Catalytic Hydrogenation of Cyclohexene

4. The Effect of Sulfur on Supported Platinum

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The rate of turnover r_t for the gas-phase hydrogenation of cyclohexene on platinum catalysts in the absence or the presence of sulfur was measured at 273 K and pressures of H_2 and C_6H_{10} equal to 9.31 and 2.66 kPa. If the number of platinum sites is measured by means of hydrogen chemisorption, r_t is found to be the same for all catalysts and equal to 0.65 s^{-1} if it is assumed that one site corresponds to one hydrogen adatom. By contrast, if the number of platinum sites is measured by means of oxygen chemisorption or dihydrogen titration of prechemisorbed oxygen, r_t is constant only for the catalysts which are not contaminated by sulfur. For the others, values of r_t scatter depending on the amount of sulfur on platinum. It appears that adsorbed sulfur takes up oxygen, thus leading to excess values of the number of platinum sites. The constancy of r_t measured by hydrogen chemisorption on platinum with or without sulfur confirms the structure insensitivity of cyclohexene hydrogenation on that metal and the adequacy of hydrogen chemisorption as a method of counting platinum sites.

INTRODUCTION

Some poisons of metallic catalysts are selective, since they decrease differently the rates of *structure-sensitive and structure-insensitive* reactions (*1*). For example, sulfur reduces the rates of structure-insensitive reactions in proportion to the amount of surface covered (*1*). But the rate of hydrogenolysis of saturated hydrocarbons, a structure-sensitive reaction, is strongly decreased by sulfur (*2*). Yet, the mode of action of poisons on metals is not well understood (*3*) and further study of poisoned catalysts is highly desirable. In fact, it is not even known if the classical methods of determination of metallic surface areas—hydrogen, oxygen, or carbon monoxide chemisorption, or hydrogen and oxygen titration—can be applied to poisoned catalysts.

A previous study (*4*) of platinum catalysts on sulfated aluminas reduced with hydrogen at various temperatures has shown that if the platinum sites are counted by dioxygen titration of preadsorbed hydrogen, the turnover frequency r_t for the hydrogenation of benzene, a well-known structure-insensitive reaction (*5–7*), is not the same for all the catalysts, but decreases with increasing temperature of reduction and increasing initial percentage of sulfate in the alumina support, i.e., when the poisoning of platinum by sulfur increases (*1*). On the other hand, if the platinum sites are counted by alkene titration of chemisorbed hydrogen, r_t is constant whatever the extent of poisoning as expected for a structure-insensitive reaction (*1*). Thus the platinum surface area available for catalytic reactions on sulfur-poisoned catalysts seems larger when preadsorbed hydrogen is titrated with oxygen than when it is reacted with alkene. The difference between the two methods can be explained in two ways. First, hydrogen could be adsorbed on platinum atoms poisoned by sulfur, and this hydrogen could react with oxygen but not with alkenes. Alternatively, oxygen could be adsorbed, not only on the *free* platinum atoms but also on sulfur covering the poisoned platinum atoms.

In the first case, the ratio between the amount of oxygen consumed by the titration of chemisorbed hydrogen (OT) and the amount of hydrogen chemisorbed on the catalyst (HC) should be the same on *clean* and poisoned catalysts. Then, neither chemisorption nor titration of hydrogen can be used to measure the platinum surface area available for catalysis. In the second case, the poisoned surface should adsorb more oxygen than hydrogen, and hydrogen chemisorption would still be a good method for determining the active platinum surface area.

This paper reports a study of the chemisorption and titration of oxygen and hydrogen on several platinum catalysts with various degrees of poisoning and compares chemisorption with activity in the gas phase hydrogenation of cyclohexene in order to select the best method for measuring the active surface area of sulfur-poisoned catalysts. The reaction was chosen because of three previous studies in our laboratory where it was shown to be structure insensitive in the gas phase (8) and the liquid phase (9).

EXPERIMENTAL

The adsorption apparatus was a conventional gas volumetric system (10). The amounts of gas adsorbed on the catalysts were determined from pressure measurements with a Texas Instrument precision pressure gauge. An oil diffusion pump allowed a nominal vacuum in the apparatus of 10^{-3}–10^{-4} Pa. The sample was protected by a liquid nitrogen trap. Calibrated and dead volumes were determined using helium. Hydrogen and oxygen were stored in 2-liter bulbs after purification by passage respectively through a Milton Roy Company palladium thimble purifier and through zeolite cooled in Dry Ice-acetone. The reduced samples were pretreated for 1 h at room temperature under flowing dihydrogen in order to remove oxygen adsorbed on platinum, then outgassed overnight for about 10 h at 753 K. They were cooled to

room temperature under vacuum. Adsorption isotherms were determined at room temperature between 5 and 33 kPa. The amount chemisorbed was obtained by extrapolation to zero pressure of the linear parts of the isotherms.

The rate measurements were carried out at 273 K (ice + water) in a batch recirculation system (8) redesigned as described in detail elsewhere (11). The gas mixture was recirculated at 3 liters min^{-1} over the catalyst with a stainless-steel welded bellow pump. Cyclohexene was purified by passing through alumina at room temperature to remove oxygen and peroxides as described by Segal et al. (8). Hydrogen was purified by diffusion through a Milton Roy palladium thimble. Helium, used as a diluent to operate at atmospheric pressure, was passed through a glass coil cooled with liquid nitrogen. About 10 mg of prereduced catalyst was used for each run. In each experiment the initial pressures of cyclohexene and hydrogen were respectively 2.66 and 9.31 kPa. The analysis of the gas phase was carried out every 360 s in a Varian Aerograph chromatograph model A 90 P, equipped with a column of firebrick impregnated with 20 wt% Reoplex. Helium was used as a carrier gas.

After several trials, we selected a procedure which gave the best reproducible results and avoided a poisoning of the catalyst by hydrocarbon vapors in the absence of hydrogen (12). This procedure consisted first in a removal of air in the reactor either by a very short outgassing (2 min) with the rough pump until the pressure reached about 10^{-5} Pa or by flushing with purified helium at room temperature for 300 s. Then the catalyst was reduced again under flowing hydrogen at room temperature for 1 h. Finally the reactor was isolated and cooled to 273 K for 600 s under static hydrogen, then the mixture of reactants was introduced at zero time. The rate of reaction was obtained from the initial slope of the curve quantity of cyclohexane produced vs reaction time. Figure 1 shows typical results
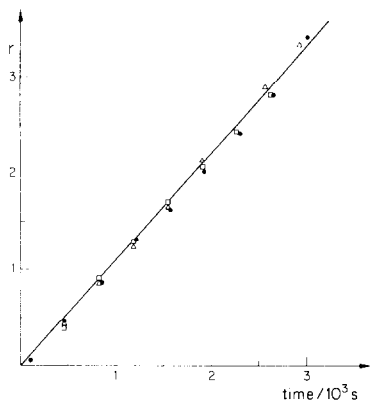
FIG. 1. Cyclohexane (10^{-2} mol g^{-1} catalyst) produced in the hydrogenation of cyclohexene vs the time of reaction for three different runs on Pt–SiO$_2$ under standard conditions.

obtained for three different runs with Pt–SiO$_2$.

Catalysts. A Pt/SiO$_2$ catalyst prepared according to the method of Benesi *et al.* (*13*) was 0.53 wt% Pt was donated by Dr. H. A. Benesi.

The Pt/Al$_2$O$_3$ catalysts were prepared as follows. A given amount of alumina was impregnated with distilled water and the appropriate amount of chloroplatinic acid to give a catalyst with 2 wt% Pt. Water was evaporated to dryness on a hot plate (or in a sand bath) while stirring and the catalyst was finally maintained overnight in an oven at about 383 K. The catalysts were reduced under flowing hydrogen at various temperatures.

Four different aluminas were used as catalyst supports: Al$_2$O$_3$ SCS9 and Al$_2$O$_3$ CBL1 available from Rhone Progil, Al$_2$O$_3$ Degussa "Oxid C," and Al$_2$O$_3$ Dispal M provided by Continental Oil Co. They were all used as powders after grinding, sieving, and washing for Al$_2$O$_3$ SCS9, and after sieving for Al$_2$O$_3$ CBL1 (granulometry 0.08 to 0.125 mm) and as obtained from the manufacturer for the two other supports. Their main characteristics are given in Table 1.

It has been shown (*1*) that when H$_2$PtCl$_6$ deposited on a sulfated alumina is reduced at temperatures higher than 573 K, the Pt

TABLE 1

Alumina Supports Used in This Work

Support	BET surface area/m^2 g^{-1}	Crystallographic form	S content (ppm)	Label
Al$_2$O$_3$ SCS 9	8	mainly α	100	A
Al$_2$O$_3$ CBL 1	180	γ	1380	B
Al$_2$O$_3$ Degussa	100	γ	0	C
Al$_2$O$_3$ Dispal M	320		50	D

catalyst thus obtained is poisoned with a *selective poison* which has been shown to act exactly as elemental sulfur (*1, 14*) and which is very probably sulfur. The amount of sulfur deposited on platinum increases with the temperature of reduction under hydrogen (*1*). When the catalyst was reduced at 573 K this selective poison was not present on platinum. *The catalysts prepared from a support containing less than 100 ppm of sulfur are called clean,* while Pt/CBL1 Al$_2$O$_3$ (Pt/B) reduced at temperatures higher than 573 K appears to be sulfur poisoned and will be referred to as such. All the *clean* platinum catalysts were reduced at 753 or 773 K.

RESULTS

The rate data are collected in Table 2. The adsorption data were obtained as follows. After outgassing a sample of reduced catalyst at 753 K and cooling it to room temperature, the first hydrogen adsorption isotherm was determined and the amount of hydrogen chemisorbed on platinum (HC) was measured. Then the sample was outgassed at room temperature for 300 s, and another hydrogen adsorption isotherm (hydrogen back sorption) was determined and its intercept is called HB. It measures the amount of hydrogen which has been desorbed during room temperature outgassing. After another 300 s evacuation at room temperature, oxygen titration (OT) was measured, then hydrogen titration (HT). By OT we mean the reaction between preadsorbed hydrogen with dioxygen followed by oxygen chemisorption. Similarly, HT is the reaction between preadsorbed oxygen

TABLE 2

Hydrogenation of Cyclohexene on Platinum
Catalysts at Total Atmospheric Pressure[a]

Catalyst	Dispersion[b] of Pt (%)	Temperature of reduction (K)	Reaction rate (μmol s^{-1} g^{-1} catalyst)
Pt/A	31	773	0.21
			0.21
			0.25
			0.24
Pt/C	68	778	0.45
Pt/D	61	753	0.38
			0.41
Pt/SiO$_2$	65	773	0.12
			0.11
			0.10
Pt/B	100	631	0.24
			0.21
			0.25
		688	0.30
			0.35
		723	0.24
			0.21
		753	0.17
		765[c,d]	0.44
			0.39
			0.42
		823	0.22
			0.29
		943[a]	0.12

[a] $T = 273$ K, $P_{C_6H_{10}} = 2.66$ kPa, $P_{H_2} = 9.31$ kPa (standard conditions).

[b] from HC, on the assumption of one H atom per surface Pt atom.

[c] After reactivation by H$_2$ at 573 K, some sulfur is removed.

[d] HC = 32 μmol g^{-1} catalyst; OC' = 22.7 μmol g^{-1} catalyst; OT = 35.3 μmol g^{-1} catalyst; HT = 85.3 μmol g^{-1} catalyst.

with dihydrogen followed by hydrogen chemisorption. The catalyst was then evacuated at room temperature then at 753 K and cooled to room temperature where oxygen chemisorption (OC) was measured, then eventually HT, HB, OT. It was checked that after outgassing at room temperature the oxygen backsorption isotherm extrapolated to zero at zero pressure. The results of hydrogen and oxygen chemisorption and titration are given in Table 3 for clean catalysts and Table 4 for sulfur-poisoned catalysts.

The differences in adsorption on clean and poisoned catalysts must be pointed out. First the equilibrium for a given pressure was reached much faster for clean catalysts (15 to 30 min) than for sulfided catalysts. On Pt-B the equilibrium was reached after 1 h for HC, but only after 10 to 12 h for OC. However, after 1 h the pressure decreased much more slowly and it was arbitrarily decided to measure OC after 1 h. This procedure gave probably slightly too low a value for OC.

Second, for clean catalysts all values of HC and OC were remarkably reproducible (Table 2), while for Pt-B reduced at temperatures higher than 723 K, HC increased slightly after OC and/or HC at room temperature, probably because of a partial cleaning of the platinum surface.

Third, a treatment under flowing dihydrogen at 473 or 573 K seemed to clean, at least in part, the sulfur-poisoned catalysts. For example Pt/B reduced respectively at 765 and 943 K gave HC = 11.7 and 2.7 μmol/g of catalyst, but when they were submitted after reduction to a pretreatment under hydrogen at 573 K the values of HC were 32–33 and 10.8 μmol/g of catalyst respectively (Table 4). Such a phenomenon was never observed for clean catalysts. It could be a result of a reduction of surface platinum sulfide into platinum and hydrogen sulfide:

$$Pt_sS + H_2 = Pt_s + H_2S \qquad (1)$$
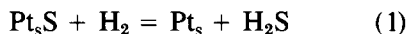
Of course, reaction (1) would also occur at temperatures higher than 573 K, but when the temperature was sufficiently high (higher than 673 K in this paper), the production of sulfur by reduction of the sulfate in the support was presumably faster than the disappearance of sulfur via reaction (1).

In Table 3 and 4 we have also calculated the values OC' = OT − 0.5 (HC − HB) and HT' = 2 OT + HB in order to check whether the stoichiometries of oxygen and hydrogen adsorption were the same for the

TABLE 3

H_2 and O_2 Chemisorption (μmol/g of Catalyst) on *Clean* Catalysts

Catalyst	Temperature of reduc- tion (K)	HC	HB	OT	OC	HT	H/Pt	OC'[a]	HT'[b]	OT'[c]	OT/HC	HT/HC	HT'/OT'	HC/OC	HC/OC'
Pt A	773	15.6	5.2	16.3	10.67	38.9	0.31		38	19	1.03		2.1	1.5	1.4
		16.1	5.2	16.1				10.9	37	19			2.1		
Pt C	778	34.8	8.3	30.6	15.1	75.8	0.68	17.4	70	35	0.88	2.2	2.2	2.3	2.0
		35.0	8.2	30.8				17.4		35	0.88		2.2	2.3	2.0
Pt C	753	51.7	9.7	48.2	20.7	107.3	1.0	27.2	106	53	0.93	2.1	2.0	2.5	1.9
Pt D	753	28.7	6.7	25.6	13.3	61.3	0.56	14.6	58	29	0.89	2.1	2.1	2.2	2.0
		28.6												2.2	2.0
Pt/SiO₂	773	8.9	2.6	7.6	5.1	18.2	0.65	4.5	18	9.0	0.85	2.0	2.0	1.7	2.0
				7.8				4.6		9.1	0.87		2.0	1.8	2.0
		9.0		7.5					18	8.8	0.84		2.1		

[a] OC' = OT − 0.5 (HC − HB).
[b] HT' = 2 OT + HB.
[c] OT' = OT + 0.5 HB.

TABLE 4

H_2 and O_2 Chemisorption (μmol/g of catalyst) on Pt-CBL1 Al_2O_3 Reduced at Various Temperatures T_r

T_r (K)	HC	HB	OT	OC	HT	H/Pt	OC'[a]	HT'[b]	OT'[c]	OT/HC	HT/HC	HT/OT'	HC/OC	HC/OC'
540	50.5	10	41		89.5	0.985	20.8	92	46	0.31	1.8	2.0		2.4
577	30	7	35.2	20.2	71	0.585	23.7	77.4	38.7	1.2	2.40	1.8	1.5	1.3
677	21.4	6.4	32.4	21.8	71.9	0.42	24.9	71.2	35.6	1.5	3.4	2.0	1.0	0.86
765	11.7	4.8	35.5	25	65	0.23	32.1	75.8	37.9	3.0	5.6	1.7	0.5	0.36
631	42.4	8.7	40	17.2	94.7	0.83	23.2	88.7	44.3	0.94	2.2	2.1	2.5	1.8
	24.8	5.3			78.5	0.48	28.4	76.5	38.2		1.9	2.3	1.4	0.87
	19.8	6.1	35.2		86	0.39				1.8	4.3	2.1	1.2	0.70
688	27.4	7.25	36.6		80.8	0.53	26.5	80.4	40.2	1.3	4.1	2.1		1.0
	24.3	6.9			84	0.47	27.9	80.1		1.5	3.1			0.87
	24.0	6.9				0.47	28.1				3.5			0.85
723	10.8	3.7	35.3	20	49.9	0.21	31.8	74.3	37.1	3.3	4.6	1.6	0.54	0.34
	13.0	3.5			60.2	0.25	30.6	74.1		2.7	4.6		0.65	0.42
	12.6	4.9				0.245	31.5	75.5			4.8		0.63	0.40
753	13.5	5.5	30.3		75.4	0.26	26.3	66.1	33.0	2.2	5.6	2.3		0.51
	15.95	5.5				0.31	25			1.9	4.7			0.64
823	12.9	4.5	35	29.9	80.5	0.25	30.8	74.5	37.2	2.7	6.3	2.2	0.43	0.42
943	17.6	5.9			81.15	0.34	29.2	75.9		2.0	4.6		0.59	0.60
	2.73[d]	1.66	8.85	9.8[d]		0.053	8.3	19.4		3.2			0.28	0.33
	10.82[d]	2.7				0.21							1.1	1.3

[a] OC' = OT − 0.5 (HC − HB).
[b] HT' = 2 OT + HB.
[c] OT' = OT + 0.5 HB.
[d] After partial regeneration under H_2 at 473 K.

first chemisorption and the titration. It can be seen, in Table 3, that, for all the clean catalysts, OC′ = OC and HT′ = HT within a reasonable margin of error, as expected, except for Pt-C reduced at 753 K, which is very well dispersed and could have been sintered to some extent during the second outgassing before OC. For sulfur-poisoned catalysts the agreement between OC′ and OC on the one hand and HT′ and HT on the other hand is less good than for clean catalysts. A rather general trend is that HT seems higher than HT′. This may be due to the very slow adsorption of dioxygen as a result of which OT and OC could be underestimated for the poisoned catalysts.

The results of adsorption on sulfur-poisoned catalysts in Table 4, show that the values of OT changed very little (OT = 35 ± 6 μmol/g catalyst) when the temperature of reduction was changed, except for the catalyst reduced at 943 K which had probably been sintered. To some extent this is true too for OC although OC increased slightly when HC decreased. On the contrary HC decreased when the temperature of reduction was increased, bringing about more poisoning. This is clearly seen in the ratios OT/HC, HC/OC, and HT/HC which were not constant but increased with poisoning and were systematically higher than the corresponding ratios for *clean* catalysts which were constant except for Pt-A irrespectively of the dispersion of platinum (Table 3).

DISCUSSION

To express rates of catalytic reactions as turnover rates r_t is advantageous because r_t is measured only in units of time, because an easy comparison is provided between catalysts both homogeneous and heterogeneous, and because the independence of r_t from surface anisotropy or particle size is a clear indication of structure insensitivity of the reaction under study.

The difficulty is to find a way to count "sites" properly so that the rate can be expressed as r_t, i.e., as the number of

molecules transformed per site per second. If chemisorption is used to count sites, the surface stoichiometry, i.e., the number of adsorbed species taken up by the surface under standard conditions should be independent from surface anisotropy or particle size and from adventitious or intentional surface contamination. The surface stoichiometry may remain unknown as the size of a catalytic site may be different from that of a chemisorption site. For a structure-insensitive reaction, the reported value of r_t will be proportional to the true value while it will be a lower bound to the true value for a structure sensitive reaction.

We are concerned here with a structure-insensitive reaction and with the problem of counting sites properly in the absence or presence of a surface contaminant. That the hydrogenation of cyclohexene on platinum and palladium is structure insensitive has been amply documented in the first three papers of this series (8, 9). It has recently been confirmed by a study of the reaction on single crystals of platinum (15) which at pressures comparable to those used in the previous work yielded values of r_t in excellent agreement with those reported on small crystallites exhibiting 100% dispersion.

If we now examine the rate data of Table 2 and plot them against the values of HC (Fig. 2), we see that all data are well
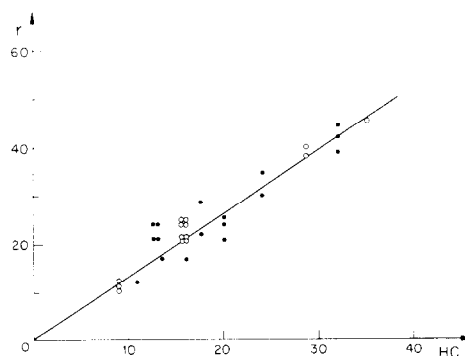

FIG. 2. Specific rate of hydrogenation of cyclohexene, r/μmol s^{-1} g^{-1} catalyst, as a function of the amount of hydrogen chemisorbed HC (μmol g^{-1} catalyst) on various Pt catalysts. ○, Clean catalysts; ●, sulfur-poisoned catalysts.
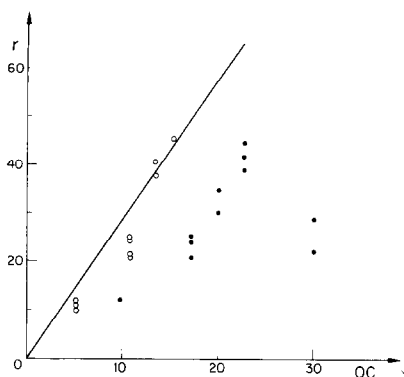
FIG. 3. Specific rate of hydrogenation of cyclohex-ene, r/μmol s^{-1} g^{-1} catalyst, as a function of the amount of oxygen chemisorbed OC (μmol g^{-1}catalyst) on various Pt catalysts. $\bigcirc$, Clean catalysts; $\bullet$, sulfur-poisoned catalysts.

FIG. 5. Specific rate of hydrogenation of cyclohex-ene, r/μmol s^{-1} g^{-1} catalyst, as a function of HT (μmol g^{-1} catalyst) on various Pt catalysts. $\bigcirc$, Clean catalysts; $\bullet$, sulfur-poisoned catalysts.

represented by a straight line the slope of which is proportional to the value of r_t under the conditions of the work. This is true for catalysts of varying dispersion, on different supports, and with or without sur-face contamination. It can also be con-cluded that the turnover rate of a structure insensitive reaction remains unaffected by massive poisoning of the surface.

By contrast, by plotting the rate data versus values of OC (Fig. 3), OT (Fig. 4), and HT (Fig. 5), we see that all data line up on a straight line only for the *clean* cata-lysts. Thus, for clean platinum surfaces, oxygen chemisorption, oxygen titration, and hydrogen titration are valid methods to
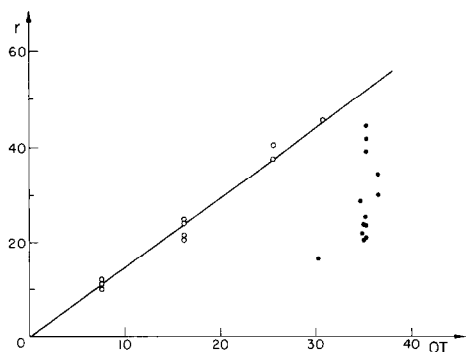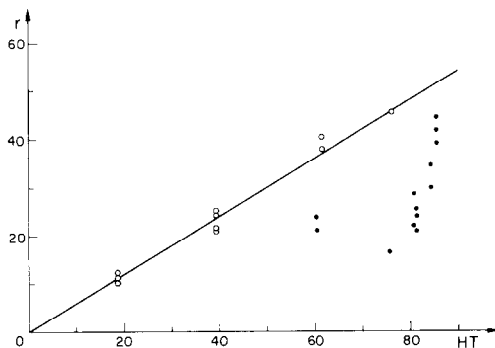
obtain values of r_t. But rate data obtained on poisoned catalysts scatter badly below the line for clean catalysts. Thus these three methods involving oxygen chemi-sorption are not suitable for counting sites on platinum contaminated with sulfur. Clearly, these methods give excess values for the number of platinum sites.
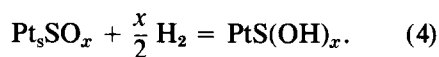
This is evident from the adsorption data presented above. Thus the values of OT and OC are consistently higher than those of HC on poisoned surfaces. The results can be accounted for by adsorption of oxy-gen on the surface platinum atoms already poisoned by sulfur:

$$Pt_sS + \frac{x}{2} O_2 = Pt_sSO_x. \qquad (2)$$
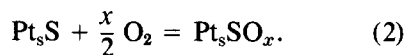
Since HT' = 20T + HB is always close to HT, oxygen atoms adsorbed by sulfur prob-ably react with hydrogen as follows:

$$Pt_sSO_x + xH_2 = Pt_sS + xH_2O \qquad (3)$$

and not according to:

$$Pt_sSO_x + \frac{x}{2} H_2 = PtS(OH)_x. \qquad (4)$$

FIG. 4. Specific rate of hydrogenation of cyclohex-ene, r/μmol s^{-1} g^{-1} catalyst, as a function of OT (μmol g^{-1} catalyst) on various Pt catalysts. $\bigcirc$, Clean cata-lysts; $\bullet$, sulfur-poisoned catalysts.

A final important result from this work concerns relative surface stoichiometry of adsorption of hydrogen and oxygen on plat-inum, a subject that has led to a considera-ble amount of controversy since the early

papers on the subject (*10, 16–18*). From the slopes of the straight lines in Figs. 2–4, we obtain relative values of r_t equal to 1, 2.3, and 5 when calculated from OC, HC, and HT, respectively. These relative values are in good agreement with the values of 1, 2, and 4 for the relative values of OC, HC, and HT on platinum proposed by Mears and Hansford (*16*), and later by Wilson and Hall (*17*) for highly dispersed supported Pt samples. They are not in good agreement with the values of 1, 1, and 3 for the relative values of OC, HC, and HT on platinum proposed by Benson and Boudart (*10*), by Wilson and Hall (*17*) for less well dispersed supported Pt samples, and by Vannice *et al.* (*18*) for Pt black powders. The interesting new result from this work is that relative uptakes do not change with metal dispersion but from values approaching 1 : 2 : 4 to values approaching 1 : 1 : 3 as samples become progressively poisoned with sulfur, as a result of the postulated Eq. (3) above. In fact, Pt/A is the only so-called *clean* catalyst different from the other *clean* catalysts in that HC : OC is 1.5 instead of 2 (Table 3). This can be explained by a slight poisoning of Pt on the A support containing 100 ppm of sulfur. On the contrary, from the HOC : OC values (Table 4), it can be inferred that Pt/D reduced at low temperatures (440 and 631 K) is almost *clean* in spite of the large amounts of sulfur in support D.

The question of relative stoichiometries of adsorption of hydrogen and oxygen, as well as their modification as a result of high temperature reduction and/or poisoning of the platinum surface by an impurity susceptible to react with oxygen, will be discussed in a forthcoming paper (*19*) which will also present new results on absolute stoichiometries of adsorption on clean platinum powders. At this moment let us conclude by mentioning that the value of r_t for the hydrogenation of cyclohexene on Pt, poisoned or not, is 0.65 s^{-1} at standard conditions as calculated from Fig. 2 with the assumption that one site corresponds to one hydrogen adatom. This value is in excellent agreement with those of other investigators (*8, 15*).

REFERENCES

1. Maurel, R., Leclercq, G., and Barbier, J., *J. Catal.* **37**, 324 (1975).

2. Maurel, R., and Barbier, J., *J. Chim. Phys.* **73**, 995 (1976).

3. Oudar, J., *Catal. Rev.* **22**, 171 (1980).

4. Leclercq, G., Barbier, J., Betizeau, C., Maurel, R., Charcosset, H., Frety, R., and Tournayan, L., *J. Catal.* **47**, 389 (1977).

5. Aben, P. C., Platteeuw, J. C., and Stouthamer, B., "Proc. 4th Int. Congr., Catal.," Vol. 1, p. 395. Akademia Kiado, Budapest, 1971.

6. Nikolajenko, V., Bosacek, V., and Danes, V., *J. Catal.* **2**, 127 (1963).

7. Mutin, R., Basset, J. M., and Prettre, M., *C.R. Acad. Sci. Ser. C* **273**, 1704 (1971).

8. Segal, E., Madon, R. J., and Boudart, M. *J. Catal.* **52**, 462 (1978).

9. (a) Gonzo, E. E., and Boudart, M., *J. Catal.* **52**, 462 (1978). (b) Madon, R. J., O'Connell, J. P., and Boudart, M., *AIChE J.* **24**, 904 (1978).

10. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).

11. McConica, C., Ph.D. Dissertation, Stanford, 1981.

12. Schlatter, J. C., and Boudart, M., *J. Catal.* **24**, 482 (1972).

13. Benesi, H. A., Curtis, R. M., and Studer, H. P., *J. Catal.* **10**, 328 (1968).

14. Barbier, J., Thesis, Poitiers, 1975.

15. Davis, S. M., and Somorjai, G. A., *J. Catal.* **65**, 78 (1980).

16. Mears, D. E., and Hansford, R. C., *J. Catal.* **9**, 125 (1967).

17. Wilson, G. R., and Hall, W. K., *J. Catal.* **17**, 190 (1970).

18. Vannice, M. A., Benson, J. E., and Boudart, M., *J. Catal.* **16**, 348 (1970).

19. O'Rear, D. J., Leclercq, G., and Boudart, M., to be published.