R. van Hardeveld and F. Hartog, Surf. Sci. 15 (1969) 189.
[23] D. Rouabah, R. Benslama and J. Fraissard, Chem. Phys. Lett. 179 (1991) 218.
[24] D. Rouabah and J. Fraissard, Solid State NMR 3 (1994) 153.
[25] T. Ito, T. Kadowaki and T. Toya, Japan J. Appl. Phys. 14 (1975) 1673.