

Supported Au-Pt Catalysts

Characterization and Hydrogen Transfer Activity between Benzene and Cyclohexane

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Two series of Au-Pt catalysts supported on SiO₂ were prepared by the incipient wetness method. In one series the total amount of metal (Au + Pt) was kept constant at about 0.7 wt% (Series A), while in a second series the amount of Pt was kept constant at about 0.7 wt% (Series B). In the latter the total amount of metal ranged between 1.03 to 6.13 wt%. The two series were characterized by H₂ and O₂ chemisorption, wide-angle X-ray scattering, and electron spectroscopy for chemical analysis. There was indication of the presence of mixed Au-Pt particles as well as of particles containing Au only. In depth compositional profile of Series B showed homogeneous composition extending to at least about 12 Å below the surface, while in Series A compositional inhomogeneities were found. The rate of the carbon-14 equilibration between benzene and cyclohexane and the rate of equilibration between H₂ and D₂ were measured on both catalyst series in a flow system at a total pressure of 1 atm. For the carbon-14 equilibration reaction the temperature was 205°C, contact time in the range of 10 to 30 sec. The influence of the ratio cyclohexane to benzene on the reaction rate was recorded. For the deuterium equilibration the temperature was -78°C and a ratio of $p_{D_2}/p_{H_2} = 1$ was employed. The rate of the carbon-14 equilibration was found to be independent of surface composition of the Au-Pt particles for Series A, while for Series B the rate increased upon addition of Au to Pt. Differences in rate up to about one order of magnitude were observed between catalysts from Series A and B possessing a similar overall Au/Pt ratio. No difference in the rate of deuterium equilibration was found between Series A and Series B catalysts. The kinetic behavior of Series B is discussed, and suggestions of the nature of the Au-Pt interaction, responsible for the enhancement of the reactivity of Pt, are advanced. The concept of reaction sensitivity to surface structure is viewed as a dynamic factor which includes the position of the reaction steady state and the corresponding degree of reaction conversion. Consequently, a reaction may be sensitive or insensitive to the surface structure depending upon its conversion.

The influence of several factors on the catalytic activity of Au was recently investigated (1). The factors studied included precursor salt, size and distribution of the Au particles, nature of the support material, and gas phase oxidation-reduc-

tion conditions. From these investigations a complex set of surface effects covering the structure and composition of the surface and the kinetics of the catalytic reaction were found. Against this background, it was felt of interest to investigate the effect of the addition to Au of a second metal with limited bulk solubility in Au. The condition of partial solubility seemed preferable to that of complete miscibility, since it appeared that in the presence of

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this condition it would be more likely to discover subtle interactions between the two metals that could be obscured by large three-dimensional alloy formation. In past studies on bimetallic systems, there has been an effort to strive for conditions leading to alloy formation, as predicted by the bulk phase diagram. This approach has been instrumental for the derivation of general schemes for the catalytic activity of supported alloys. It may also be argued that bimetallic compositions with large miscibility gap may, indeed, be important for throwing light on the genetic steps of bimetallic particles as they grow from the decomposition products of separate metal salts, on the possible existence and characterization of metal-metal interactions precursor to alloying, on the stabilization of genetic intermediates, on nonequilibrium particle morphology (anisotropic and two-dimensional growth). This is a vast area, whose microscopic details are largely unknown; yet it comprises steps which conceivably have a controlling role on the reactivity of bimetallic supported particles.

Following these considerations, it was felt that Pt would be a good candidate for the study of its effect on supported Au. In fact, the catalytic activity of Pt is generally orders of magnitude higher than that of Au and considerable research has already been carried out on supported (2-5) and unsupported (6-14) Au-Pt compositions. In the course of past research it was found that depending upon the procedure employed for the preparation of supported Au-Pt, alloying did or did not take place (3, 4).

The Au-Pt system displays a miscibility gap, within which a Pt-rich and an Au-rich phase coexist (15). At 400°C the latter, extending up to about 18 wt% Pt, is a disordered substitutional solid solution. Under conditions of thermal equilibrium it is expected that Au will segregate at the surface, due to its lower

sublimation energy. This has been confirmed in studies on Au-Pt films by H₂ chemisorption and work function measurements (10, 12). It was also found (11) as expected, that surface composition remained essentially constant as the bulk composition was modified within the range of the miscibility gap. Adsorption-desorption of H₂ and CO has been employed to derive a more detailed picture of the film surface (9, 10). From these studies it was concluded that Au acted as a diluent for Pt, which formed atomic "ensembles" of different sizes. Au additions simply influenced the number of the smaller Pt "ensembles," causing variations in the relative intensity of the desorption peaks. In supported Au-Pt (particle size 500-2000 Å) these conclusions seemed to be confirmed (4, 5), but questions on the possible influence of the size of the smaller particles, of the preparative conditions, and of the catalytic reaction itself remained unresolved. Indeed, with very small particles ($\lesssim 25$ Å) the surface composition may become controlled by surface tension effects, or if thermal equilibration is not achieved, particle nucleation and growth effects may be determinant. If nucleation rates are appreciably different between the two metals one type of metal particle will be formed initially to be subsequently covered, partially or totally, by the other metal, irrespective of thermodynamic predictions. Nucleation and growth of the two metal particles may also be dependent upon the type of support employed and its pretreatment prior to contact with metal precursor salts. If under pretreatment of the catalyst and during reaction rate measurements no appreciable sintering or thermal equilibration takes place, surface composition is essentially fixed by preparative manipulations. The reaction employed to test the activity of the catalytic surface reflects the geometrical and electronic requirements of controlling adsorption-desorption steps,

and surface models thus developed are dependent upon reaction kinetic characteristics. It becomes necessary to test these models with investigations on several reactions, possessing alternate requirements.

In view of these considerations it was deemed interesting to submit the supported Au-Pt system to further scrutiny in view of seeking answers to the following questions: If alloys are not formed, as indicated by standard characterization methods, does the catalytic activity vary with overall composition in a way that it may be expected from a noninteracting particle of different catalytic activity? Within the phenomena controlling the physicochemical behavior of small metal particles on a ceramic support, is alloy formation the catalytically important interaction or are there more subtle ones which escape detection by the standard techniques employed for the definition of alloy formation? This question seems especially relevant, since in the range of small supported particles every physical technique employed for particle characterization yields results biased by the effect underlying the technique employed. Is the nature of the catalytic step an important consideration for the observation of interactions between the two metals outside the range of alloy formation?

These questions prompted us to investigate the catalytic activity of supported Au-Pt preparations in hydrogen and oxygen transfer reactions. This communication summarizes the results obtained in the preparation and characterization of supported Au-Pt samples and in their catalytic activity for hydrogen transfer reactions, while in a subsequent communication we shall present the results on oxygen transfer reactions. Because of the interest in employing well-defined and constant gas phase redox reaction conditions, isotopic exchange reactions have been used throughout.

EXPERIMENTAL

Materials

Reagent grade Au and Pt chlorides, SiO₂ (Davison Grade 62, surface area 340 m²/g), high purity (99.99%) H₂ and He were employed. H₂ was used after purification by passage through Pd asbestos at 400°C, followed by a molecular sieve trap, kept at liquid N₂ temperature, while He was passed through Cu turnings, 400°C, followed by a charcoal trap cooled at liquid N₂ temperature. Reagent grade benzene (BE) and cyclohexane, CHA, 14C-BE (*BE), 0.5 mCi (radioactive purity 99.3%) were employed without further purification. *BE was diluted with BE to about 0.1 mCi as needed. Supported Au-Pt catalysts were prepared by impregnation of the support with a solution of H₂PtCl₆ and HAuCl₄ of the desired concentration. The amount of the impregnated solution was slightly greater than the pore volume of the silica gel (1.15 cm³/g). After impregnation the catalysts were dried at 120°C for about 24 hr.

Two series of catalysts with various Au/Pt ratios were prepared. In one series the total amount of metal was kept constant at about 0.7 wt% (Series A), while in a second series the amount of Pt was kept constant at about 0.7 wt% (Series B). In the latter the total amount of metal ranged between 1.03 and 6.13 wt%. Two sets of SiO₂-supported catalysts containing Au or Pt only were also prepared. A summary of the pretreatments before adsorption and reaction rate measurements is presented in Table 1. Preparation and pretreatment of the Pt- or Au-supported catalysts were identical to those employed for the Au-Pt series. Catalyst composition was determined by atomic absorption and neutron activation analysis. In the latter analysis separation of the neutron irradiated components in the Au-Pt series was carried out by dissolution in HNO₃; radiation counting was performed sepa-

TABLE 1
Preparation and Pretreatment Conditions of Supported Au-Pt Catalysts

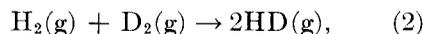
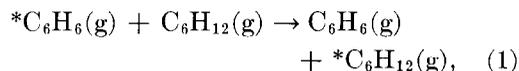
Total metal (wt%)	Au (atom %)	Treatment		
		H ₂ adsorption	O ₂ adsorption	Reaction
Series A				
0.55	100	Heated in air, 70 Torr,	After measurement of	(BE + CHA)
0.59	70	300°C 1 hr; heated	H ₂ adsorption, heated	Heated in H ₂ , 400°C,
0.53	52	in H ₂ , 70 Torr, 400°C,	in vacuum, 450°C,	2 hr; in He, 1 hr,
0.83	23	1 hr; evacuated	30 min, cooled to	cooled to reaction tem-
0.51	0	450°C, 30 min, cooled	200°C	perature
		to room temperature		
Series B				
6.13	89			(H ₂ + D ₂)
2.31	68			Heated in H ₂ , 400°C,
1.40	45			2 hr; cooled to reac-
1.03	28			tion temperature

rately on the Au and Pt fractions. It was found that the results of both methods of analysis differed by less than ± 2.4 wt%.

Catalyst characterization included H₂ and O₂ adsorption, wide-angle X-ray scattering (WAXS) and electron spectroscopy for chemical analysis (ESCA). Adsorption measurements were carried out in a conventional glass vacuum system employing a thermocouple vacuum gauge. The experimental details of the adsorption apparatus have already been reported (16). WAXS spectra were obtained by means of an X-ray diffractometer with a resolution of 0.005°; crystallite size was calculated with the aid of the Scherrer expression, after correction for the instrument contribution (17). CuK α wavelength was used. The ESCA patterns were recorded with a Physical Electronic Industries Spectrometer in which unmonochromatized MgK α line was the exciting radiation. An electron flood gun was used to control charging effects. Samples were prepared by compacting the catalyst powder on an In base (18). For all samples the measurement sequence and procedure was the same. The sequence of the spectral lines observed was O (1s), Si (2p), Pt (4f), and Au (4f). A 20-eV range was recorded

in each case. Signal intensity was obtained by integrating the area under the recorded peaks. It was felt that the most reliable comparison between samples would be obtained by using the Si (2p) intensity as an internal reference for each sample. In fact, it was found that the absolute magnitudes of the Si (2p) intensities for several of the samples ranged over a few percent only. By means of averaging values from several measurements a relative standard deviation of $\pm 1.5\%$ was computed.

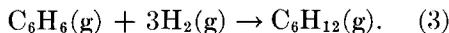
Catalytic activity for hydrogen transfer reactions was assessed by measuring the rate of the isotopic exchange reactions:



where *C is a carbon-14 atom.

A conventional flow system was employed for both reactions. The apparatus included metering valves, flow meters, gas purifying devices, constant temperature saturators and tubular reactor. It was operated at 1 atm total pressure. For reaction (1) known amounts of BE, CHA, and *BE were introduced into the reactor using He as a carrier gas. The rate of

reaction (1) was measured under conditions of equilibrium for the hydrogenation of BE,



This condition was fulfilled by feeding to the reactor, in addition to BE and CHA, H_2 corresponding to the partial pressure in equilibrium (3). The establishment of reaction equilibrium (3) was ascertained by analyzing the composition at the reactor inlet and the reactor outlet and obtaining similar values. Furthermore, whenever the H_2 partial pressure in the feed was changed from the equilibrium value the reactor inlet and outlet compositions differed, indicating the occurrence of a net reaction (3). The reactor temperature was 205°C, contact time in the range of 10 to 30 sec; from 1 to 3 cm³ of 100 to 170-mesh catalyst (0.4–1.2 g) was employed. Product analysis for reaction (1) was performed by an in-line gas chromatograph (HP Model 5750 with flame detector) equipped with a 5-ft column filled with 5% B34 + 5% DIPP on Chrom-W (60–80 mesh). Fractions eluting from the g.c. were collected in a solution of PPO in toluene for liquid scintillation analysis. No side reactions were detected. Experiments were performed at various flow rates and gas phase compositions to ascertain the absence of diffusional limitations. For each set of conditions, several runs were carried out.

From these experiments it was estimated that the error in the rate coefficient k_c (see below) was $\pm 20\%$ and in the pressure exponent m was $\pm 5\%$.

For reaction (2) prepurified H_2 and D_2 (CP grade) were passed through Pd asbestos at 400°C and molecular sieve traps kept at liquid N_2 temperature. High purity N_2 , employed as carrier gas, was further purified by passage through Cu turnings at 400°C, followed by a liquid N_2 molecular sieve trap. Reactor temperature was generally kept at -78°C . Gas analysis was carried out mass spectroscopically. The mass spectrometer (AEI-MS10) was calibrated with known amounts of H_2 and D_2 . The ms sensitivity for HD was assumed to be the average between that for H_2 and for D_2 . Generally 10 mg of catalyst mixed with 0.2 g of SiO_2 were employed. A constant ratio $p_{\text{D}_2}/p_{\text{H}_2} = 1$ was used throughout. From 2 to 4 runs were carried out for each set of conditions; the error in the rate coefficient k_{D} (see below) was estimated at $\pm 30\%$.

RESULTS

Catalyst Characterization

H_2 and O_2 adsorption isotherms were measured on supported Pt and supported Au–Pt, while on Au the adsorption of O_2 was carried out. O_2 adsorption on Au was found to be a reliable method for the

TABLE 2
 H_2 and O_2 Adsorption on Pt– SiO_2

Pt (wt%)	H_2 uptake ^a $\left[\frac{\text{cm}^3 \text{ (STP)}}{\text{g cat}} \right] \times 10^2$	O_2 uptake ^b $\left[\frac{\text{cm}^3 \text{ (STP)}}{\text{g cat}} \right] \times 10^2$	$\frac{\text{O}_2}{\text{H}_2}$	Percentage exposed	Particle diameter (Å)
0.26	4.73	8.5	1.8	32.1	35
0.51	15.3	19.6	1.3	52.9	21
1.14	24.0	30.3	1.3	36.8	31
1.28	20.8	—	—	28.4	40
3.25	57.8	80.1	1.4	31.0	37

^a 20°C, p_{H_2} 0.15–0.20 Torr.

^b 200°C, p_{O_2} 0.2–0.7 Torr.

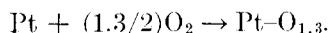
TABLE 3
 H₂ and O₂ Chemisorption on Au-Pt-SiO₂ Preparations

Total metal (wt%)	Au overall (atom %)	H ₂ uptake ^a $\left[\frac{\text{cm}^3 \text{ (STP)}}{\text{g cat}} \right] \times 10^3$	O ₂ uptake ^b $\left[\frac{\text{cm}^3 \text{ (STP)}}{\text{g cat}} \right] \times 10^3$		Percentage exposed		Surface composition (Au %)
			Total metal	Au only	Pt	Au	
Series A							
0.59	70	1.46	3.50	1.60	14.5	13.7	69
0.53	52	4.35	7.60	1.95	29.5	24.9	47
0.83	23	10.30	17.40	4.01	28.0	74.2	44
Series B							
6.13	89	3.96	7.30	2.15	10.0	1.53	52
2.31	68	11.30	15.20	0.51	26.5	1.14	8
1.40	45	14.20	19.70	1.24	32.2	6.92	15
1.03	28	15.50	21.20	1.05	36.4	12.70	12

^a 20°C, p_{H_2} 0.15–0.20 Torr.

^b 200°C, p_{O_2} 0.2–0.7 Torr.

calculation of the Au particle size (16). To obtain separate values of the surface area of the two metals in the bimetallic preparations, independent measurements of O₂ adsorption and H₂ adsorption were carried out. The assumption was made that the H₂ and O₂ stoichiometry found on supported Pt and the O₂ stoichiometry found on supported Au did not change in the mixed Au-Pt supported preparations. From the H₂ uptake on Au-Pt, the percentage of Pt exposed was calculated using the adsorption stoichiometry $\text{Pt} + \frac{1}{2}\text{H}_2 \rightarrow \text{Pt} - \text{H}$. H₂ chemisorption was measured at 20°C and H₂ partial pressure of 0.15 to 0.20 Torr (1 Torr = 133.33 N m⁻²). No adsorption of H₂ could be detected on the SiO₂ support or on the Au preparation. The O₂ adsorption was measured at 200°C and O₂ partial pressure of 0.2 to 0.7 Torr. Under these conditions, O₂ is chemisorbed on both Pt and Au. The Pt-O surface stoichiometry at 200°C was established by using Pt catalysts of known surface area (determined by H₂ chemisorption). The average O₂ stoichiometry found at 200°C was



A summary of experimental results on Pt-SiO₂ is presented in Table 2. O₂ adsorbed on Au in the Au-Pt preparations was calculated by subtracting the amount of O₂ adsorbed on Pt, determined by the Pt-O stoichiometry at 200°C, from the total O₂ uptake.

The percentage of Au exposed was calculated by using the O₂ adsorption stoichiometry: $2\text{Au} + \frac{1}{2}\text{O}_2 \rightarrow \text{Au}_2\text{O}$. Au surface area derived from this stoichiometry were found to be consistent with the results from WAXS and Transmission Electron Microscopy (16). In Table 3 the results obtained using the above procedure are reported. From the percentage exposed of both metals, the surface composition was calculated and it is reported in the last column of Table 3. The percentage of Pt exposed is plotted versus the overall composition in Fig. 1.

No Pt was detected in the WAXS analysis of Series A and Series B preparations. This is taken as an indication of small particle size of Pt in agreement with the conclusions from H₂ adsorption (Table 2). An extensive Au-Pt alloying is clearly absent, since the lattice constant

of Au in the Au-Pt preparations was found to be similar to that of Au. In contrast to Pt, Au was easily detectable by WAXS (Table 4). In some Au preparations, diffraction from different crystal planes yielded different particle dimensions, indicating large anisotropy in particle growth. This effect was also reported in an earlier study of the supported Au (19). Most likely, these observations are an indication of differences in nucleation and growth rate between Au and Pt particles. Indeed, the equivalent particle diameter of Pt in the Au-Pt preparations, calculated from the Pt surface area, is one order of magnitude (or more) smaller than that of Au, irrespective of bulk composition. This is taken as an indication that Pt nucleation was faster than that of Au, and, consequently, local depletion of Pt salt during particle growth set in. These events will eventually lead to a mixed Au-Pt crystal particle.

Analysis of the ESCA results was carried out by dividing the areas of the O_{1s} , Si_{2p} , Pt_{4f} , and Au_{4f} peaks, by the corresponding photoelectric cross sections (20), and expressing them as percentages. The percentage exposed of Pt and Au was calculated by means of the expression: $D = R/W \cdot K$ where R is the metal-Si ratio, from ESCA peak ratios, W is the weight percent of the metal, D is the percentage exposed, and K is a constant. The value of K , characteristic for each

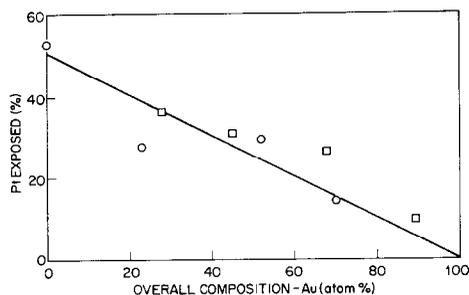


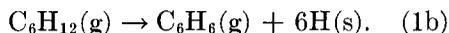
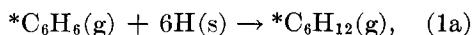
FIG. 1. Percentage of Pt exposed from H_2 chemisorption versus overall composition, in SiO_2 -supported Au-Pt; \circ , Series A; \square , Series B.

TABLE 4
WAXS Characterization of Au-Pt- SiO_2
Preparations

Total metal (wt%)	Au (atom %)	Au crystallite diameter (\AA)				
		(111)	(200)	(220)	(311)	(222)
Series A						
0.55	100	450	347	261	—	—
0.59	70	450	335	—	—	—
0.53	52	477	332	—	—	—
0.83	23	240	—	—	—	—
0.51	0	—	—	—	—	—
Series B						
6.13	89	363	260	248	246	234
2.31	68	242	230	212	213	—
1.40	45	215	186	—	—	—
1.30	28	318	—	—	—	—

element, is obtained using a sample with known values of W and D . From the percentage exposed of Pt and Au the surface composition was calculated (Table 5). The results obtained are plotted in Figure 2 together with the values of surface composition from H_2 , O_2 chemisorption.

Hydrogen transfer between benzene and cyclohexane. It is assumed that reaction (1) takes place via the following sequence of adsorption-deposition steps (1):



Since reaction step (1b) is the reverse of reaction step (1a) and equilibrium conditions prevailed during the course of reaction (1), the rate of the latter and the

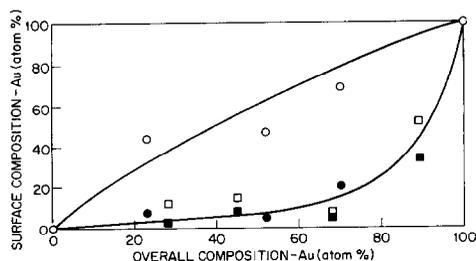


FIG. 2. Surface versus overall composition of SiO_2 -supported Au-Pt particles. Series A: \circ , by H_2 , O_2 chemisorption; \bullet , by ESCA. Series B: \square , by H_2 , O_2 chemisorption; \blacksquare , by ESCA.

TABLE 5
ESCA Characterization of Au-Pt-SiO₂
Preparations

Total metal (wt%)	Au overall (atom %)	Surface composition ^a (Au atom %)
Series A		
0.55	100	100
0.59	70	20
0.53	52	5
0.83	23	8
0.51	0	0
Series B		
6.13	89	34
2.31	68	6
1.40	45	8
1.03	28	3

^a Calculated by means of the expression $1/(1 + D_{Pt}(Pt)_t/D_{Au}(Au)_t)$, where D_{Pt} , D_{Au} are the Pt and Au dispersion, respectively, and $(Pt)_t$, $(Au)_t$ are the total Pt and Au atoms, respectively.

rates of reaction steps (1a) and (1b) are similar. Considering reaction step (1a), its rate is given by:

$$\frac{1}{W} \frac{dn_{*CHA}}{dt} = k_c p_{*BE} - k'_c p_{*CHA} \quad (4)$$

where W , n_{*CHA} , p_{*BE} , and p_{*CHA} are the catalyst weight, moles of *CHA, and partial pressures of *BE and *CHA, respectively, and k_c , k'_c are the forward and reverse rate coefficients of reaction step (1a). Introducing the equilibrium condition and integrating Eq. (4) for a flow reactor one obtains (1):

$$k_c = \frac{\dot{V}}{WRT} \frac{1}{1 + 1/\beta} \ln \frac{1}{1 - \alpha_e} \left[\frac{\text{moles}}{\text{g} \times \text{sec} \times \text{atm}} \right], \quad (5)$$

where \dot{V} is the total volumetric flow rate measured at the temperature T , R is the gas constant, $\beta = p_{CHA}/p_{BE}$, the reaction conversion $\alpha_e = p_{*CHA}/(p_{*CHA})_e$; the suffix e refers to equilibrium conditions. The

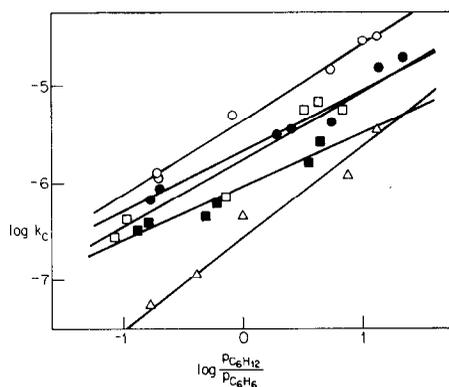


FIG. 3. Rate coefficient, k_c , for reaction (1) as a function of $\beta = p_{CHA}/p_{BE}$, 205°C, catalyzed by Au-Pt-SiO₂; Series A: ○, 0.51 wt% Pt; ●, 0.61 wt% Au-Pt; □, 0.83 wt% Au-Pt; ■, 0.53 wt% Au-Pt; △, 0.59 wt% Au-Pt.

influence of the gas phase composition β , upon the rate coefficient k_c , for catalysts of Series A at 205°C is shown in Fig. 3. Similar results for Series B catalysts and for Pt-SiO₂ are reported in Figs. 4 and 5. In all cases, k_c increased with β .

In the derivation of the Eq. (4), the reaction rate was assumed to be first order in p_{*BE} and p_{*CHA} . The actual dependence is obtained from rate measurements at

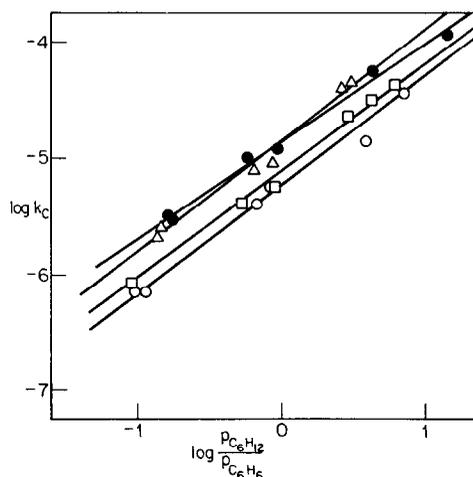


FIG. 4. Rate coefficient, k_c , for reaction (1) as a function of $\beta = p_{CHA}/p_{BE}$, 205°C, catalyzed by Au-Pt-SiO₂; Series B: ○, 6.13 wt% Au-Pt; △, 2.31 wt% Au-Pt; ●, 1.40 wt% Au-Pt; □, 1.03 wt% Au-Pt.

various β 's. The results are expressed by means of the equation

$$k_e = k_e^\circ \beta^m \quad (6)$$

where k_e° is the rate constant for reaction (1) and $0 < m < 1$. The values of k_e° and m calculated from Eq. (6) are reported in Table 6 for all three set of catalysts examined. Under the experimental condition used, the rate of reaction (1) on Au was found to be negligible.

H₂-D₂ equilibration. Since the results on the rate of reaction (2) showed that the rate increased with $(p_{H_2})_{total}$, it was assumed that a likely reaction scheme was the following:



Consider the rate of reaction step (2a)

$$\frac{V}{WRT} \frac{dp_{HD}}{dt} = k_D p_{H_2} - k_D^b p_{HD} \quad (7)$$

where V , k_D , k_D^b are the volume of the catalyst bed and the forward and backward rate coefficient of reaction step (2a),

TABLE 6

Rate Constant, k_e° , [Eq. (6)], Exponent m [Eq.(6)], Surface Collision Efficiency γ_e [Eq. (10)], for Reaction (1) Catalyzed by Pt-SiO₂ and Au-Pt-SiO₂ Preparations, 205°C

Total metal (wt%)	Au (atom %)	k_e° [$\frac{\text{molecules}}{\text{Pt(s)} \times \text{sec} \times \text{atm}}$]	m	$\gamma_e \times 10^9$
0.26	—	0.47	0.79	4.75
0.51	—	0.29	0.76	2.93
1.28	—	0.42	0.76	4.25
3.25	—	0.20	0.81	2.02
Series A				
0.55	100	^a	^a	^a
0.59	70	0.22	0.94	2.22
0.53	52	0.33	0.56	3.34
0.83	23	0.15	0.73	1.52
0.51	0	0.29	0.76	2.93
Series B				
6.13	89	1.64	0.95	16.58
2.31	68	1.39	0.94	14.05
1.40	45	1.12	0.83	11.32
1.03	28	0.45	0.94	4.55

^a No detectable reaction on Au.

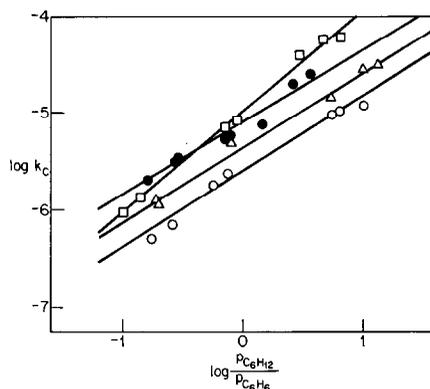


FIG. 5. Rate coefficient, k_e , for reaction (1) as a function of $\beta = p_{CHA}/p_{BE}$, 205°C, catalyzed by Pt-SiO₂; O, 0.26 wt% Pt; Δ , 0.51 wt% Pt; \bullet , 1.28 wt% Pt; \square , 3.25 wt% Pt.

respectively. Introducing the reaction conversion $\alpha_D = (\gamma_t - \gamma_0)/(\gamma_e - \gamma_0)$, where $\gamma = p_{HD}/(p_{H_2})_0$, eliminating k_D^b and integrating, Eq. (7) yields:

$$k_D = \frac{V}{WRT\tau} \gamma_e \ln \frac{1}{1 - \alpha_D} \left[\frac{\text{moles}}{\text{g atm sec}} \right], \quad (8)$$

where τ is the contact time.

The validity of Eq. (7) was tested at various τ 's and the calculated values of k_D were found to be within $\pm 30\%$. Typical values of k_D for catalyst 2.31 wt% (68% Au) on SiO₂ at -78°C are plotted versus $(p_{H_2})_{total}$ in Fig. 6. The values of the rate constant k_D° for both series of

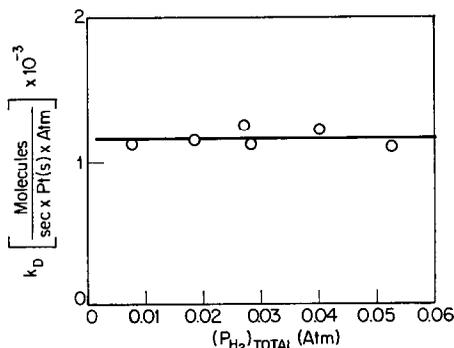


FIG. 6. Rate coefficient, k_D , for reaction (2) as a function of $(p_{H_2})_{total}$, -78°C , catalyzed by 2.31 wt% Au-Pt on SiO₂.

TABLE 7

Rate Constant for Reaction (2), k_D° , and Collision Efficiency γ_D , for Au-Pt-SiO₂ Preparations, $T = -78^\circ\text{C}$

Total metal (wt%)	Au (atom %)	k_D° molecules [Pt(s) × sec × atm]	$\gamma_D \times 10^7$
Series A			
0.55	100	—	—
0.59	70	525	5.4
0.53	52	575	6.0
0.83	23	630	5.5
0.51	0	1130	11.7
Series B			
6.13	89	775	8.0
2.31	68	1150	11.9
1.40	45	1300	13.5
1.03	28	625	6.4

Au-Pt preparations are reported in Table 7. K_D° is defined by the expression $k_D = k_D^\circ (p_{\text{H}_2})_{\text{total}}^n$ (9). In all cases the value of $n = 0$. In the range $10 < p_{\text{H}_2} < 100$ Torr, $-78 < T < 30^\circ\text{C}$ the calculated activation energies were 2.5 to 3.0 kcal/mole. This value is to be compared with earlier determinations on wire, sponge, and Pt black ranging between 0.5 to 7.5 kcal/mole (21), between 0.5 to 3.0 (21) kcal/mole on Pt-SiO₂ and between 2.5 to 3.0 kcal/mole (22) on Pt films.

DISCUSSION

Catalyst Characterization

The significant experimental results reported in the previous section on catalyst characterization are:

1. In Series A and B, the addition of Au caused a decrease in the percentage of Pt exposed (Fig. 1);

2. Pt crystallites and Au-Pt alloy formation could not be detected by WAXS;

3. largely nonspherical Au particles, with size ranging between 200 and 500 Å, have been detected by WAXS. Particles became more spherical as the Au content increased;

4. the surface compositions in Series B preparations deduced from H₂ and O₂

chemisorption and from ESCA were similar and indicated a Pt enrichment at the surface (Fig. 2). In Series A the H₂ and O₂ chemisorption yielded a surface composition higher in Au than that deduced from ESCA (Fig. 2).

Results under item 1 may be explained by means of two hypotheses, namely, that (a) upon increasing the amount of Au, Pt particle size increased and the percentage of Pt exposed decreased; (b) particles of mixed Au and Pt were formed and Au covered Pt. Since Pt crystallites with size $\lesssim 25$ Å could not be detected by WAXS (item 2 above), hypothesis (a) may be ruled out.

In earlier studies on SiO₂ supported Au-Pt catalysts, it was found that alloy formation could be achieved by coreduction of the mixed Au and Pt salt solution at 80°C with hydrazine but not by support coimpregnation and high temperature (450°C) reduction with H₂. The coimpregnation catalysts did not show alloying even after treatment at 610°C for 84 hours (3). However, if oxidation at 77°C and reduction at 200°C were repeatedly performed on the coimpregnated catalysts, alloy formation was obtained (4).

Since from the WAXS spectra of Au there was no evidence of alloy formation (item 2 above), we conclude that two kinds of particles were present containing aggregates of Au and Pt atoms and of Au atoms only. There was no direct evidence for the presence of particles containing Pt atoms only. The Au aggregates were considerably larger than those containing Pt and Au. We envision that, initially, both metals nucleated separately on the support surface; assuming that Pt had a faster nucleation rate than Au, a larger number of Pt embryos were formed. At a later stage of the particle formation as a consequence of local enrichment in the Au salt, and/or higher mobility of Au particles already formed (lower melting point and/or

higher vapor pressure, whichever transport mechanism may have been responsible for Au aggregation) deposition of Au upon the Pt particles occurred.

The presence of particles containing atomic aggregates of Au and Pt raises the question of composition of their surface. To this end we shall compare the results from H_2 chemisorption and from ESCA. Since we estimate that the ESCA sampling depth was about 12 Å, a comparison between the percentage of Pt exposed derived from ESCA and that obtained from H_2 chemisorption is indicative of the compositional profile in the immediate subsurface. In contrast to the samples of Series B, in those of Series A the composition was not uniform. The comparison may be easily carried out using the results presented in Fig. 2. Indeed, inspection of Fig. 2 shows that for Series A samples, there was disagreement between surface composition from chemisorption and from ESCA.

In conclusion, Series A and B preparations included particles of mixed Au-Pt aggregates, of individual Au aggregates and, likely, of individual Pt aggregates also. The central part of the mixed Au-Pt particles was constituted by Pt or by a Pt-rich Au-Pt alloy. In Series A preparation, an Au enrichment at the surface layer was found, but it was not clear how morphologically this enrichment was distributed at the surface itself (uniform layer versus rafts or islands). Thus, depending upon the interplay of conditions prevailing during particle formation and growth, subtle variations in composition and local morphology at the surface of mixed aggregates of Au and Pt were induced into preparations possessing similar overall Au/Pt ratios. Since the single different condition between Series A and Series B was the concentration of the original salt solution, there is a strong implication that the dissimilar surface composition obtained in the two series

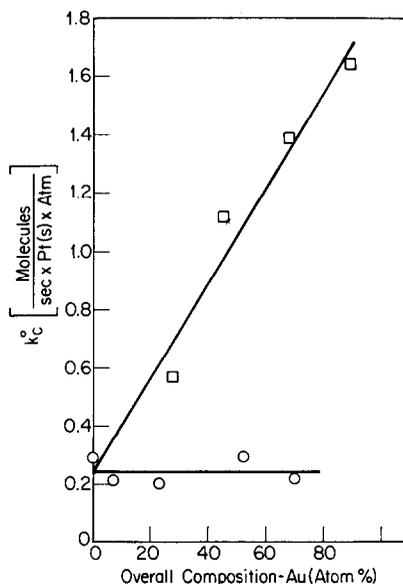


Fig. 7. Rate constant, k_c^0 , for reaction (1) [Eq. (6)] versus overall composition in Au-Pt-SiO₂ preparation, 205°C; ○, Series A; □, Series B.

reflects the interplay of the nucleation and growth rates of the two metals at the support surface.

Hydrogen transfer between BE and CHA. The significant conclusions which may be derived from an inspection of Figs. 3, 4, and 5 and Table 6 are the following:

- (a) Reaction (1) took place readily at 205°C under the conditions of reaction equilibrium (3) on all catalysts investigated, except for Au. There was no detectable presence of side reactions;
- (b) the rate of reaction increased with the ratio $\beta = p_{CHA}/p_{RE}$ (Figs. 3, 4, 5);
- (c) catalysts of Series A and B showed differences in the reaction rate (Table 6). The activity of catalysts of Series A, when expressed in terms of surface Pt atoms, was independent of the overall particle composition and similar to that measured for supported Pt, while that of Series B increased with increasing Au content (Fig. 7);
- (d) in Pt-SiO₂ the rate of reaction was independent of the amount of Pt (Table 6);

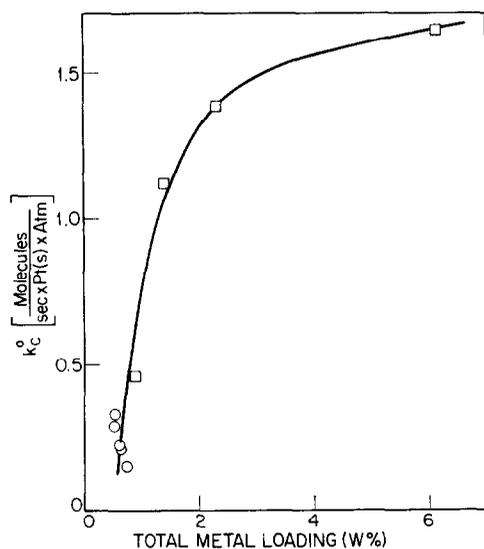


FIG. 8. Total amount of metal and rate constant, k_c^0 for reaction (1) in Au-Pt-SiO₂ catalysts; ○, Series A; □, Series B.

(e) for all catalysts studied the value of m (Eq. 6) was constant over a range of β of about two orders of magnitude, and $0.56 < m < 0.95$ (Table 6).

Results under (a) are consistent with earlier conclusions on the rate of reaction (1) over several noble metal catalysts, which showed comparable activity at temperatures as low as 117°C (1). The only difference between the two studies is in the value of the equilibrium hydrogen partial pressure; in the earlier investigation the hydrogen partial pressure was on the order of 10^{-3} Torr, molecular H₂ was not fed with BE and CHA. In the present study, because of the higher temperature and the desirability of directly assessing the establishment of equilibrium (3), molecular hydrogen corresponding to the equilibrium partial pressure of reaction (3) was fed with BE and CHA. Also, in the earlier work it was found that the reaction rate increased with β [item (e) above]. The fact that the activity of Series A catalysts was independent of the Au content and similar to that of supported Pt only indicates that Pt sites responsible for

the reaction were similar, geometrically and energetically, on all these catalysts. The compelling conclusion is that Au simply acted as a diluent and no interaction between Au and Pt was evident. This role of Au is consistent with previous studies on Au-Pt films and foils (10).

This situation, however, is not reflected in the activity of catalysts of Series B. In these preparations increasing overall Au content increased their catalytic activity. At the Au/Pt ratio of 7/3, the value of k_c^0 on Series B was seven times higher than the value on the catalyst of similar Au/Pt ratio from Series A. It should be mentioned that in previous studies on supported Ru-Cu and Os-Cu catalysts for ethane and cyclohexane hydrogenolysis, it was found that the activity (per surface Ru atom) decreased with increasing Cu, while it was not modified for cyclohexane dehydrogenation (23).

It is tempting to relate the effect of Au on catalytic activity of Series B to the subtle differences, as exemplified by the homogeneous composition of the surface layers of the mixed Au-Pt particles found in preparations B in contrast to the non-homogeneous composition of Series A and discussed in the previous section. The analysis of the experimental results does not permit a detailed topological description of the differences in composition. It is, however, conceivable that the compositional homogeneity of Series B formed the basis for Au-Pt interaction which modified the surface reactivity of Pt. In earlier studies on supported Fe-Pt catalysts, it was concluded that the extent of formation of mixed aggregate of Fe and Pt varied monotonically with the Fe concentration at constant Pt concentration (24). If a similar effect was present in the Au-Pt supported preparations, it may be concluded that the extent of the interaction between Pt and Au should increase with the amount of Au at constant Pt content. The results of the reaction rate

constant plotted against total metal content for Series A and B support this contention (Fig. 8). Further insight into the Au-Pt interaction may be obtained by consideration of the work function of Pt and its variation upon additions of Au. From previous work function measurements on equilibrated Au-Pt films (12) it may be concluded that upon additions of Au to Pt the Fermi level of Pt increases quite sharply initially, leveling off for larger Au additions. We shall assume that in our preparations whenever an electronic interaction between Au and Pt sets in, it involved the raising of the Fermi level of Pt with increasing amount of Au. To find out the effect of the resulting more electron rich Pt surface site on the catalytic activity of the site for reaction (1) we need to turn to information derived from the exponent m [Eq. (6)]. To this end, we shall consider that the rate of reaction (1) increased with β (m positive) indicating that the concentration of the controlling surface intermediate increased with the ratio $p_{\text{CHA}}/p_{\text{BE}}$. In the reaction sequence (1a), (1b) the intermediate has been formally indicated as H(s), electronically, however, it may involve both CHA and BE. We shall assume that the bonding of this intermediate included electron backdonation from the metal to the adsorbate. Finally, it should be realized that the value of m governed the nature of the adsorption isotherm,

$$[\text{H(s)}] \propto (p_{\text{CHA}}/p_{\text{BE}})^m,$$

in such a way that for a given $p_{\text{CHA}}/p_{\text{BE}}$ ratio, $[\text{H(s)}]$ increased with m . Since the value of $[\text{H(s)}]$ corresponded to the fraction of surface covered under a given $p_{\text{CHA}}/p_{\text{BE}}$ ratio, we may employ the values of m to ascertain variations in surface coverage of the reactive intermediate.

We have now the possibility to explore qualitatively the effect of a more electron rich Pt site (as a consequence of Au interaction) on the rate of reaction (1).

Indeed, under the conditions described, raising the Pt Fermi level increased the coverage of the surface, since more electrons flow into the lower-lying surface level of the adsorbate, whose energy was fixed by the $p_{\text{CHA}}/p_{\text{BE}}$ ratio which was held constant throughout the course of reaction (1). An increase in surface coverage upon additions of Au to Pt should result, as indicated previously, in a higher m value. We turn now to the computations reported in Table 6. The average value of m for Pt is 0.77, while for Series B it is 0.92. The change is in the expected direction. For Series A the average value of m is 0.75. For the latter series, in which no evidence of Au-Pt interaction was found, the value of m is practically similar to that for Pt. This is considered significant.

The reaction collision efficiency, γ_c , was calculated with the aid of the expression (1)

$$\gamma_c = k_e^\circ (2\pi MkT)^{\frac{1}{2}}, \quad (10)$$

where M and k are the average molecular mass and the Boltzman constant, respectively. The computed values are collected in Table 6. The values ranging between about $(1 \text{ to } 15) \times 10^{-9}$ are an indication of the low probability of occurrence of reaction (1).

H₂-D₂ equilibration. The results reported in Fig. 6 and in Table 7 may be summarized as follows:

1. The rate of the H₂-D₂ equilibration at -78°C was first order in $(p_{\text{H}_2})_{\text{total}}$;
2. when expressed in terms of surface Pt atoms, the catalytic activity of Series A and Series B was quantitatively similar;
3. the activity was independent of the overall composition of the sample (Fig. 9);
4. surface collisional efficiencies at -78°C were about 10^{-7} , or two orders of magnitudes higher than those for reaction (1) at 205°C.

These conclusions have a rather simple and direct interpretation. Indeed, assuming

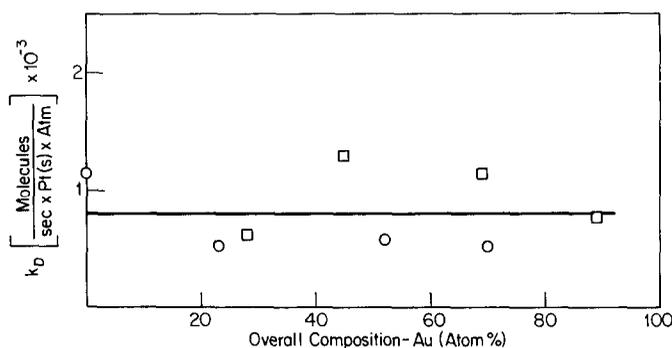


FIG. 9. Rate Constant, k_D° , for reaction (2) and overall composition in Au-Pt-SiO₂ preparations, -78°C , $10 < (p_{\text{H}_2})_{\text{total}} < 100$ Torr, $p_{\text{H}_2}/p_{\text{D}_2} = 1$; \circ , Series A; \square , Series B.

that H₂ adsorption is represented by the reaction $\text{H}_2 \rightleftharpoons 2\text{H}$, its Langmuir formulation gives $\theta = bp_{\text{H}_2}^{1/2}/1 + bp_{\text{H}_2}^{1/2}$, where θ is the fraction of surface covered by H₂ and b the adsorption equilibrium constant. Taking $bp_{\text{H}_2}^{1/2} \gg 1$, $\theta \cong \text{constant}$ and the rate of reaction (2) $\propto \theta p_{\text{H}_2} = \propto p_{\text{H}_2}$ (item 1 above). The possible influence of electronic interactions between Au and Pt on the surface population of the reactive intermediate cannot be kinetically detected whenever the steady state surface coverage corresponds to a bare or to a fully covered surface. The experimental observation that in this instance $n = 0$ (Eq. (9)) indicates that reaction (2) took place on a fully covered surface. Collision efficiencies at -78°C were about two orders of magnitude higher than the collision efficiencies recorded for reaction (1) at 250°C .

CONCLUSION

The concept of sensitivity of a catalytic reaction to the structure of a surface implies the requirement for surface sites with specific coordination and characteristic two-dimensional structure. As the results of this study have shown, reaction (1) can be sensitive and insensitive to the composition of the surface layers and, consequently, to the structure of Pt aggregates in these layers. It has been argued that the presence or absence of sensitivity depends, *inter alia*, upon the extent of

surface covered by the reactive intermediate during reaction. There is no reason to believe that this condition is not shared by all catalytic reactions and that surface reactions may be responsive or not to the structure of the surface, depending upon kinetic conditions controlling the composition of the surface under steady state conditions, or, in other words, upon the extent of reaction conversion. Thus, the concept of reaction sensitivity should not be viewed as a set of static requirements between adsorbate molecules or molecular fragments and atomic surface sites but rather as a dynamic relationship which is a function of the extent of surface covered by the adsorbate molecules. This coverage, in turn, depends upon the position of the reaction steady state, and the reaction conversion. Two consequences follow from this view; namely, that (a) a reaction may be observed as structure sensitive or insensitive depending upon the extent of conversion, and (b) structure sensitive reactions may become, as a limiting case, structure insensitive at full surface coverage.

Stable bimetallic supported catalysts may be prepared with different surface activity from similar overall compositions. Preparative conditions may influence subtle distribution patterns of the two metals in the top surface layer and in the sub-surface. Whether this possibility implies

a kinetic role of the few atomic layers underneath the topmost is unclear. However, instances of interplay between surface catalytic activity and compositional variations in the subsurface resulting from the catalytic reaction are well known. Related to this latter possibility is the definition of the catalytic activity per surface Pt atom. Indeed, in this study a reaction rate constant (per surface Pt atom) on Pt-Au higher than on Pt has been observed. This realization brings forth the close correlation between the geometrical arrangements of the atoms, the morphology of the juxtaposition of the two metal aggregates, the composition of the particle surface and the electronic interactions between the two atomic species.

Effects deriving from particle morphology have already been described for unsupported bimetallic preparations (25), and this study has shown that they are also present in supported bimetallic preparations.

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