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The Influence of Particle Size on the Catalytic Properties of Alumina-Supported Rhodium Catalysts

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The catalytic activities of rhodium for benzene hydrogenation and cyclopentane hydrogenolysis have been investigated as a function of the state of dispersion. The specific surface area of rhodium was varied by changing the conditions of preparation: metal content, rhodium salt, and temperature of reduction. The dispersion of rhodium was determined by measurements of hydrogen and oxygen chemisorption, by H_2 titration of preadsorbed oxygen, and by direct examination of the distribution of particle sizes by electron microscopy. The stoichiometries of adsorption are found to correspond to Rh H and Rh O, whatever the dispersion of rhodium. The turnover number for hydrogenation is approximately constant and independent of dispersion in the range of 20 to 90% dispersion. An eightfold increase in the turnover number for hydrogenolysis is found when the dispersion decreases from 95 to 20%. The selectivity of hydrogenolysis also changes. The particle size effect is attributed to the formation of dense crystallographic planes at the surface of the large particles.

INTRODUCTION

The relation between catalytic properties and the state of dispersion of a metal remains a basic but controversial question in the field of catalysis by metals. An influence of the dispersion on the specific activity has been reported on hydrogenolysis of ethane on silica-supported nickel (*1*) and rhodium (*2*), on hydrogenolysis of neopentane on platinum (*3*), and of cyclohexane on Ru/SiO_2 (*4*). However, opposite results have been reported on nickel (*5*), since it was found that over a wide range of dispersions the specific activity for the hydrogenolysis of ethane was independent of the metal particle size and the method of catalyst preparation. Maurel *et al.* (*6*) demonstrated that hydrogenolysis of cyclopentane is not dependent on particle size for platinum catalysts sintered under hydrogen and that trace amounts of sulfur contained by the support could selectively inhibit that reaction. Similar results were recently obtained on Pd/Al_2O_3 (*7*) and it was found that iron impurities could induce changes in selectivity; an apparent change of the specific activity of Pd/SiO_2 with dispersion was in fact due to an accidental contamination by iron.

It therefore appears necessary to compare the results on several metals, supports, and reactions to establish the influence of particle size on a firm experimental basis. Since the hydrogenolysis of ethane on Rh/SiO_2 had been previously investigated by Yates and Sinfelt (*2*), a study of

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TABLE 1

Characteristic Features of the Catalysts Used in this Work

Catalyst		Thermal treatments		Method of preparation	Dispersion (%)
Number	Percentage Rh	T (°C)	(hr)		
52	0.08	500	5	Exchange $RhCl_3$	100
22	0.22	400	5	Exchange $RhCl_3$	94
41	0.44	550	16	Exchange $RhCl_3$	87
61	2.35	730	16	Exchange $RhCl_3$	68
63	2.3	800	48	Exchange $RhCl_3$	48
81[a]	1.85	600	60	Impregnation $Rh(NH_3)_5Cl_3$	22
82	1.85	550	4	Impregnation $Rh(NH_3)_5Cl_3$	30
84[a]	1.85	830	48	Impregnation $Rh(NH_3)_5Cl_3$	7.5
85[a]	1.85	750	16	Impregnation $Rh(NH_3)_5Cl_3$	20

[a] Reduced in hydrogen saturated by water (pressure of water ≃30 Torr).

Rh/Al_2O_3 was undertaken with the objective to reexamine the influence of the state of dispersion of rhodium and of trace amounts of iron and sulfur. Two reactions were used in this work, benzene hydrogenation which is known to be structure insensitive and cyclopentane hydrogenolysis which could be structure sensitive.

EXPERIMENTAL

Catalysts and Catalyst Treatments

The various rhodium catalysts used in this study are listed in Table 1. The support was a γ-Al_2O_3 made in the laboratory, of surface area 320 m^2/g, containing traces of iron (140 ppm). The rhodium salts were purchased from Merck.

Two methods of preparation were used: (i) ion exchange using an acidic solution of $RhCl_3 \cdot 3H_2O$ in HCl at pH ~ 2. The solids were left overnight in contact with the solution, then filtered and dried at 110°C. (ii) Impregnation by an aqueous solution of $RhCl(NH_3)_5Cl_2$: the support was poured into the solution and left in contact for 1 hr. The solution was then evaporated slowly to dryness at 70°C. The catalyst was dried at 110°C overnight and stored.

Both types of catalyst were then reduced in flowing hydrogen at various temperatures. Table 1 shows that the resulting dispersion is a function of the metal loading, mode of deposition, and temperature of reduction. As expected, ion exchange yields well-dispersed catalysts when the temperature of reduction is moderate. However, that type of catalyst appears resistant to sintering. Water is known to increase sintering, and therefore some samples were reduced in hydrogen saturated by water (partial pressure ~30 Torr). In that case lower dispersions are indeed obtained.

Sintered rhodium samples can be obtained by reducing impregnated catalysts. In such a case, the interaction between the rhodium salt and the support is lowered and the resulting catalyst presents a distribution of particle sizes centered around 50 Å.

The distributions of particle sizes are represented in Fig. 1 for three characteristic samples. Homogeneous distributions are obtained. Sample 41 contains mainly small particles and Sample 81 mainly large particles.

The influence of sulfur and iron was investigated on samples of γ-alumina impregnated by known amounts of contaminants in the form of $(NH_4)_2SO_4$ and $FeCl_3$.

Dispersion Measurements

The degree of exposure of rhodium atoms was determined by hydrogen and oxygen chemisorption and by titration of preadsorbed oxygen by hydrogen, using a volumetric method at room temperature. The measurements were carried out in a conventional static apparatus equipped with a quartz spiral Bourdon gage (Texas Instruments).

The sample was first reactivated in 20 Torr H_2 at 500°C for 2 hr, then evacuated

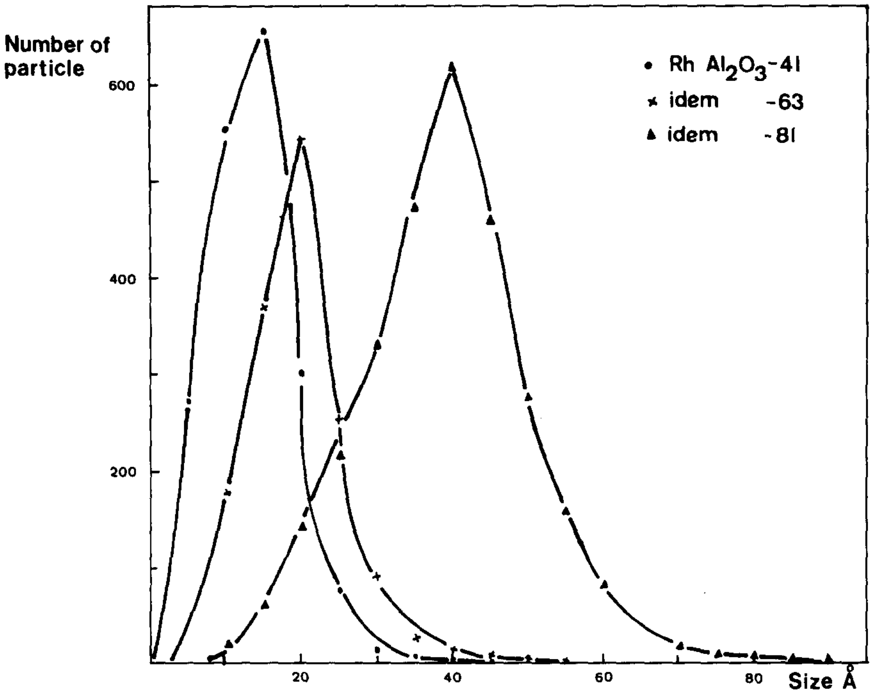

FIG. 1. Distribution of particle sizes on three characteristic rhodium catalysts.

($P < 10^{-5}$ Torr) at the same temperature for 2 hr.

The isotherms were measured for each gas between 0 and 15 Torr and the volume adsorbed was determined by extrapolating to zero pressure the linear part of the curve as proposed by others (*8–10*). Adsorption isotherms of H_2 and O_2 at room temperature on sample 52, containing 0.08 wt% Rh, are shown in Fig. 2.

The particle size distribution of the rhodium crystallites was determined on

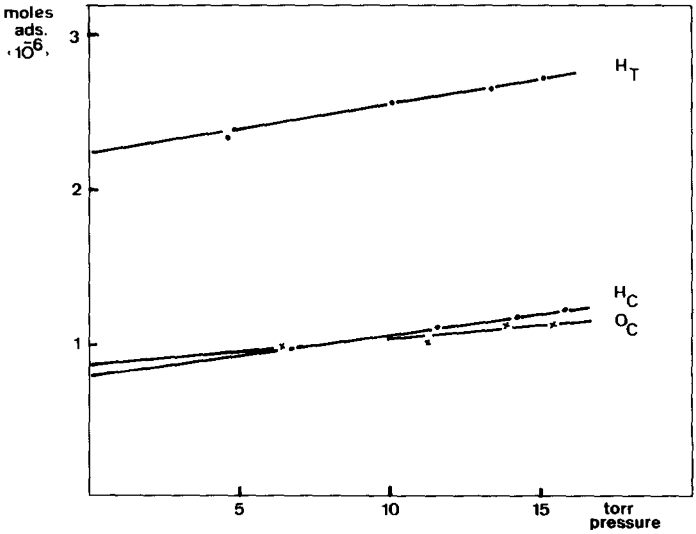

FIG. 2. Adsorption isotherms of oxygen (denoted O_c), hydrogen (H_c), and titration of preadsorbed oxygen by hydrogen (H_T). Room temperature. Sample 52, weight of sample: 200 mg.

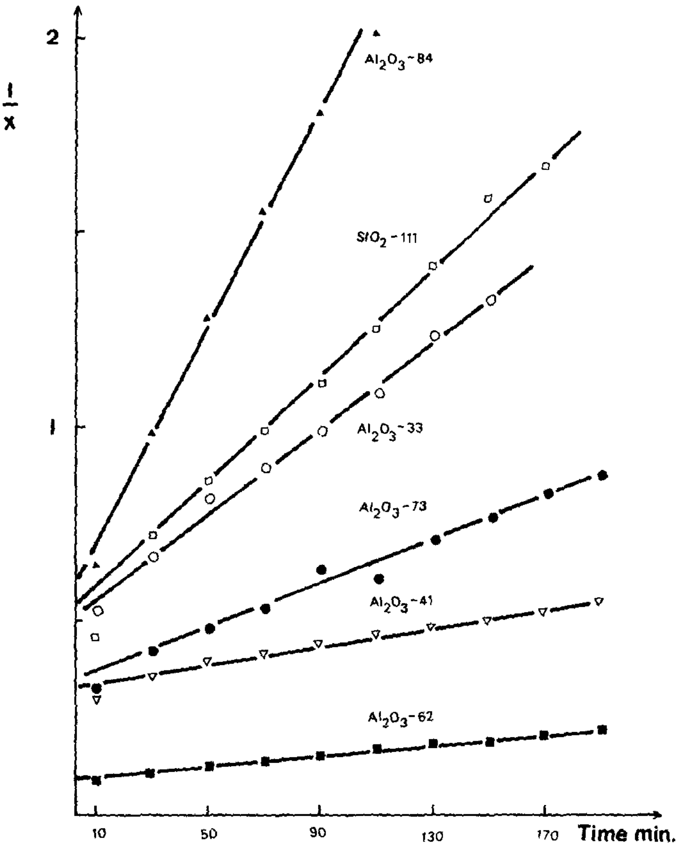

FIG. 3. Determination of the initial catalytic activity by extrapolation of the second order law of deactivation, x = percentage conversion of cyclopentane.

four samples. These were examined by electron microscopy (JEM 100C) using a carbon replica techniuque. The resolution of the apparatus is 2 Å, and permits the detection of particles 5 Å in size.

Fifteen to twenty micrographs were obtained with each sample. Photographic enlargement to 10^6 was used to provide a suitable image for particle size counting. To obtain a good representation of the sample 2500 to 3000 particles were counted.

Dispersions determined by chemisorption (H/Rh ratio) were converted to rhodium surface areas assuming a site density of 1.3×10^{19} atoms/m^2 which corresponds to an equal distribution of (110) and (111) crystal planes at the surface. This is equivalent to the assumption used by Yates and Sinfelt (*2*) of a rhodium atom occupying an area of 7.6 Å at the surface. Crystallite sizes can then be calculated from the rhodium surface area assuming a spherical or cubic shape. These sizes were compared to the surface average size ($\Sigma n_i d_i^3 / \Sigma n_i d_i^2$) obtained from electron micrographs.

Catalytic Measurements

Catalytic activities were determined on an aliquot of the sample used for dispersion measurements. The sample was reactivated in flowing H_2 for 2 hr at 400°C.

The rates were measured in a conventional flow reactor at low conversion (less than 2%) to avoid heat and mass transfer limitations.

For benzene the conditions were temperature range 30 to 50°C, partial pressure of hydrocarbon 56 Torr, and partial pressure

TABLE 2

Stoichiometric Ratios for the Adsorption of Hydrogen, Adsorption of Oxygen, and Hydrogen Titration of Preadsorbed Oxygen on Rh/Al_2O_3 Catalysts[a]

Catalyst		T_R (°C)	H/Rh ADS	O/Rh ADS	H/Rh Titration	Average dispersion (%)
Number	Percentage Rh					
41	0.44	550	0.8	0.92	2.65	87
63	2.3	800	0.45	0.49	1.52	48
85	1.85	750	0.20	0.20	0.61	20
81	1.85	600	0.22	0.20	0.67	21
84	1.85	830	0.082	0.072	0.22	7.5
61	2.35	730	0.58	0.74	2.18	68
82	1.85	550	0.30	0.24	1.07	30
52	0.08	500	0.99	1.06	2.89	100

[a] H/Rh represents the ratio of the number of hydrogen atoms chemisorbed to the number of rhodium atoms of the sample.

of H_2 704 Torr. Under these conditions the reaction is found to follow a zero order relative to benzene.

For cyclopentane, the reaction temperature was 225°C, pressure of hydrocarbon 100 Torr, and pressure of hydrogen 660 Torr. The reaction order relative to cyclopentane was found to be close to zero. The products of the reaction are paraffins ranging between methane and *n*-pentane. The selectivity S_i, relative to product i, is defined as the rate of formation of product i to the rate of conversion of the reactant.

Catalysts suffer deactivation in the conversion of cyclopentane; the initial activity, which is taken as characteristic of the fresh sample, was determined by extrapolation of the catalytic activity to time zero, using the law of deactivation previously described (*7*). An illustration of this procedure is given in Fig. 3. Deactivation affects activity but only slightly affects selectivity.

RESULTS

Determination of the Dispersion of Rhodium

The results obtained for the different stoichiometries of adsorption are given in Table 2. It may be noted from Fig. 2 that the slope of the isotherm is small, indicating a saturation at low pressure. Such a behavior is characteristic of an adsorption on a clean metallic surface.

The stoichiometric ratios H/Rh or O/Rh are close to unity on well-dispersed catalysts. Moreover, the agreement between both values is good for the whole series of catalysts; therefore these adsorptions may be represented as Rh–H and Rh–O surface compounds. The stiochiometric ratio obtained for the titration of preadsorbed oxygen agrees well with this hypothesis.

However, it was observed that diluted catalysts reduced at low temperature give irreproducible results which were dependent on the temperature used for reactivation. This is indicative of an incomplete reduction. Reduction at 500°C gave reproducible results; thus it can be inferred that complete reduction is then reached. Reduction above 500°C was therefore used in the present work. When adsorption is carried out at 110°C, the hydrogen uptake decreases while the oxygen uptake increases. This increase of oxygen uptake has been interpreted previously (*10*) as bulk oxidation of the particles, which renders both oxygen adsorption and hydrogen–oxygen titration unsuitable for surface area determination. Finally, it was observed that repeated cycles lead to a decrease of both oxygen and hydrogen uptakes. This reflects an inhibiting effect of water, as reported by Wanke and Dougharty (*10*).

From the distributions of particle sizes reported in Fig. 1, average particle sizes

TABLE 3

Comparison of Chemisorption Data with Electron Microscopic Determination of the Average Size

Catalyst	Percentage D Chem.	ϕ (Å) Chem.	ϕ (Å) Electron microscopy
81	22	48	48
41	87	13	17
63	48	22	24
84	7.5	140	150

FIG. 4. Electron micrograph (× 1.2 × 10^6) of Sample 41, containing 0.44 wt% Rh.

were computed which are compared to chemisorption data in Table 3. These two independent determinations agree rather well and this is an evidence that chemisorption can be used confidently to measure the rhodium surface area.

TABLE 4

Turnover Number for the Hydrogenation of Benzene and Hydrogenolysis of Cyclopentane as a Function of the Degree of Dispersion

Catalyst		Dispersion (%)	Turnover number for benzene (hr^{-1}) at 50°C	Turnover number for cyclopentane (hr^{-1}) at 225°C
Number	Percentage Rh			
52	0.08	100	281	459
33	0.44	100	330	—
41	0.44	87	700	973
61	2.35	70	609	1128
63	2.3	48	756	2150
82	1.85	30	763	1928
81	1.85	23	944	2630
81	1.85	23	944	3200
85	1.85	20	908	3096
84	1.85	7.5	554	651

Shape of the Rhodium Particles

The shape of the particles is not easy to define on well-dispersed catalysts (Fig. 4) and a spherical shape can be supposed. However, Sample 81 which has been reduced at higher temperature in the presence of water shows many particles presenting a hexagonal shape, as can be seen in Fig. 5. This indicates a facetting of the particle with formation of dense crystallographic planes which should be the most stable ones. It can therefore be seen here that sintering changes not only the size of the metallic particle but also the surface structure.

Catalytic Properties

Catalytic activities are reported in Table 4 in terms of turnover numbers, or numbers

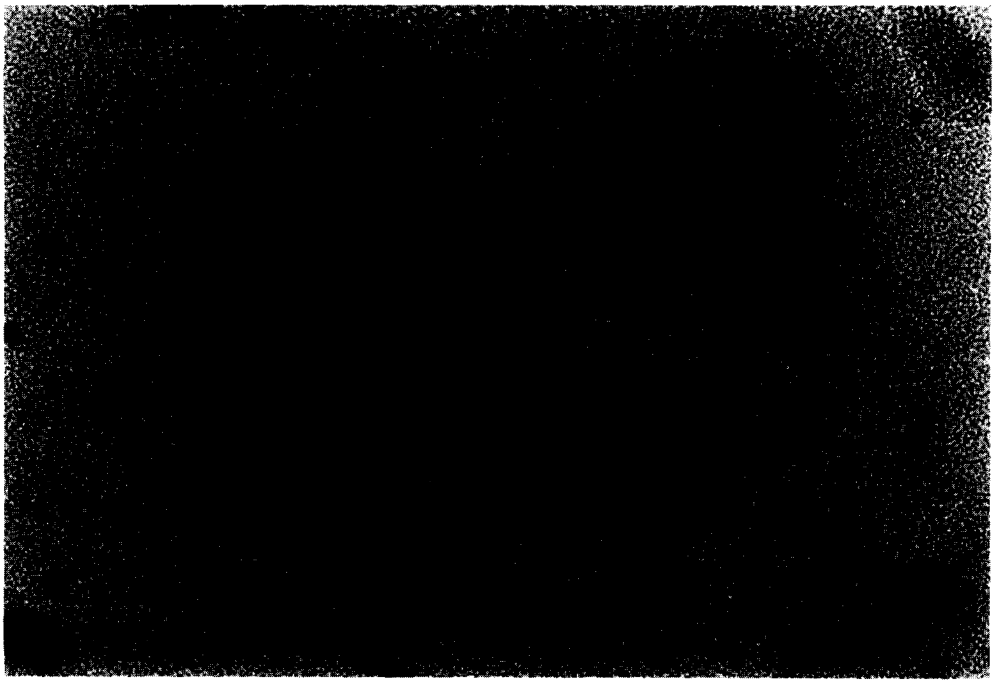

FIG. 5. Electron micrograph (×1.2 × 10^6) of Sample 81, showing hexagonal rhodium particles.

of molecules reacting per hour and per surface rhodium atom. For the conversion of cyclopentane, our data can be compared to those reported by Leclercq and Maurel (*11*) on similar catalysts (Table 5). The good agreement found between these values indicates that no large artefact can exist (traces of poison in cyclopentane, for example).

The selectivity in hydrogenolysis is also affected by sintering, as is illustrated in Fig. 6, which reports the selectivities for methane and *n*-pentane. A maximum for *n*-pentane, corresponding to a minimum for methane, appears at intermediate dispersion. The variations are small, but we believe that the threefold change from 5 to 15% observed for methane is beyond experimental error.

TABLE 5

Comparison of the Activity for Hydrogenolysis of Cyclopentane of Sample 52 and a Similar Sample from Reference (*11*).

Catalyst	Percentage Rh	Reduction	Catalytic activity at 225°C (× 10^3 mol sec^{-1} g^{-1} Rh)	E_a (kcal/mol)
52	0.08	500°C	1.24	23
Ref. (*11*)	0.0745	500°C	1.51 (extrapolated)	26

The influence of iron was investigated on a sample containing 0.39 wt% Rh contaminated by 0.1 wt% Fe in the form of $FeCl_3$ and reduced at several temperatures. The catalytic activities of these catalysts are listed in Table 6, in which Sample 41, of similar Rh content, represents the blank run. It appears that iron has only a small influence on catalytic activities, whatever the temperature of reduction, and moreover it cannot affect the selectivity. Therefore the particle size effect cannot be explained by a contamination by iron.

The influence of sulfur was examined on a sample containing 0.44% Rh contaminated by $(NH_4)_2SO_4$ in order to introduce 0.32 wt% of sulfur, and similarly reduced

TABLE 6

Catalytic Activities ($\times 10^5$ mol sec^{-1} g^{-1} Rh) of Rh/Al_2O_3 Samples Contaminated with Iron

Catalyst	T (°C) reduction	Activity A_2 for cyclopentane	Activity A_1 for benzene	$R = A_1/A_2$
41	550	210	130	0.62
71	400	232	91	0.40
72	500	180	89	0.49
73	600	198	131	0.66
74	300	210	130	0.62

at several temperatures. The results are summarized in Table 7 and show that sulfur severely inhibits both activities. A surprising fact is that hydrogenolysis decreases continuously when the temperature of reduction increases while the activity for hydrogenation can be partly restored by reduction at high temperature. In connection with the present work, sulfur contamination cannot explain the results obtained when varying the particle size since (i) the most active catalysts are those reduced at high temperature, (ii) sulfur preferentially represses hydrogenolysis.

DISCUSSION

The stoichiometries of the adsorption of oxygen and of hydrogen and the titration of preadsorbed oxygen have been investigated before by several authors (*2*, *9*, *10*, *12*, *13*). However, no independent determination of particle sizes was made, except by X-ray line broadening which is limited to particles larger than 30 Å.

One of the points of controversy is the stoichiometry of hydrogen adsorption, which is reported to exceed unity by two groups of authors (*10*, *13*). Our data on well-dispersed catalysts, which are in good agreement with electron microscopy, show no evidence of such behavior and therefore support the conclusions reached by Yates and Sinfelt (*2*) and Kikuchi *et al.* (*9*), which favor a stoichiometry corresponding to Rh-H.

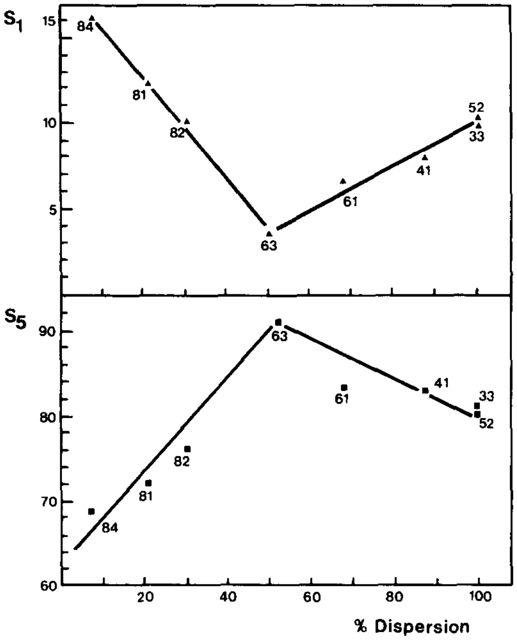

FIG. 6. Selectivity for methane (S_1) and for *n*-pentane (S_5) plotted as a function of the dispersion.

The stoichiometry for oxygen adsorption is also found equal to unity on well-dispersed catalysts, and the ratio hydrogen adsorption/oxygen adsorption is close to unity on all the catalysts investigated here. Our conclusion that the surface oxidation stoichiometry is 1.0 agrees with previous work by Buyanova *et al.* (*12*), but is in contradiction with Yao *et al.* (*13*) who

TABLE 7

Catalytic Activities ($\times 10^{-5}$ mol sec^{-1} g^{-1} Rh) of Sulfate Contaminated Samples)

Catalyst	T (°C) reduction	Activity		$R = A_1/A_2$
		A_1 for benzene at 50°C	A_2 for cyclopentane at 220°C	
41	550	130	210	0.62
94	300	0.82	4.9	0.17
91	400	4.0	3.3	1.21
92	500	9.45	1.0	9.45
93	600	14.7	1.2	12.25

concluded that there was an adsorption in the form of Rh_2O_3. Stoichiometries higher than 1 are probably associated with the oxidizability of rhodium. The authors (*10, 13*) who have reported such a stoichiometric ratio for oxygen have carried out the oxygen adsorption at pressures of 100 Torr or above. Buyanova *et al.* (*12*) used a chromatographic pulse method in which the actual reactant pressure is low, or low oxygen pressures ($5 \leqslant P \leqslant 30$ Torr) in static volumetric determinations.

In the present work the experimental conditions are similar to the latter ones and similar results were obtained. This allows us to believe that the pressure range may have some importance and that higher pressures favor bulk oxidation of the rhodium particles.

A surprising fact is that rhodium does not show any change in the stoichiometry of oxygen adsorption at high dispersion, such as is known for platinum (*8*) or palladium (*7*). The electron-deficient character of small metallic particles is therefore restricted to the more noble metals. Rhodium, like nickel, can be oxidized in the bulk at low temperature; it is therefore not surprising that its behavior should be different from that of Pt or Pd in that respect.

The titration of preadsorbed oxygen on rhodium at room temperature also proceeds according to a simple stoichiometry which corresponds to the reaction:

$$RhO + \tfrac{3}{2}H_2 \rightarrow RhH + H_2O$$

This proposition agrees well with the data reported by Kikuchi *et al.* (*9*) and also by Wanke and Dougharty (*10*) for similar metal loadings. The discrepancies arising at low metal loadings may reflect an incomplete reduction to the metallic state as suggested by the data presented by Yao *et al.* (*13*) and our own experiments.

However, it can be emphasized here, as has been done in the case of platinum (*8*), that the error introduced by using a wrong stoichiometry such as

$$Rh_2O_3 + 4H_2 \rightarrow Rh - H + 3H_2O$$

cannot exceed 25%. Therefore the order of magnitude of the metallic area will be correct whatever equation is used.

The turnover number for benzene hydrogenation shows a small variation ($N = 750 \pm 200$ hr^{-1}) when the dispersion is varied from 90 to 20%. Such a behavior was expected for a reaction classified as facile by Bourdart's definition (*3*). At higher dispersions a lower turnover is observed, which appeared to be reproducible. This decrease at high dispersion may be tentatively attributed to a high state of dispersion, since on similar systems Yates *et al.* (*14*) have reported the existence of clusters of a few atoms. The decrease of turnover number with dispersion is indicative that the very small particles are less active. It is known from homogeneous catalysis that organometallic clusters do not catalyze the hydrogenation of aromatics, so some indications exist that highly dispersed rhodium catalysts may be less active for hydrogenation of benzene than catalysts containing large particles.

The turnover number for hydrogenolysis shows a clear variation as a function of dispersion since an eightfold change is obtained, which is beyond experimental error. Such a variation cannot be explained by a contamination of rhodium by iron or sulfur impurities from the support.

These results agree with those previously reported by Yates and Sinfelt (*2*) for hydrogenolysis of ethane. A particle size effect does exist on carbon–carbon bond rupture. A maximum for specific activity was reported in that previous work at 50% dispersion for Rh/SiO_2. In the present work a maximum is observed at 25% dispersion ($\Phi \sim 50$ Å) for Rh/Al_2O_3 but the tendency is the same, namely, large particles exhibit a higher catalytic activity per surface metal atom than small particles.

The changes in selectivity also suggest a particle size effect and it appears that large particles favor hydrogenolysis to methane. Similar results were recently reported by Yao *et al.* (*15*) for the hydrogenolysis of *n*-pentane which was found to present a greater selectivity for methane formation on large particles.

Growing experimental evidence therefore supports the existence of a particle size effect in the case of rhodium, since it is now established for three reactions involving C–C bond rupture, on silica-supported and alumina-supported catalysts.

It is worth recalling here that no particle size effect has been found on Pd/Al_2O_3 catalysts in the same range of dispersion as that investigated here for rhodium. Therefore, a simple interpretation assuming that edge, corner, and face atoms have different properties appears inadequate, since the situation would be the same for palladium and rhodium which exhibit different catalytic behaviors. Catalytic activity is not connected with the number of low-coordinated atoms which exist on small particles (*16*).

The sintered Rh/Al_2O_3 catalysts are unique on the point that they show some evidence of crystallization. A small particle can be imagined as a rough plane, while a facetted particle will expose low index planes. Experimental work on single crystals (*17–19*) gives plenty of evidence that both classes of surface exhibit differences in catalytic properties. Therefore, different turnover numbers may be expected on spherical and facetted particles. Results from this laboratory (*20*) suggest that the catalytic activity for C_2H_6 hydrogenolysis per surface nickel atom depends on the morphology of the particle, and this work presents similar evidence for small rhodium particles.

In that hypothesis, sintering induces complex transformations of the metallic particle which cannot be reduced to an increase of the particle size, because the shape of the particle will be a function of size, nature of the support, and sintering atmosphere (*21*).

If our hypothesis is realistic, "particle size effects" can be expected on those metals which exhibit differences in catalytic activities for the different crystal planes and this appears to be the case for platinum (*22*) and nickel (*20*).

The behavior of palladium may be understood if we take into account that: (i) palladium is easily sintered at low temperatures, so the temperature used for reduction is insufficient to produce facetting and the shape of the particles remains spherical; (ii) no crystal plane specificity was found on this metal for the oxidation of CO (*23*).

It can be concluded that the dispersion of the metallic phase, or size of the particles, does indeed have some influence, but it is not the fundamental factor governing the catalytic properties.

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