JOURNAL OF CATALYSIS 86, 210–214 (1984)

Polyamide-Supported Platinum–Gold Catalysts for Selective Hydrogenation of Benzene

Polyamide-supported noble metal catalysts exhibit activity and selectivity patterns significantly different from those observed when the same metals are deposited on more traditional materials, such as silica, alumina, or charcoal (*1*). Such catalysts appear to be particularly effective for the selective hydrogenation of benzene into cyclohexene (*1–4*). Nevertheless, the nature of their active sites is still controversial. Harrison and Rase (*3*) advocated, for Pt/nylon catalysts, a particular geometric arrangement of platinum metal atoms on the surface of the support, whereas Dini *et al.* (*4*), for similar catalysts, postulated the formation of a stable bivalent platinum coordination complex, produced during the activation step. Strong evidence has been gained in our laboratory in favor of the presence of active metallic sites on the support for Pt/nylon and Pd/nylon catalysts (*5, 6*). Their unusual selectivity in the partial hydrogenation of benzene has then been attributed to an electron transfer from the polyamide support toward the metal (*2, 6, 7*).

The present work has sought to gain further information on the active sites of Pt supported on polyamide by examining the effect of "alloying" by gold on the catalytic properties of Pt in the partial hydrogenation of benzene.

Catalysts were made by refluxing (reflux temperature: 100°C) polyamide-66 (nylon-66) powder (0.1–1 mm size; 12 $m^2 g^{-1}$) with aqueous solutions of metal chlorides (H_2PtCl_6 and/or $AuCl_3$, NaCl) for 30 min, followed by filtering, washing with water and methanol (*8*). After drying in air at 120°C, the solids were reduced in a hydrogen flow at 160°C for 1 h. Catalyst composition was determined by atomic absorption photometry.

The hydrogenation of benzene was carried out in a flow differential reactor described elsewhere (*9, 10*). The total conversion level was in all cases maintained below 2%.

The platinum surface areas of catalysts were determined by hydrogen–oxygen titration following a pulsed chromatographic method previously reported (*5*). Under the experimental conditions used, no hydrogen consumption via H_2–O_2 titration was observed on gold. Therefore, it was assumed that H_2–O_2 titrations measured only platinum area. Electron microscope examination of catalyst particle cuttings was performed, as previously described (*11*), with a JEM 100 B model.

The composition of the catalysts and the corresponding composition of the impregnation solutions are provided in Table 1.

For impregnation solutions containing more than 17% Au, the catalysts exhibit a large excess of gold. This is particularly obvious for the Pt–Au-9 sample for which Au/Pt = 10 whereas the corresponding impregnation solution has a Au/Pt ratio of only 2 (column 3). This result confirms the reducing character of polyamide-66 (*6, 12*), since it is well known that Au(III) complexes are powerful oxidizing agents (*13*), probably stronger than H_2PtCl_6.

The results obtained from H_2–O_2 titration and kinetic measurements are summarized in Table 2. The hydrogenation of benzene (B) was performed at $T = 433$ K, with $P_B = 60$ Torr, $P_{H_2} = 700$ Torr, total flow rate: 30 $cm^3 min^{-1}$, and catalyst weight = 3 to 20

0021-9517/84 $3.00

TABLE 1

Composition of Nylon-Supported Catalysts versus Composition of Impregnation Solutions

Catalyst	Total metal (wt %) on catalyst	In impregnation solution (atom %)		On catalyst (atom %)	
		Pt	Au	Pt	Au
Pt-100	1.5	100	0	100	0
Pt–Au-95	2.0	91	9	95	5
Pt–Au-85	1.3	83	17	85	15
Pt–Au-34	1.2	67	33	34	66
Pt–Au-9	2.3	33	67	9	91
Au-100	3.4	0	100	0	100

mg. Kinetic measurements were obtained by extrapolating the activity vs time on stream curves to time zero. In all cases, the conversion of benzene decreased smoothly with time and no significant stabilizing effect of gold was observed in this respect.

As can be seen from Table 2, the addition of Au causes a decrease in the percentage of Pt exposed (decrease of Pt specific surface area, column 2). A similar effect was reported for silica-supported Au–Pt catalysts and was ascribed to the coverage of Pt by Au (*14*). From wide-angle X-ray scattering (WAXS) and transmission electron microscopy (TEM), the authors concluded that mixed aggregates of Au and Pt atoms and the aggregates of Au atoms only were both present, the latter being considerably larger than the former (*14*).

TABLE 2

Platinum Surface Area, Turnover Frequency, and Selectivity to Cyclohexene (CHE) of Polyamide-Supported Catalysts

Catalyst	S ($m^2\ g^{-1}$ Pt)	Conversion (%)	S_{CHE}[a]	N[b] (h^{-1})
Pt-100	62	1.68	0.20	2330
Pt–Au-95	45	0.80	0.26	287
Pt–Au-85	39	0.54	0.46	253
Pt–Au-34	32	0.05	0.80	68
Pt–Au-9	22	0.0	—	0

[a] Selectivity to cyclohexene expressed as cyclohexene/cyclohexane.

[b] Turnover frequency in molecules of benzene converted per surface Pt atom per hour.

For Pt–Au-95 sample (95% Pt–5% Au), the TEM micrograph shows the presence of homodispersed particles of 3–4 nm and a few aggregates of 1 order of magnitude (or more) larger (Fig. 1). These large aggregates become dominant on Au-rich catalysts as can be seen in Fig. 2, which especially exhibits large particles of 20–40 nm for the Pt–Au-9 sample (9% Pt–91% Au). For the monometallic Au sample (Au-100), even larger particles with definite geometric shapes (triangles, squares, rectangles . . .) are present (Fig. 3). Therefore, large particles may especially result from aggregation of Au, since the mobility of Au particles is higher than that of Pt particles (lower melting point for Au). Nevertheless, the presence of Pt in bimetallic catalysts partially inhibits the growth of large particles and the formation of their facets (compare Fig. 2 with Fig. 3). This tends to show that these large particles of Fig. 2 are bimetallic clusters, in the Sinfelt sense (*15*), rather than aggregates of Au atoms only (*14*), although the reduction temperature of Pt–Au/nylon catalysts never exceeded 160°C. This assumption may be explained by a close contact between Pt and Au on the polyamide

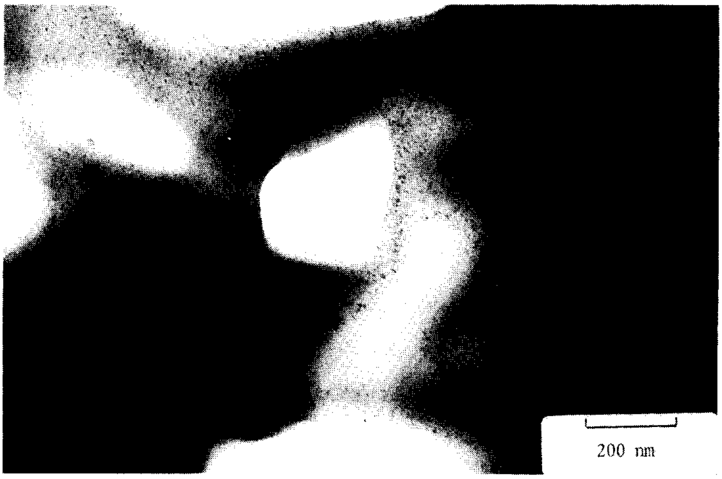

FIG. 1. Electron micrograph of Pt–Au-95 catalyst (5 atom% Au).

support, since $AuCl_3$ and H_2PtCl_6 are both powerful oxidizing agents (*13*) and should therefore adsorb on the same reducing sites (amide groups) of the polyamide carrier. However, the endothermic formation of Au–Pt alloy is unlikely at 160°C.

An inspection of Table 2 (column 5) clearly shows that the turnover frequency (N) of Pt very strongly decreases by the addition of 5% Au. A dramatic decrease of the catalytic efficiency of Pt resulting from such a small content of Au therefore suggests an electronic effect rather than a screening effect by gold. Further additions of Au result in a less-pronounced decrease of the turnover which finally becomes negligible for the Pt–Au-9 sample (91% Au). The variation of the selectivity to cyclohexene (S_{CHE}) with the total conversion level for different catalysts is shown in Fig. 4. This type of curve allows the comparison of the selectivity of catalysts of various compositions exhibiting a strong decrease of selectivity with an increasing conversion level (*10*). Indeed, the same curve as that shown in Fig. 4 was established for the monometallic Pt/nylon catalyst (Pt-100) in the same range of conversions. This behavior

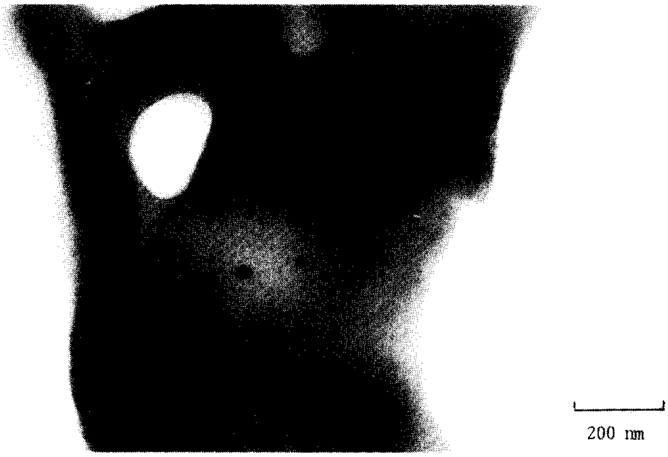

FIG. 2. Electron micrograph of Pt–Au-9 catalyst (91 atom% Au).

FIG 3 Electron micrograph of Au-100 catalyst

strongly suggests that the *selectivity* characteristics, of bimetallic Pt–Au/nylon catalysts in the partial hydrogenation of benzene are identical to those of pure Pt on nylon which were explained by a kinetic scheme (*2*) Therefore, both electronic (donation from Au to Pt) and ensemble size (dilution by Au) effects play only a secondary role, if any, in the *selectivity* of Pt–Au/nylon catalysts for the partial hydrogenation of benzene

In summary, bimetallic Pt–Au clusters can be formed at low temperature (160°C) on a reducing organic carrier such as the polyamide-66 powder used in this work The lack of an ensemble (or dilution) effect, due to the addition of gold, on the selectivity of Pt/nylon catalysts strongly suggests that the adsorption sites for benzene molecules involve one Pt atom only In such a case, the observed decrease of the activity per accessible Pt atom (turnover frequency) by addition of Au may be due to the electronic effect (*16*) and/or more simply, to a decrease of the accessibility of benzene molecules to Pt atoms screened by Au The kinetic scheme which, as for monometallic Pt catalysts, favors the selectivity to cyclohexene when the conversion level decreases, remains the same for Pt–Au catalysts

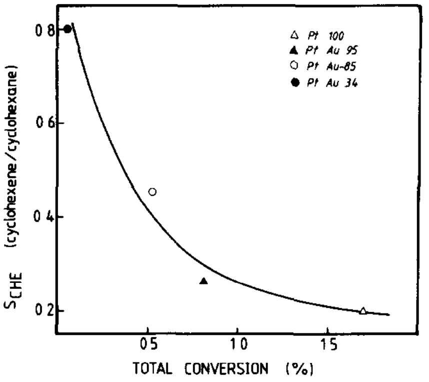

FIG 4 Variation of S_{CHE} (cyclohexene/cyclohexane) with the total conversion

REFERENCES

1 Teichner, S J , Hoang-Van, C , and Astier, M *in* "Metal-Support and Metal-Additive Effects in Catalysis" (B Imelik *et al* , Eds), p 121 Elsevier, Amsterdam, 1982

2 Hoang-Van, C , Tournier, G , Michel, C , and Teichner, S J , "Proceedings, 7th International Congress on Catalysis (Tokyo 1980)," p 1508 Kodansha/Elsevier, Tokyo/Amsterdam, 1981

3 Harrison, D P , and Rase, H F , *Ind Eng Chem Fundam* **6,** 161 (1967)

4 Dini, P , Dones, D , Montelatici, S , and Giordano, N , *J Catal* **30,** 1 (1973)

5 Bernard, J R , Hoang-Van, C , and Teichner, S J , *J Chim Phys* **72,** 1217 (1975)

6 Michel, C , Hoang-Van, C , and Bozon-Verduraz, F , *Nouv J Chim* **2,** 575 (1978)

7 Hoang-Van, C , Michel, C , Teichner, S J , and Bozon-Verduraz, F , "Proceedings, 6th Ibero-American Symposium on Catalysis (Rio de Janeiro 1978)," Veritas' Multiplicadora e Copiadora LTDA Pub , Part II, p 45 Rio de Janeiro, 1978
8 Bernard, J R , Hoang-Van, C , and Teichner, S J , *J Chim Phys* **72,** 729 (1975)
9 Bernard, J R , Hoang-Van, C , and Teichner S J , *J Chim Phys* **73,** 988 (1976)
10 Michel, C , Hoang-Van, C , and Teichner, S J , *J Chim Phys* **75,** 819 (1978)
11 Michel, C , Hoang-Van, C , and Teichner, S J , *J Chim Phys* **78,** 241 (1981)
12 Hoang-Van, C , Michel, C , and Teichner, S J , *C R Acad Sci Paris C* **289,** 325 (1979)
13 Cotton, F A , and Wilkinson, G , "Advanced Inorganic Chemistry," p 1049 Interscience, New York, 1966
14 Galvagno, S , and Parravano, G , *J Catal* **57,** 272 (1979)
15 Sinfelt, J H , *J Catal* **29,** 308 (1973)
16 Lam, Y L , Criado, J , and Boudart, M , *Nouv J Chim* **1,** 461 (1978)

C HOANG-VAN
G TOURNIER
S J TEICHNER

Laboratoire de Catalyse Appliquee
et Cinétique Heterogene
Laboratoire Associe au CNRS (L A 231)
Universite Claude Bernard (Lyon I)
43 Bd du 11 Novembre 1918
69622 Villeurbanne Cedex, France

Received April 28, 1983