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Pd/SiO_2

III. Activity and Selectivity Patterns for Methylcyclopropane Hydrogenolysis and Cyclopentane Exchange with Deuterium: Comparison with Pt/SiO_2

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Results of studies of the interaction of hydrogen and oxygen and of the activity and selectivity for hydrogenolysis of methylcyclopropane and for deuterium exchange with cyclopentane are given for a series of Pd/SiO_2 catalysts previously described (Nandi, R. K., Pitchai, R., Wong, S. S., Cohen, J. B., Burwell, R. L., Jr., and Butt, J. B., *J. Catal.* **70,** 298, 1981; Nandi, R. K., Georgopoulos, P., Cohen, J. B., Butt, J. B., Burwell, R. L., Jr., and Bilderback, D. H., *J. Catal.* **77,** 421 (1982)). A comparison with prior studies of a similar series of Pt/SiO_2 (Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **53,** 414, 1978) is also given. Exchange patterns of the two series with cyclopentane are similar, although some differences in the details of D_{6-10} suggest that reaction via α,α-diadsorbed cyclopentane is relatively more important on Pt than on Pd. The turnover frequencies for i-butane formation in the hydrogenolysis reaction are six to eight times higher for Pt/SiO_2 than for Pd/SiO_2, while *n*-butane formation on the two is about the same. As a result, the selectivities, iso/normal, are much lower on Pd. The patterns of structure sensitivity for this reaction on the two series also differ considerably, with an apparent maximum being observed for Pd/SiO_2 for a catalyst of 65.5% exposed. Finally, the dependence of the nature of hydrogenolysis structure-sensitivity on conditions of pretreatment, very pronounced on Pt/SiO_2, is less on Pd/SiO_2.

INTRODUCTION

We have prepared a series of Pd/SiO_2 catalysts in which the average particle size of the palladium particles for the various elements of the series varies over a wide range. In Part I of this series (*1*) *in situ* X-ray diffraction experiments on these catalysts were described in which we determined the degrees to which the individual metallic particles were converted to β-palladium hydride during catalysis of methylcyclopropane (MCP) hydrogenolysis. Part II (*2*) reported the effects of pretreatment upon the structure and size of the palladium particles. In the present paper, we describe the results of the interaction of hydrogen and oxygen with the palladium particles, the activity and selectivity of the catalysis for hydrogenolysis of MCP, and for deuterium exchange with cyclopentane. We also provide a comparison between Pt/SiO_2 and Pd/SiO_2 catalysts for these reactions.

EXPERIMENTAL

Preparation of Pd/SiO_2 catalysts. The catalysts of primary interest in the present work, designated Pd/SiO_2-IV, were prepared by the ion exchange at pH 9.5–10.0 for 2 h of 100 g of Davison grade 62 silica gel with $Pd(NH_3)_4(NO_3)_2(aq)$ by the method previously described for Pt on the same support (*3*). The exchanged gel was then

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dried for 48 h at 90°C. The material designated as Pd/SiO_2-V differed from Pd/SiO_2-IV in that ion exchange was effected from a solution of $Pd(NH_3)_4Cl_2$ and in much more concentrated NH_4OH: 100 cm^3 of concd NH_4OH in 600 cm^3 water for 100 g silica gel. Preparation of the series Pd/SiO_2-I, -II, and -III has been previously described (*4*).

Preliminary experiments indicated that reduction with hydrogen at 300 or 450°C, either directly or after calcining at 300°C, led to high D_h (percentage exposed of Pd as measured by the chemisorption of H_2) but that the presence of water during reduction led to smaller values of D_h. It also appeared that increase in the Pd loading from 0.5 to 1.5 wt% led to a small decrease in D_h. The effect of water means that a concentration gradient of water through the reactor in a fixed-bed reduction could lead to an increase in palladium crystallite size from entrance to exit. Accordingly, Pd/SiO_2-IV catalysts were reduced in a fluidized bed with an internal diameter of 35 mm. The individual samples are as follows:

79.1-Pd/SiO_2-IV. (The first number is D_h.) Here, 0.49 wt% Pd was reduced by He,300°,1;He,50°;$H_2$50° to H_2,450°,1;cool H_5.[5] Temperature elevations were programmed at 4°C min^{-1}.

65.5-Pd/SiO_2-IV. Pd (2.09%) was reduced by the sequence He(saturated with water at 25°C),25°,1;H_2,450°,1;cool He. Again, the temperature was elevated at 4°C min^{-1}.

49.8-Pd/SiO_2-IV. Pd (1.56%) was reduced by H_2 (saturated with water at 40°C), 450°,1;cool H_2. Temperature elevation in this experiment was 1°C min^{-1}.

29.3-Pd/SiO_2-IV. Pd (2.09%). A sample of 20 g of exchanged silica gel plus 1.5 cm^3 of water was stored in a closed container for 3 days and then reduced in the same way as 65.5 Pd/SiO_2-IV.

13.8-Pd/SiO_2-IV. Also 2.09% Pd. A sample of 20 g of ion exchanged silica gel plus 5.5 cm^3 of water stored for 1 day and then reduced H_2 (saturated with water at 25°C) to 300°C at a programming rate of 0.5°C min^{-1}, to 450° at 4 min^{-1}, hold 1 h, then cool in He.

65.8-Pd/SiO_2-IV. Pd (1.56%) was reduced by He,25°,0.25;He to 300° at 3° min^{-1};He, 300°,1;cool to 50° in He;H_2 to 450° at 3° min^{-1};H_2,450°,1;cool in H_2. The amount of water to which the 65.5% catalyst was exposed was thus too small to have had a significant effect.

INTERACTION WITH HYDROGEN AND OXYGEN

Measurement of Percentage Exposed

D_h was measured by the adsorption of hydrogen from pulses of hydrogen in flowing, ultrapure (0.02 ppm of O_2) argon in the fashion previously described for Pt/SiO_2 (*3*). However, the adsorption was effected at 60°C rather than 25°C on the view that the higher temperature might help to avoid trouble from formation of the β-Pd hydride phase. Adsorption of hydrogen was preceded by a "standard" pretreatment, O_2,300°,0.5;H_2,300°,1; Ar,450°,1,cool in Ar, a procedure which prepares a clean surface of Pd. The measurement of adsorption was followed by measurement of the desorption of hydrogen during heating in flowing argon to 450°C (*3*). Consistently good checks were obtained between adsorption and desorption. In addition, D_h was also measured for several catalysts by using deuterium at 60°C rather than hydrogen. The agreement was good; D_h was also in good agreement with values measured by wide angle X-ray scattering (*2*).

The adsorption of hydrogen on 82.8-Pd/SiO_2-V (0.51 wt% Pd), 49.8- and 13.8-Pd/SiO_2-IV, and 7.3-Pd/SiO_2-III (1.52 wt% Pt) was measured at several temperatures between 25 and 100°C (0 and 100°C for 49.8-Pd/SiO_2-IV). As the temperature was increased the amount of hydrogen adsorbed decreased smoothly and approximately linearly in much the same fashion as previously noted for Pt/SiO_2 and Pt/Al_2O_3 (*3, 5*). The amount of adsorption of hydrogen de-

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[5] In the code for treatment procedures, for example, He,300°,1 means the catalyst was exposed to flowing He at 300°C for 1 h.

creased by about 16% in the interval 25–100°C, but probably catalysts of large D_h exhibited a decrease smaller than this and catalysts of $D_h < 20\%$ exhibited a slightly larger decrease. In these experiments, after the first run, the catalyst was treated Ar,450°,0.5 as a preparation for the next measurement. Since the order of temperatures employed was random, it could be established that the treatment Ar,450°,1 led to negligible decrease in D_h.

In our pulse technique the exposure of the catalyst to hydrogen totals about 30 s and this is followed by an argon sweep for about 7 min. As shown by X-ray examination (*1*), 13.8 and 29.3-Pd/SiO_2-IV are largely converted to the β-hydride by H_2(1 atm),25°, but the same conditions fail to convert 49.8-Pd/SiO_2-IV. Thus, formation of hydride would not have occurred at all for catalysts of $D_h > 49.8\%$, and if hydride was formed for catalysts of $D_h < 49.8\%$ it was decomposed early in the 7 min of flushing.

Interaction with Oxygen

Two variants of the hydrogen–oxygen titration were examined. In one, a catalyst was exposed to the standard pretreatment and the amount of oxygen chemisorbed at 25°C from five pulses of oxygen was measured. The adsorbed oxygen was then titrated with pulses of hydrogen at 60°C. The catalyst was then heated to 450°C to measure the amount of hydrogen which was desorbed in the flowing argon. The ratio O_{ads}/H_{ads}, where O_{ads} is at 25°C and H_{ads} is that measured on clean catalyst at 60°C, was 0.75 ± 0.05 except that it was 0.66, 0.62, and 0.58 for 22.5-Pd/SiO_2-III, 13.8-Pd/SiO_2-IV, and 7.3-Pd/SiO_2-III, respectively. Had any oxygen remained unreduced to water by the pulses of hydrogen, less than that amount of hydrogen corresponding to adsorption on clean palladium at 60°C would have been desorbed. Since all desorptions checked the values of D_h, the adsorbed oxygen was fully removed by pulses of hydrogen at 60°C.

The following experiment was run to compare our results with those of Lam and Boudart (*6*), who exposed their catalysts to O_2(60 kPa),100°,0.5 before titration with hydrogen. In the present work 79.1-Pd/SiO_2-IV was subjected to the standard pretreatment and then to O_2(100 kPa),100°,1. The catalyst was then titrated by pulses of H_2 at 100°C and then heated to 450°C to desorb the hydrogen, all in a stream of flowing argon. Thus, oxygen adsorbed equals hydrogen consumed minus hydrogen desorbed. It was found the O_{ads}/Pd (total) was 0.81, in good agreement with D_h and the findings of Ref. (*6*). The value of H_2 (desorbed/Pd (total) was 0.62, or converted to 60°C, 0.70. This is somewhat smaller than the 0.791 expected and suggests that the oxygen monolayer had been nearly but not completely removed by five pulses of H_2 at 100°C.

All of our pretreatments start with O_2,300°,0.5 which we have regularly used to oxidize any possible adsorbed organic impurities (*3, 7*) even though every effort has been made to prepare and maintain the catalysts as asceptically as possible. Two sets of experiments on 13.8-, 29.3-, 49.8-, and 79.1-Pd/SiO_2-IV were run, the first to evaluate the degree of oxidation which follows O_2,300°,0.5, and the second to measure the degree of reduction of the oxide formed by O_2,300°.

In the first set, three sequential measurements were made starting with a fresh catalyst.

A. O_2,300°,0.5; cool in Ar to 60°C; trap a pulse of H_2 at 60°C for 15 min; release and measure exit pulse; isolate catalyst; heat rapidly to 400°C; restore Ar flow and measure evolved pulse; titrate residual surface oxide with pulses of H_2 at 400°C (*5*).

B. Following A: H_2,300°,1;Ar,450°; cool in Ar, then repeat A.

C. Following B: H_2,300°,1;Ar,450°, then repeat A.

The moles of oxygen atoms adsorbed in O_2,300°,0.5 are equal to the moles of hydrogen adsorbed at 60°C minus that released at 400°C plus that consumed in the pulse titration at 400°C. Results are given in Table 1.

Lam and Boudart (*6*) reported that Pd/

TABLE 1

Oxygen Sorbed at 300°C by Pd/SiO_2

Treatment	D_h (%)			
	13.8	29.3	49.8	79.1
	Oxygen sorbed as O/(total Pd)			
A	41	73	87	105[a]
B	42	70	86	—
C	53	76	87	—
A	—	73[a]	—	—

[a] In these runs the pulse of H_2 trapped at 60°C was so large that some hydrogen desorbed at 400°C and adsorption from pulses of H_2 at 400°C would have been zero. In the other runs, no H_2 desorbed at 400°C and pulses of H_2 were passed at 400°C. See Ref. (*5*) for the technique employed.

SiO_2 catalysts were fully oxidized upon treatment in oxygen at 300°C or less. They employed Davison grade 950 silica gel which has a nominal pore diameter of 2.5 nm. The percentage exposed of their catalysts was 15.3 and 57% and the average particle diameters were accordingly about 7 and 2 nm. Although it is difficult to decide as to the exact meaning of calculated pore diameters for porous objects whose pore space resembles that of a cemented, loose gravel bed, it is reasonable to say that the immediate environment of a crystallite of palladium in Davison grades 62 and 950 would be quite different.

To determine the degree to which H_2,25°,1 removes oxygen added by O_2,300°,0.5, fresh catalyst was pretreated O_2,300°,0.5;Ar,300° → 25°;H_2,25°,1;Ar,25°, 0.5; isolate catalyst, heat rapidly to 450°C, restore flow of Ar, and measure evolved H_2 (*3*). As noted above, the amount of H_2 adsorbed on clean Pd at 60°C (this gives D_h) is about 0.91 of that at 25°C. After correcting for the amount of H_2 released upon heating from 25 to 450°C to that expected for 60 to 450°C, the value of H(desorbed)/D_h for the four catalysts was 0.99 ± 0.05. Thus, since the coverage by H_2 following O_2,300°,0.5;H_2,25°,1 was essentially the same as that after adsorption of H_2 on the catalyst following standard pretreatment, all O(ads) had been removed by H_2,25°,1. In drawing this conclusion, we assume that it is unlikely that following H_2,25°,1 all surface areas are exactly that much larger as to compensate for some retained surface oxygen. Our conclusion as to reducibility by H_2,25°,1 accords with the previous report of Lam and Boudart.

RESULTS AND DISCUSSION—CATALYTIC EXPERIMENTS

Isotopic Exchange between Cyclopentane and Deuterium

Isotopic exchange was investigated in a flow reactor by the techniques previously described (*8*). Mn^{2+}/SiO_2 traps were used to reduce the content in oxygen to below 0.02 ppm and to measure the amount of oxygen in H_2, D_2, and He flows at the catalyst. About 0.2 g of catalyst was employed and flow rates of deuterium were varied in the range 8 to 100 cm^3 min^{-1} to keep total conversions in the vicinity of a few percents. The molar ratio, deuterium/cyclopentane, was 13.

A fresh sample of catalyst was first exposed to the standard pretreatment. At 40°C, the flow of He was replaced by a flow of D_2. After 15 min, the flow of D_2 was replaced by one of D_2 + C_5H_{10} and three or four samples were collected for mass spectroscopy over an interval of about 16 min. The first point was sometimes a little exceptional, otherwises changes in conversion and selectivity were small over the runs. Values of rates, expressed as N_t, the turnover frequency for loss of cyclopentane-d_0 per Pd_s in s^{-1}, and isotopic distribution patterns were averaged over a run and corrected for isotopic dilution (*9*). After the run at 40°C, the temperature was raised to 55°C and after 0.5 h an exchange run was started. The temperature was similarly changed to 70°C and then back to 40°C. The change in rate between the first and second run at 40°C was usually less than 10%. Two runs were made on each catalyst and averaged values are presented. Samples of cata-

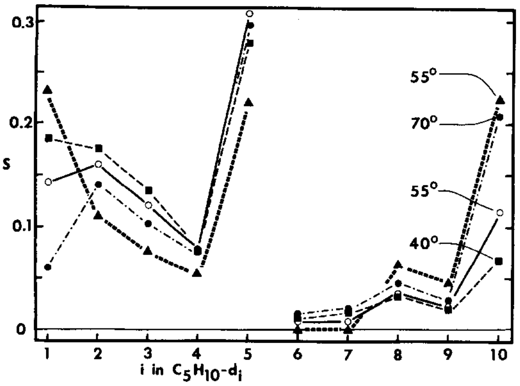


FIG. 1. Isotopic distribution patterns of cyclopentane exchanged with deuterium on Pd/SiO_2 of D_h = 29.3%, thinner lines (●, at 70°C; ○, at 55°C; and ■, at 40°C), and on a Pd/Al_2O_3 (see text) at 55°C, thicker dashed line (▲, at 55°C). x-Axis; i in $C_5H_{10-i}D_i$; y-axis; fraction of $C_5H_{10-i}D_i$ in total exchanged cyclopentane.

lyst were also run after D_2,450° (O_2, 300°,0.5;D_2,450°,1; cool in D_2), but only on one sample of each catalyst and only at 55°C.

As shown in Fig. 1 the general effects of increasing the temperature of isotopic exchange runs for catalysts given the standard pretreatment were increases in all D°_6–D°_{10}, little change in D°_5, and decreases in D°_1–D°_3, particularly D°_1. Here D°_i is the fraction of exchanged cyclopentane molecules, with i atoms of hydrogen exchanged, obtained after the standard pretreatment. Catalyst 79.1-Pd/SiO_2-IV behaved somewhat differently in that D°_2 was less than D°_1 and D°_3 at all temperatures, and D°_2 increased with increasing temperature while D°_1 and D°_3 decreased. The apparent activation energy E°_a, was 88 ± 6 kJ mol^{-1} and without trend to within our rather low precision. The turnover frequency after standard pretreatment, N°_t, at 55°C varied approximately linearly with D_h from 1.5×10^{-3} s^{-1} for D_h = 29.3% to 8.8×10^{-3} s^{-1} for D_h = 79.1%. The effect of D_h upon the isotopic distribution patterns is shown in Fig. 2 and detailed in Table 2. The major effect of increasing D_h is a decrease in D°_{10} and an increase in D°_1–D°_4.

D_h had less effect upon N_t and the isotopic distribution pattern after D_2,450° than after the standard pretreatment (Table 2). At 55°C, N_t was $2.5 \pm 0.5 \times 10^{-3}$ s^{-1} with no clear dependence upon D_h. At 55°C, the patterns for D_h = 49.8 and 65.5% were of the same type as that at 55°C in Fig. 1, but for 29.3%, and particularly for 79.1%, D_1 was greater than D_2 and, where D_1 was large, D_2 was proportionately small. Varia-

TABLE 2

Isotopic Distribution Patterns for Exchange at 55°C

D_h (%)	D_1–D_4	D_5	D_6–D_9	D_{10}	D_5/D_{10}
	A (standard pretreatment)				
29.3	0.504	0.310	0.072	0.115	2.6
49.8	0.485	0.305	0.102	0.111	2.7
65.5	0.565	0.292	0.078	0.065	4.5
79.1	0.608	0.268	0.090	0.037	7.3
	B (treatment D_2,450°C)				
29.3	0.542	0.321	0.084	0.055	5.8
49.8	0.510	0.330	0.090	0.071	4.7
65.5	0.493	0.340	0.099	0.068	5.0
79.1	0.598	0.265	0.086	0.051	5.2

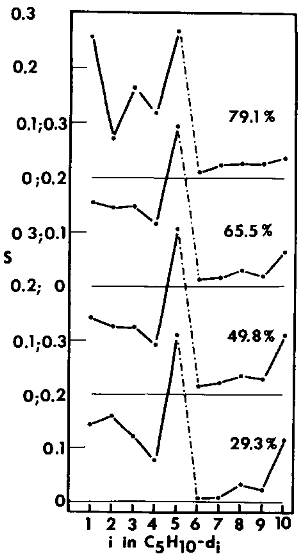


FIG. 2. Isotopic distribution patterns of cyclopentane exchanged with deuterium at 55°C on Pd/SiO_2 catalysts of the percentages exposed shown in the figure. x-Axis; i in $C_5H_{10-i}D_i$; y-axis; fraction of $C_5H_{10-i}D_i$ in total exchanged cyclopentane.

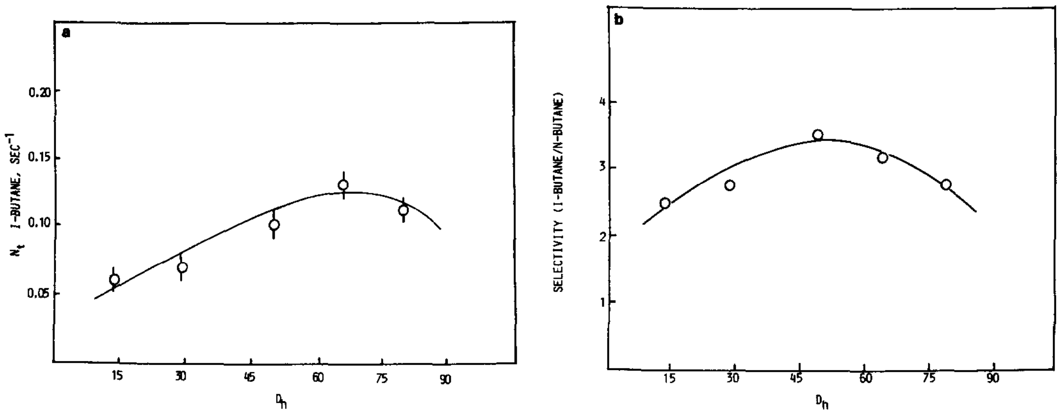


FIG. 3. (a) N_t vs D_n after standard pretreatment. (b) Selectivity vs D_h after standard pretreatment.

tion in D_h had only a small effect upon the other D_i's.

Hydrogenolysis of Methylcyclopropane

Turnover frequencies and selectivities for the hydrogenolysis of methylcyclopropane (MCP) were determined in a differential flow reactor system previously described (*10*).

The effect of D_h on activity and selectivity following the standard pretreatment is presented in Figs. 3a and b in terms of N_t^o of formation of the principal product, isobutane, and the selectivity $S = (i\text{-}C_4/n\text{-}C_4)$. The activities and the selectivities maximized in the vicinity of 60%. Curiously, N_t^o for *n*-butane is roughly the same on both Pd/SiO_2 and Pt/SiO_2, but the larger value of N_t^o for isobutane on Pt/SiO_2 results in S being about 3 for Pd/SiO_2 and 20 for Pt/SiO_2.

Prior work with Pt/SiO_2 has also indicated that the apparent activation energies were independent of D_h. In the present work E_a was evaluated from N_t^o for i-C_4 and n-C_4 at four points in the range $0 \leq T \leq 35$°C for Pd/SiO_2 given the standard pretreatment. For $13.8 \leq D_h \leq 79.2$ the values are 37.0 ± 2.8 and 42.8 ± 3.7 kJ mol^{-1}, respectively. Corresponding values for Pt/SiO_2 were 38.3 ± 1.3 and 43.7 ± 4.2. The similarity is striking but caution is necessary since the relatively generous experimental error could allow for significant differences.

Effect of Pretreatment by Hydrogen

In prior work with Pt/SiO_2 (*10*) and Pt/Al_2O_3 (*11*) the temperature of pretreatment in hydrogen had a more pronounced effect on the structure-sensitive behavior of MCP hydrogenolysis than did D_h. Indeed, a change in that temperature led to qualitative changes in the course of the variation of N_t with D_h. It was, therefore, of interest to investigate this effect for the Pd/SiO_2 series, particularly in view of the structure sensitive nature of the formation of β-hydride observed for these catalysts.

In the present work, fresh samples of catalyst were subjected to O_2,300°,0.5; He,300°,0.25; cool He. These were then successively pretreated in H_2 for 1 h at temperatures ranging from 25 to 450°C, cooled to 0°C (reaction temperature) in H_2, and N_t for MCP hydrogenolysis measured. This is similar to the procedure employed previously for Pt/SiO_2 and Pt/Al_2O_3. A summary of the results obtained for Pd/SiO_2-IV is given in Figs. 4 and 5. It is evident that although the temperature of pretreatment does indeed influence the absolute level of N_t and S, the basic pattern of structure sensitivity, maximum at ~50%, is unaltered. The Pd catalysts, thus, differ qualitatively

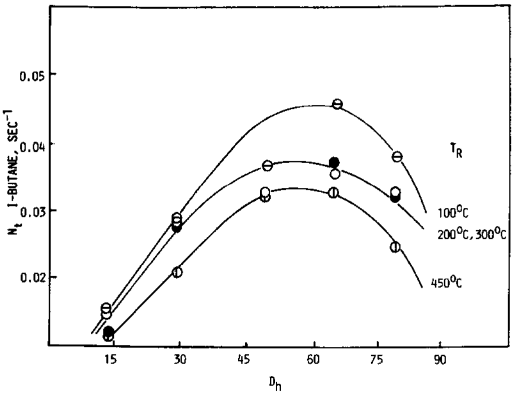


FIG. 4. Summary of structure sensitivity for i-butane formation as a function of pretreatment temperature in H_2.

from the Pt series, in that the structure sensitivity pattern is not changed by pretreatment temperature, so D_h becomes the primary factor correlating structure sensitivity for Pd/SiO_2.

Effect of Pretreatment by Oxygen

Catalyst Pd/SiO_2 also differs markedly from Pt/SiO_2 in response to O_2 pretreatment. In the results above the catalysts were always subjected to O_2,300°,0.5 before subsequent treatment. However, substantial dependence of the rate of MCP hydrogenolysis with O_2 pretreatment temperature has been observed on the Pt/SiO_2 series (*12*). This was investigated here for D_h = 13.8 and 79.1%, using O_2,300°,0.5 or O_2,450°,0.5, after which the material was either reduced H_2,450°,1, cool H_2 or reduced H_2,300°,1;He,450°,1,cool He to reaction temperature. The results shown in Table 3 demonstrate that the activity was the same for O_2,300° and O_2,450°, which contrasts with the threefold increase in N_t for high D_h (81%) measured for Pt/SiO_2 over the same range of O_2 pretreatment temperatures.

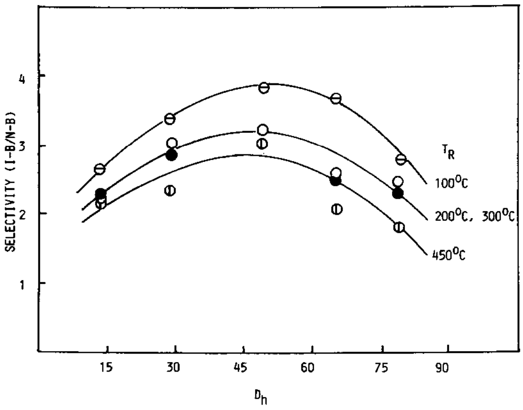


FIG. 5. Summary of structure sensitivity of selectivity of methylcyclopropane hydrogenolysis as a function of pretreatment temperature in H_2.

TABLE 3

Effect of Oxidation Temperature on Catalytic Activity[a]

Catalyst	Treatment			
	O_2,300°,0.5; H_2,450°,1; cool H_2		O_2,450°,0.5; H_2,450°,1; cool H_2	
	$(N_t)_{i-b}$	$(N_t)_{n-b}$	$(N_t)_{i-b}$	$(N_t)_{n-b}$
13.8-Pd/SiO_2-IV	0.011	0.005	0.0115	0.0065
79.1-Pd/SiO_2-IV	0.025	0.014	0.021	0.011
	O_2,300°,0.5; H_2,300°,1; He,450°,1; cool He		O_2,450°,0.5; H_2,300°,1; He,450°,1; cool He	
	$(N_t)_{i-b}$	$(N_t)_{n-b}$	$(N_t)_{i-b}$	$(N_t)_{n-b}$
13.8-Pd/SiO_2-IV	0.061	0.024	0.058	0.024
79.1-Pd/SiO_2-IV	0.11	0.039	0.094	0.035

[a] Reaction conditions, 0°C, 1 atm, H_2/MCP = 16.

Formation of β-Hydride

Boudart and Huang (*13*) found that the solubility of H_2 in supported Pd at given pressure and temperature decreased with decreasing particle size, that is the formation of β-hydride on small particles of Pd is structure-sensitive. As mentioned previously, in the present work the Pd catalysts of $D_h \leq 29.3\%$ were partially converted to the hydride, but no hydride was detected for $D_h \geq 49.8\%$ after the treatment H_2(1atm),25°C. Nandi *et al.* have investi-

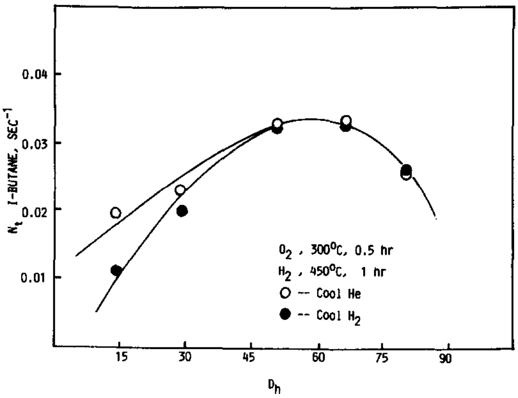


FIG. 6. Comparison of N_t i-butane for cool He and cool H_2 experiments.

gated this under reaction conditions for MCP hydrogenolysis and demonstrated that the extent of hydride formation for catalysts of low D_h was dependent upon the initial state of the catalyst before reaction. Some results are shown in Fig. 6 for two series of experiments in which the series of catalysts were treated prior to reaction by O_2,300°,0.5;He,300°,0.25;H_2,450°,1, followed by cooling either in H_2 (I) or He (II) to the reaction temperature of 0°C. For cool He any hydride formed during H_2,450° would be decomposed, however, this would not occur for cool H_2. One can see from the figure that there is an approximate twofold difference in activity for 13.8-Pd/SiO_2-IV after the two pretreatments, with the material which initially contained hydride being less active. There is also a depression of activity for 29.3-Pd/SiO_2-IV, less substantial but still outside the range of experimental error (*14*). Conversely, there is no difference for $D_h > 49.8\%$, indicative of the absence of hydride formation in these samples.

Several factors should be considered here.

(1) The X-ray results of Nandi *et al.* (*1*) demonstrated that after pretreatment (I) 13.8-Pd/SiO_2-IV was a mixture of 90% $PdH_{0.7}$ and 10% metallic Pd. Upon exposure of this material to H_2/MCP = 16 for 15 min the diffraction pattern revealed ca. 50% $PdH_{0.7}$ and 50% Pd. There is thus evidence that the virtual pressure of H_2 at the surface under reaction conditions is not the same as in the pretreatment. Temperature control in the *in situ* cell was not precise, but the actual reaction temperature was probably between 10 and 20°C. At 25°C the conversion of bulk hydride to Pd occurs only at $P_H < 0.01$ atm (*15*), so the virtual pressure of H_2 in the reaction experiments must be greater than this.

(2) An initial impulse is to associate the twofold decrease in activity for the hydride form of 13.8-Pd/SiO_2-IV with the approximately 50–50 hydride-Pd material observed in the *in situ* X-ray experiments. Nandi *et al.* (*1*) present indirect evidence for uniform dispersion of the hydride throughout the metal (there was no change in particle size upon hydride formation), so the direct correlation of decrease in activity with extent of hydride formation would imply that $PdH_{0.7}$ has no activity. Quantitative data on other low D_h catalysts comparing activity change with fraction hydride formation would be required to check this, but there are a number of factors that cast doubt on such a simplistic interpretation as discussed below.

(3) Results must be visualized in terms of the rather wide distribution of metal particle sizes in these catalysts. For example, data were presented in (*1*) showing a variation in particle size for 29.3-Pd/SiO_2-IV from 1.5 up to 14.0 nm. Approximately 50% of these particles were larger than 5.0 nm, thus a substantial fraction of the large particles may exist as hydride while smaller particles in the distribution remain metallic Pd. For 13.8-Pd/SiO_2-IV there is even a higher proportion of larger particles.

(4) In sum, it seems reasonable to say that the β-hydride phase may possess some activity for hydrogenolysis, but that it is less than that of metallic Pd. Some years ago Couper and Eley (*16*) proposed that vacant *d* levels of Pd would be filled by 1*s* electrons from the hydrogen, weakening chemisorptive bonding and thus diminishing activity.

Benedetti *et al.* (*17*), investigating Pd/C for hydrogenation of benzene, attributed the diminution of activity via β-hydride formation to a possible combination of changes in surface morphology induced by the strained hydride phase and "hydrogen poisoning," the latter presumably related in some way to the electronic interactions proposed by Couper and Eley. While various effects associated with surface morphology may be postulated, they are not easily identified experimentally on supported catalysts and the Couper–Eley postulate remains as viable as any at present.

Comparison of Results on Pd/SiO_2 and Pt/SiO_2

In general, platinum and palladium catalysts exhibit rather similar activity for the two reactions studied in the present investigation, although N_t^o is larger for Pt in both cases. Both catalysts lead to the same type of isotopic distribution patterns of exchanged cyclopentane, in particular the substantial maxima at D_5 and D_{10}. The reactivity behavior is also similar for the hydrogenolysis of methylcyclopropane; both Pd and Pt give only primary hydrogenolysis to butanes and no double hydrogenolysis (cleavage of two bonds in the cyclopropane ring to give, for example, methane plus propane) that accompanies single hydrogenolysis on nickel (*18*) and a number of other transition metal catalysts (*19*). The catalytic characteristics of the two series do, of course, differ in detail. A simple explanation for this may not be easy to advance because relativistic effects are apt to be a major contributor. The relativistic effect is major in the case of platinum but much smaller in that of palladium. The net result of the effect is likely to make binding of organic species to platinum stronger than for palladium, and bond distances shorter (*20*). It has long been recognized that the binding of olefins to platinum is considerably stronger than to palladium.

Isotopic exchange. With both Pt/SiO_2 and Pd/SiO_2 there are substantial maxima at D_5 and D_{10} and D_5/D_{10} steadily decreases as the temperature of the exchange run increases. However, there are some differences. The value of D_{6-10} on Pd/SiO_2 is only about one-half that on Pt/SiO_2. D_8 is usually a distinct maximum on Pd but not, or less clearly, a maximum on Pt. D_6 is rather large on Pt and the values of D_6 through D_9 decline steadily, whereas D_6 is small on Pd.

Alternation between mono- and α,β-diadsorbed cyclopentane can exchange all of the atoms of hydrogen on one side of the cyclopentane ring and lead to a large value for D_5. Transfer of the position of adsorption to the other side of the ring can lead to more extensively exchanged cyclopentanes. Two mechanisms for this seem to be likely, one proceeds via an intermediate α,α-diadsorbed cyclopentane, the other by rollover of α,β-diadsorbed cyclopentane (*8*). Conversion of the α,α-diadsorbed to a monoadsorbed cyclopentane could put the position of adsorption into the original, already isotopically exchanged side of the ring or into the unexchanged side. The former process would necessarily lead to a significant value of D_6. One rollover process would generate D_8 as the most exchanged species, and thus, rollover could result in a clear maximum at D_8. Both processes probably occur on Pt and Pd, but reaction via α,α-diadsorbed cyclopentane is relatively more important on Pt than on Pd. This follows from the relative values of D_6 and D_8 noted above and accords with the weaker bonding of adsorbed hydrocarbon species to Pd.

After the standard pretreatment, Pd/SiO_2 was structure-sensitive in a simple, monotonic fashion as D_h increased from 29.3% both with respect to N_t^o and the D_i^o's. This behavior is summarized in Table 4 and Fig. 2. Table 4 also summarizes the results with Pt/SiO_2 (*8*). The pretreatment D_2,450° led to Pd/SiO_2 catalysts which were nearly structure insensitive both for N_t and for the D_i's. The isotopic distribution patterns rather resembled that of 65.5-Pd/SiO_2-IV after standard pretreatment. 79.1-Pd/SiO_2-IV diverged somewhat from the others, but

TABLE 4

Behavior of Pd/SiO_2 and Pt/SiO_2 in the Isotopic Exchange of Cyclopentane at 55°C[a]

	Pd/SiO_2		Pt/SiO_2
	As D_h 29.3 → 79.1%[b]		As D_h 16 → 81%[b]
D_{10}°	× 1/3		× 1[c]
D_5°	× 0.86		× 1[c]
D_{1-4}°	× 1.2		× 2
N_t°, s^{-1}	$1.5 \rightarrow 8.8 \times 10^{-3}$		0.015[c]
N_t, s^{-1}	$2.5 \pm 0.5 \times 10^{-3}$[c]		0.015[c]
D_{10}	× 1[c]	D_{10}/D_{10}°	0.5
D_5	× 1[c]	$D_{6-10}/D_{6-10}^{\circ}$	<1
D_{1-4}	× 1[c]	D_{1-4}/D_{1-4}°	>1

[a] D_i° and N_t° are after the standard pretreatment, D_i and N_t are after D_2,450°.

[b] Effect of increasing the value of D_h over the listed range.

[c] Nearly independent of D_h.

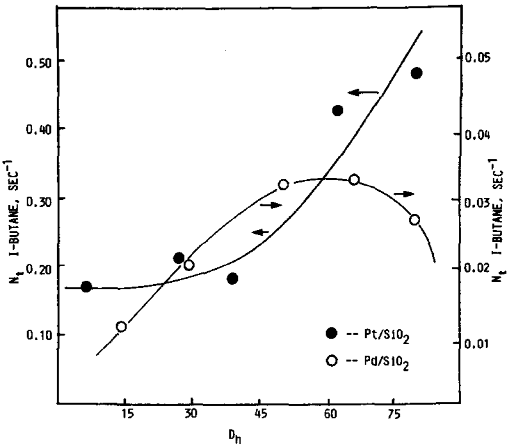


FIG. 7. Comparison of N_t i-butane for Pt/SiO_2 after O_2,300°,0.5; H_2,450°,1;cool H_2.

much of the difference resulted from a larger value for D_1.

The main effect of increasing D_h in Pt/SiO_2 was increase in D_{1-4}° and decrease in D_{6-9}° with little change in N_t°. Change from the standard to the D_2,450° pretreatment led to catalysts which were not very structure-sensitive either with respect to N_t or to the D_i's. The isotopic distribution patterns were, however, significantly different from those obtained after the standard pretreatment, but this difference was smaller with Pt/Al_2O_3 (*11*). N_t/N_t° was larger than unity except at the lowest D_h.

We reran a Pd/Al_2O_3 which had been used some years before (catalyst stock IV-VI of Ref. (9)). It had been made by impregnation with HCl + $PdCl_2$ and in the present work was given the standard pretreatment. Results appear in Fig. 1. The value of D_{10} was much larger than with Pd/SiO_2 in accordance with the much larger ratios D_{10}/D_5 seen in previous work with Pd/Al_2O_3. However, the chloride content of this Pd/Al_2O_3 makes interpretation of the differences rather difficult.

Methylcyclopropane hydrogenolysis. Comparison with our prior results for Pt/SiO_2 (*10*) is given in Figs. 7 and 8 for MCP hydrogenolysis after O_2,300°,0.5;H_2,450°,1,cool H_2. The i-butane N_t's are six to eight times higher for Pt/SiO_2 than for Pd/SiO_2, while the *n*-butane values are roughly the same for the two. Thus, the selectives shown in Fig. 8 are much lower for Pd/SiO_2, as has been reported previously (*21*).

A major difference between Pt/SiO_2 and Pd/SiO_2 is the effect of H_2 pretreatment on activity, shown in Fig. 9 for N_t for i-butane on two catalysts of similar D_h. Although N_t remains nearly constant for Pd/SiO_2, there is a wide variation for Pt/SiO_2. A similar behavior is observed for N_t for *n*-butane and for comparisons between comparable

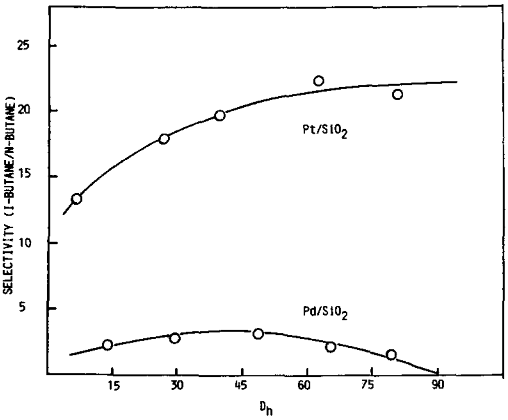


FIG. 8. Comparison of selectivity for methylcyclopropane hydrogenolysis between Pt/SiO_2 and Pd/SiO_2. Pretreatment as in Fig. 7.

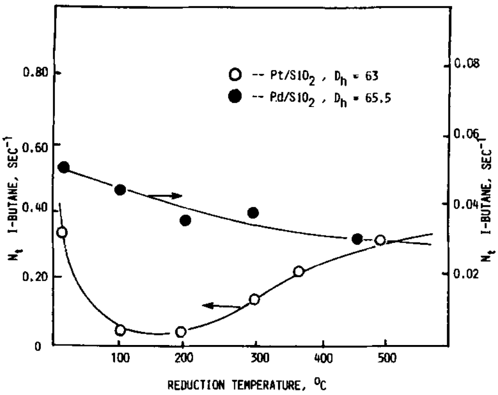


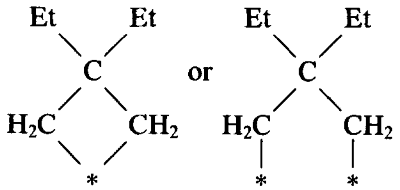
FIG. 9. Comparison of activity response to variation in H_2 pretreatment. Temperature for Pt and Pd catalysts of similar D_h.

platinum and palladium catalysts of other D_h. One might question the comparison at the lowest H_2 pretreatment temperature of 25°C, since we have not specifically investigated the extent of reduction of Pt/SiO_2 after H_2,25°,1. However, both series of catalysts are certainly reduced at temperatures above 100°C (*3*).

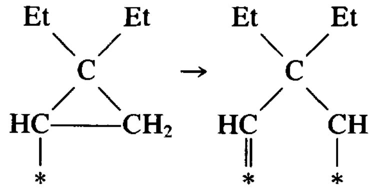
The reduction of Pd/SiO_2 after H_2,25°,1, indicated by the H_2–O_2 experiments described before, is verified by the pretreatment catalytic experiments summarized in Table 5, comparing H_2,300°,1 with H_2,25°,1. As can be seen, N_t's for both products are essentially the same for the two conditions.

These comparisons indicate substantial differences in selectivity and effect of pretreatment between Pt/SiO_2 and Pd/SiO_2, although both catalyze only single hydrogenolysis. The higher total activity of Pt/SiO_2 correlates with the stronger bonding to Pt than to Pd if often is on the left side of the typical volcano curve representing activity vs bond strength. Dalla Betta *et al.* (*22*) also report Pt to be more active than Pd for cyclopropane hydrogenolysis in accord with present results. Although on the basis of these data we cannot assert that stronger bonding leads to increased activity, the results is not inconsistent with this postulate.

What is the origin of the much larger selectivity to i-butane on Pt? Chevreau and Gault have studied the hydrogenolysis with deuterium of 1,1-diethylcyclopropane on a number of metals (*23*). The only product on Pd is $(C_2H_5)_2C(CH_2D)_2$, a result which strongly supports initial adsorption as (*18*)



A similar intermediate predominates on Pt films, but in addition to d_2 (82%) there was also d_3 (13%) and d_4 (5%). They assigned d_3 to the sequence



Pt/Al_2O_3 gave less d_2, but that catalyst contained chloride which could have complicated matters. The additional process on Pt might contribute to the higher selectivity for i-butane in the hydrogenolysis of methylcy-

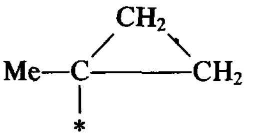
TABLE 5

Effect of Hydrogen Pretreatment at Low Temperatures on Methylcyclopropane Hydrogenolysis[a]

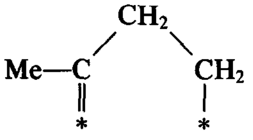
	Treatment			
	O_2,300°0.5; H_2,25°,1; cool H_2		O_2,300°,0.5; H_2,300°,1; He,450°,1; cool He to 25°C; H_2,25°,1; cool H_2	
Catalyst	$(N_t)_{i-b}$	$(N_t)_{n-b}$	$(N_t)_{i-b}$	$(N_t)_{n-b}$
13.8-Pd/SiO_2-IV	0.018	0.006	0.021	0.006
29.3-Pd/SiO_2-IV	0.021	0.007	0.019	0.007
65.5-Pd/SiO_2-IV	0.051	0.014	0.063	0.014
79.1-Pd/SiO_2-IV	0.022	0.010	0.024	0.010

[a] Reaction conditions as in Table 3.

clopropane on Pt, but, even if all of the additional process gave i-butane, that could not convert a selectivity of 3 (i-C_4/*n*-C_4) on Pd to one of 15 on Pt. It appears probable then that the higher selectivity for formation of i-butane on Pt than on Pd results from a larger degree of steric interaction in the transition state between the surface and the methyl group on Pt than on Pd. Hydrogenolysis on Pt via initial adsorption as



is unlikely since this would lead exclusively to



and then to *n*-butane.

The large difference in sensitivity to the temperature of pretreatment in H_2 between the two series is not well understood at this point. One cannot directly ascribe it to the formation of hydride in Pd/SiO_2, since across the range of D_h we have catalysts that both do and do not form hydride, yet their behavior is similar. Possible site blockage by water formation, not removed by treatment at the lower temperatures, could affect activity patterns, but again this should be similar for the two series. A possible explanation may reside simply in consideration of the relative lattice energies, 91 kcal/mol for Pd vs 135 kcal/mol for Pt (*25*). It is known that treatments such as O_2,300°,0.5 are sufficient to create significant surface disorder in Pt (*26*). The decrease in N_t for Pt/SiO_2 with increasing temperature of pretreatment in H_2 at temperatures up to ca 200°C, such as that shown in Fig. 9, has been attributed to a combination of removal of water and progressive annealing of such surface vacancies. Given the 30% smaller lattice energy for Pd, it could well be that hydrogen adsorbed at higher temperature (450°C) leads to a surface morphology that is not as reactive as that resulting from the lower temperature treatment. This can be seen directly upon comparing Figs. 3 and 6. The pretreatment O_2,300°;H_2,300°;He,450° leads to activities for all Pd/SiO_2 catalysts which are about four times greater than those resulting from the pretreatments O_2,300°H_2, 450°;cool in H_2 or O_2,300°;H_2,450°;cool in He. Exposure to hydrogen at 450°C must lead to a surface morphology which is less active than that resulting from exposure to hydrogen at 300°C, but the reason for this is not clear.

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