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Rh/SiO_2: Catalyst Characterization and Study of the Hydrogenolysis of Methylcyclopropane

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The adsorption of hydrogen, carbon monoxide, and oxygen and X-ray line profile analysis have been investigated on a series of Rh/SiO_2 catalysts made by ion exchange with $Rh(NH_3)_5(H_2O)^{3+}$ and by impregnation with $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$. The percentage exposed (D_h) of the series of catalysts as measured by hydrogen chemisorption at 25°C varied from 11 to 108%. Ease of reduction of the oxidized catalysts decreased as D_h increased and reduction in hydrogen was incomplete in hydrogen at 25°C except for the catalysts of smallest D_h. The rates of hydrogenolysis of methylcyclopropane (MCP) at 0°C decreased with increasing D_h by a factor of about 9 over the range of D_h of the series of catalysts for catalysts pretreated O_2,300°,0.5;H_2,300°,1;He,450°,1 where the last number in each triad was the time of exposure in hours. Omission of He,450°,1 led to decreased rates and augmented structure sensitivity, but H_2,25°,1 without He,450°,1 led to inverted structure sensitivity, presumably because of residual oxygen on rhodium. The activation energy for hydrogenolysis was about 37 kJ mol^{-1}. The ratio of isobutane to butane in the products was about 20 for $D_h = 11\%$, declined rapidly with increasing D_h, and became about 3.5 for $D_h > 50\%$. Pretreatment conditions (temperature of pretreatment by H_2, presence or not of terminal He,450°,1) had little effect on the ratio.

INTRODUCTION

We previously have reported the physical characterization of two series of catalysts of a wide range of percentages exposed, Pt/SiO_2 (*1, 2*) and Pd/SiO_2 (*3*). The methods of characterization included X-ray line profile analysis (*4–6*), hydrogen chemisorption, and reaction of adsorbed hydrogen with oxygen (*1–3*). The hydrogenolysis of methylcyclopentane, the hydrogenation of propylene, and isotopic exchange between cyclopentane and deuterium were studied on these catalysts (*7–9*). Rates and selectivities in these reactions were affected both by the percentage exposed and by the conditions of pretreatment of the catalysts. The role of pretreatment was dominant with Pt/SiO_2 but somewhat less important with Pd/SiO_2. It appeared desirable to extend this investigation to the case of Rh/SiO_2 catalysts. We present here the preparation, physical characterization, and catalytic activity for the hydrogenolysis of methylcyclopropane on a series of Rh/SiO_2 catalysts. Temperatures during initial reduction of the catalysts and during pretreatments have not exceeded 450°C.

EXPERIMENTAL AND RESULTS

Catalyst Preparation

Davison Grade 62 wide-pore silica gel, 80–100 mesh, was employed as the support. Its characteristics and the method of pretreatment have been reported (*1, 4*).

The catalysts were prepared by two methods: ion exchange with $Rh[(NH_3)_5(H_2O)]Cl_3$ and impregnation to incipient wetness with solutions of $Rh_6(CO)_{16}$ and $Rh_4(CO)_{12}$ (Strem Chemicals). Preparation by ion exchange followed

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TABLE 1

Catalysts

Catalyst[a]	wt% Rh	Calcination[b]	Reduction[c]
11-SiO_2-Rh_6	0.50	60°,0.75[d]	60°,0.5;250°,1
27-SiO_2-Rh_4	1.40	250°,1	250°,1
31-SiO_2-Rh_4	0.60	250°,1	250°,1
37-SiO_2-Rh_6	0.60	250°,1[e]	250°,1
50-SiO_2-Rh_4	0.60	400°,1	140°,1
52-SiO_2-Rh_4	0.55	None	250°,1.2[f]
53-SiO_2-Rh-IonX	0.78	None	450°(H_2O),1;450°,1[g]
58-SiO_2-Rh-IonX	0.78	None	370°,3[h]
108-SiO_2-Rh-IonX	0.78	400°,3[i]	135°,2[j]

[a] Catalyst code: the beginning number is D_h (Table 2), Rh_6 designates preparation by impregnation with $Rh_6(CO)_{16}$, Rh_4 designates impregnation by $Rh_4(CO)_{12}$, IonX, ion exchange.

[b] Treatment, if any, by O_2 before reduction in H_2.

[c] Reduction in H_2. This was followed by flushing with N_2 at 25°C before exposure to air.

[d] Nine impregnations. After each impregnation and removal of solvent, the material was treated O_2,60°,0.75.

[e] Seven impregnations. The catalyst was exposed to oxygen only after the last impregnation.

[f] H_2 was introduced at 25°C after impregnation and removal of solvent. The catalyst was then treated H_2,100°,0.7;H_2,250°.

[g] During the first hour at 450°C and during warming to 450°C, the H_2 was saturated with H_2O at 25°C.

[h] Heated to 370°C at 20°C min^{-1}.

[i] Heated to 400°C at 1°C min^{-1}.

[j] Heated from 25 to 135°C at 0.5°C min^{-1}.

the procedure used for $Pt(NH_3)_4^{2+}$ (*1*). $Rh_6(CO)_{16}$ is very sparingly soluble in most solvents and, even with chloroform, multiple impregnations were required to secure the desired loadings of rhodium. $Rh_4(CO)_{12}$, however, was sufficiently soluble in pentane that a single impregnation sufficed. Impregnations were effected in a stream of oxygen-free nitrogen in a modified rotary evaporator. The solvent was evaporated by the stream of nitrogen with the assistance of warming by an infrared lamp. The chloride in $[Rh(NH_3)_5(H_2O)]Cl_3$ should have been removed completely during ion exchange at a pH of 9.5. This would not be true with $[Rh(NH_3)_5Cl]Cl_2$, which sometimes has been employed. Thus, the catalysts should have been free of chloride barring possible introduction of chloride from the chloroform solvent used with $Rh_6(CO)_{16}$. The list of catalysts appears in Table 1. As will be noted, the ion-exchanged catalysts had the highest percentage exposed (D_h).

The catalysts made via rhodium cluster carbonyls were prepared for comparison with mixed metal catalysts made via Rh–Co cluster carbonyls (*10*). Preparation of Rh/SiO_2 from rhodium carbonyls previously has been reported (*11, 12*), and the chemistry of the interaction between carbonyl and silica has been studied (*13–15*).

Percentage Exposed of Rhodium

Hydrogen chemisorption was measured by the technique previously described, except that a trap of MnO/SiO_2 rather than of Cr^{3+}/SiO_2 was used to reduce the oxygen in

TABLE 2

Percentage Exposed of Rh/SiO_2 Catalysts

Catalyst	D_h[a] (%)	D_{25}[b] (%)	D_{375}[c] (%)	D_{CO}[d] (%)	$\langle L \rangle$[e] (nm)	D_x[f] (%)
11-SiO_2-Rh_6	11	13	17	8	9.3	11.5
27-SiO_2-Rh_4	27	28			3.8	28.5
31-SiO_2-Rh_4	31	34	36.5	35	8.4	13
37-SiO_2-Rh_6	37	40	46	31	3.7	29
50-SiO_2-Rh_4	50	53	62	53		
52-SiO_2-Rh_4	52	55	60	53		
53-SiO_2-Rh-IonX	53	60	67			
58-SiO_2-Rh-IonX	69	83	96	82		
108-SiO_2-Rh-IonX	114	125	145	172		

[a] Measured by desorption to 375°C after pulse adsorption of H_2 at 25°C on O_2,250°,0.5;H_2,250°,1;H_2,375°,1;Ar,375°,1.

[b] Measured by desorption to 375°C after H_2,25°,1 on a catalyst of the same pretreatment as above.

[c] As in *b*, but after H_2,375°,1; cool in H_2 to 25°C.

[d] Measured by pulse chemisorption of CO at 25°C; see text.

[e] Average Rh particle diameter from X-ray line profile analysis done after H_2,300°,1.

[f] Computed from $\langle L \rangle$ as in Ref. (*4*).

the argon carrier to less than 0.03 ppm. Further, the purged Carle switching valve that permitted bypassing and isolation of the catalyst during heating to 450°C for measurement of hydrogen desorption was altered by insertion of a needle valve in the bypass loop. This permitted the resistance in the bypass line to be set equal to that of the catalyst bed and thus to avoid any flow upset at 450°C when the switching valve was returned to the position giving flow through the catalyst bed. Hydrogen was purified by passage through a Deoxo unit (Engelhard), a silica gel trap (Davison Grade 62) cooled to −197°C, and an MnO/SiO_2 trap just preceding the catalyst. The oxygen employed was Linde 99.999%, less than 0.5 ppm hydrocarbons. During catalyst pretreatments, the rate of temperature rise was set at 4–10°C a minute by a temperature programmer. Catalyst weights were 0.1 to 0.4 g, and the argon flow rate was about 25 cm^3 min^{-1}.

Quantities of H_2 chemisorbed on the catalysts of Table 1 under various conditions are presented in Table 2. A catalyst was initially treated O_2,250°,0.5;H_2,250°,1; H_2,375°,1;Ar,375°,1, where O_2,250°,0.5; designates treatment in flowing oxygen at 250°C for 0.5 h, and the semicolon separates elements of the overall pretreatment. Five pulses of H_2 separated by 7 min each were passed over the catalyst at 25°C in oxygen-free argon, and the amount of hydrogen adsorbed was calculated (*1*). The catalyst then was isolated by means of a switching valve, the temperature was raised and held at 375°C by means of a preheated furnace, the argon flow was reestablished, and the amount of desorbed H_2 was measured (*1*). Previously (*1, 3*), the percentage of metal exposed had been calculated from the amount of H_2 adsorbed from the pulses with the assumption that H_{ads}/M_s was unity and symbolized D_h. The behavior of Rh/SiO_2 was less satisfactory than that of Pt/SiO_2 and Pd/SiO_2, because desorption of hydrogen following the passage of a pulse of H_2 tailed more than with Pt/SiO_2 and Pd/SiO_2 with consequent reduction in accuracy of measurement of the amount of hydrogen adsorbed. Accordingly, with Rh/SiO_2 we define D_h as that measured by the desorption peak. Divergence between D_h measured by adsorption and by desorption was not large. Values of D_h in Table 2 are an average of two or, more usually, three determinations. Catalysts 58- and 108-SiO_2-Rh-IonX were also examined in the same fashion after O_2,300°,0.5;H_2,300°,1;Ar,450°,1. Ar,450°,1 in this pretreatment vs Ar,375°,1 in the pretreatment used in general led to some decrease in percentage exposed. H_2,550°,14;Ar,450° led to a value of D_h for 108-IonX of 62%, whereas with 58-IonX the coarsening effect of H_2,550°,14 was smaller, about 15%.

Since O_2,300°,0.5;H_2,300°,1;Ar(or He), 450°,1 has been our "standard" pretreatment, and since it preceded many of the catalytic runs, we use D_h measured by desorption after that pretreatment for calculating turnover frequencies for the catalysts with the highest two percentages exposed, 58- and 108-SiO_2-Rh-IonX. D_h's also are used in the catalyst code for these two catalysts. Differences between D_h's measured after the standard pretreatments and after the O_2,350°;H_2,375°;Ar,375° pretreatment should be less with catalysts of smaller D_h.

We doubt that there are any specific conditions under which exactly one atom of hydrogen is attached to each M_s atom (*1*). However, there may be conditions under which H(average)/M_s is in general near unity. If so, measurement of H/M under appropriate conditions could provide an empirically useful method of measuring M_s/M (*1*). The measured value of H/M declines with increasing temperature for Pt (*1*), Pd (*2*), and Rh (*16*, *17*); thus, the temperature of adsorption at which H/M = D_h can be selected only by calibration against some "absolute" method of measuring percentage exposed or particle size, such as X-ray line profile analysis, small-angle X-ray scattering, or electron microscopy.

The assumption that H/Rh_s = 1.00 at 25°C has been used in the past (*18–20*), but evidence for this assumption is less abundant than for supported Pt, and there are reports that H/Rh_s can significantly exceed unity at 25°C for Rh particles of D_h near 100% (*16*, *21*), presumably because of the presence of a significant fraction of Rh atoms in low coordination number capable of holding two H atoms. We have measured the average diameters of Rh crystallites in four catalysts by X-ray line profile analysis using techniques previously described (*4*). Values are shown in Table 2 along with the derived percentages exposed, D_x. Agreement between D_h and D_x is excellent in two cases, but, for unknown reasons, poor for 31-SiO_2-Rh_4.

Following the measurement of D_h (which terminated in Ar,375°), catalysts were treated H_2,25°,1, and desorption by Ar,375° was measured and expressed as D_{25}, i.e., H/Rh in percent. Values of D_{25} appear in Table 2. In most cases D_{25} was about 10% larger than D_h. Following measurement of D_{25}, catalysts were treated H_2,375°,1, cooled in H_2 to 25°C, and flushed with Ar, and the amount of H_2 desorbed by Ar,375° was measured and expressed as D_{375} (H/Rh in percent). The ratio D_{375}/D_{25} was near 1.16 for many catalysts.

Chemisorption of Oxygen

The chemisorption of oxygen at 25°C on 58- and 108-IonX after H_2,450°,14;Ar,450° was measured by the pulse technique and expressed as O/Rh. The adsorbed oxygen was titrated with H_2 at 25°C (*1*), and the catalyst then was heated to 450°C in flowing Ar to measure the amount of H_2 desorbed. For 108-IonX, O/Rh was 143%. The Rh nearly had been converted to Rh_2O_3(ads). Upon desorption, H/Rh was only 27%. Thus, the surface rhodium oxide had been partly but incompletely reduced by five pulses of H_2 at 25°C. Following titration, the catalyst contained H(ads) and unreduced oxygen, and the amount of H(ads) was large enough fully to remove the residual oxygen during heating to 450°C in Ar.

The sequence of experiments was repeated on the same sample of catalyst. O/Rh was only 130%, and the desorbed H_2 corresponds to H/Rh = 14%. Apparently the sequence leads to coarsening. On 58-IonX, O/Rh was 104%, and the amounts of H_2 desorbed corresponded to H/Rh = 48%, a value well below 58%. Repetition led to lower values of O/Rh and of H(desorbed)/Rh.

Values for O/Rh_s of 1.4–1.5 previously have been reported following exposure of Rh catalysts to O_2,25° (*16, 17*). However, Fuentes and Figueras (*19*) reported that H/Rh_s and O/Rh_s at 25°C were equal and that the hydrogen–oxygen titration proceeded satisfactorily. The origin of the disagreement between their work and that reported here might lie in the low pressures of oxygen to which the catalysts of Ref. (*19*) appear to have been exposed initially, only a few Torr. Conceivably, there was a larger rise in the temperature of the rhodium particles upon first exposure to oxygen in the present work, and this would have led to more adsorption of oxygen (*16*).

Experiments on 108-IonX showed that H_2,25°,1 does not completely reduce 108-IonX;O_2,300°,0.5. After O_2,300°,0.5;H_2, 25°,1, the catalyst was flushed with Ar at 25°C, and the amount of H_2 liberated during heating in Ar to 450°C was measured. The quantity was zero; thus, after H_2,25°,1, the degree of removal of oxygen is such that the amount of H(ads) is insufficient to remove residual oxygen during Ar,450°. However, Ar,450° leaves the residual oxygen in a more readily removable form. Thus, five pulses of hydrogen resulted in a consumption of H_2 larger than the amount liberated by then heating the catalyst to 450°C in Ar. Upon repetition of pulse adsorption and desorption, values became normal. It appears that H_2,25°,1 led to partial reduction of what was probably Rh_2O_3/SiO_2, that enough adsorbed hydrogen was present following H_2,25°,1 nearly to remove oxygen during Ar,450°, and that the residual oxygen after Ar,450° was in a form much more readily removed by H_2,25°. 58-IonX behaved similarly, except that some hydrogen desorbed during the last step in O_2,300°;Ar flush; H_2,25°;Ar, 25°;Ar,450°. Thus the extent of reduction by H_2,25°,1 is larger for 58- than for 108-Rh-IonX, but still incomplete. O_2,300°,0.5 also must largely convert less highly dispersed Rh/SiO_2 to oxide. Thus, 27-SiO_2-Rh_4, after storage in air, exhibited an Rh(111) reflection in X-ray diffraction that corresponded to an average Rh particle diameter of 2.8 nm. After O_2,300°,0.5 no diffraction from metallic rhodium could be detected. H_2,300°,1 restored the Rh(111) peak, and to an intensity twice that of the stored catalyst. The calculated average Rh particle diameter was 3.8 nm. Thus, the stored catalyst appears to have had a metallic core surrounded by a layer of oxide. O_2,300° oxidized the metallic core, and subsequent H_2,300°,1 fully reduced the rhodium oxide/SiO_2. These results resembled those observed with high-resolution scanning transmission electron microscopy on Rh particles evaporated on a planar surface of amorphous silica (*22*). In that work, heating in air produced particles with oxide outer layers and metallic cores. However, it appeared that 500°C was needed for complete oxidation of 5.0-nm particles of Rh, whereas 300°C appeared to suffice for 3.8-nm particles in the present work.

Chemisorption of CO

Adsorption of CO was measured at 25°C by the pulse technique after pretreating catalysts in H_2 at 250–300°C followed by flushing with Ar at 375–450°C. Results are expressed as D_{CO} (CO/Rh) in Table 2. Agreement with D_{h} is fairly good for $D_{\mathrm{h}} <$ 52%, but CO/H becomes considerably larger than unity for Rh/SiO_2's with larger D_{h}'s. Such behavior has been reported before (*16, 18, 20, 23*).

Two items of controversy have arisen with respect to Rh/support materials. One question relates to the morphology of small crystallites of Rh. Prestridge and Yates have interpreted the results of electron microscopic examination of Rh/SiO_2 (*24*) and Rh/Al_2O_3 (*23*) as showing that Rh occurs as monolayer clusters ("rafts") on these supports; see also Ref. (*12*). On the contrary, Yacamán *et al.* (*25*), recognized the presence of no rafts on Rh/SiO_2, but rather icosahedral (non-fcc) particles for catalysts of percentages exposed of 80% and cubooctahedral (fcc) particles for percentages exposed of 50%. With $Rh/\gamma\text{-}Al_2O_3$, Newcomb *et al.* (*26*) report the absence of rafts and the presence of fcc clusters of Rh that are spheroidal down to somewhat less than 1.0 nm in diameter.

The other question relates to the location and identity of surface $Rh(CO)_2$ formed during adsorption of CO on supported Rh. References (*27, 28*) are leading references to the rather extensive literature dealing with IR absorption spectroscopy of CO adsorbed on Rh/support. Absorption bands ascribed to $Rh(CO)_2$ have been observed in these studies. The $Rh(CO)_2$ units have been assigned to isolated atoms of Rh (probably +1) (*29, 30*) and to edge sites of low CN (*31*). van't Blik *et al.* (*28*) have reported an EXAFS study that relates to both questions using $Rh/Al_2O_3\text{–}Cl$ made by impregnation to incipient wetness with $RhCl_3$ followed by H_2,300°,1. H/Rh was 1.7 and CO/Rh was 1.9. EXAFS and other data indicated that all rhodium was reduced and in clusters of 15–20 atoms with an average CN of 5 ± 0.5. Upon exposing the catalyst to CO at 25°C, only $Rh(CO)_2$ pair bands appeared, and EXAFS indicated that the Rh clusters had been drastically disrupted. It was proposed that only small clusters of Rh would be drastically disrupted and the Rh in $Rh(CO)_2$ was probably oxidized to Rh^+ by surface OH groups.

Catalytic Experiments

The experimental apparatus and procedures were essentially the same as those employed previously for studies of supported Pt and Pd (*1, 2*). Methylcyclopropane was supplied by K & K Company, 98% pure, and was further purified by removal of olefins, predominantly *n*-butene (*1*). Ultrahigh purity hydrogen (Linde, 99.999%) was used after further purification by MnO/SiO_2 for removal of trace oxygen; in catalytic experiments, the hydrogen contained less than 1 pm H_2O and less than 0.1 ppm O_2. Oxygen (Linde, 99.999%, less than 0.5 ppm hydrocarbon) was used for catalyst pretreatment without further purification. Helium (99.999%) was passed through a silica gel trap at −197°C to remove possible impurities.

Measurements of turnover frequency for MCP hydrogenolysis were carried out in a flow reactor under differential conversion conditions (<10% conversion). Hydrogen was saturated with MCP by passing it through a thermostated bed of porous Filtros FS-140 containing the MCP (*7, 8*). Feed composition was maintained at approximately $H_2/MCP = 16$ in all experiments, although there was some variation in this ratio and the actual ratio was determined analytically for each experiment. The reactor consisted of a $\frac{1}{4}$-in.-o.d. Pyrex glass U-tube containing 0.01 to 0.2 g of catalyst; in most experiments the reactor was immersed in an ice bath to maintain the reaction temperature at 0°C. Warm water or ethanol–Dry Ice baths were employed to obtain the other temperatures needed to measure activation energies. The absence of temperature gradients was verified experimentally by use of the thermocouples in the catalyst bed. Analytical procedures were the same as described previously (*1, 2*).

Prior to experiments, catalysts were pretreated O_2,300°,0.5 to remove any carbonaceous contaminants on the Rh (*1*), and then He,300°,0.25;H_2,T_H,1;cool in H_2. The temperature T_H was in the range 25–450°C. One group of experiments employed the "standard" pretreatment, O_2,300°,0.5;H_2,300°,1; He,450°,1;cool in He. In this last case, the catalyst was free of adsorbed hydrogen when first exposed to hydrogen at $T \sim 0°C$.

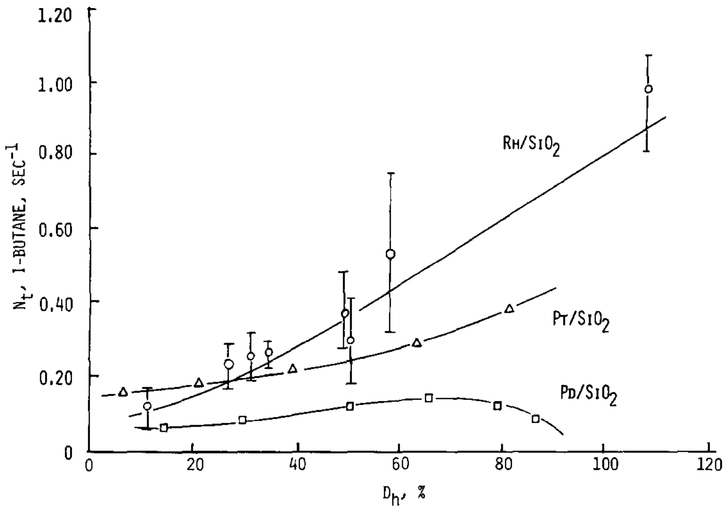

FIG. 1. N_t for i-butane *vs* D_h for Rh/SiO$_2$ and comparison with Pt/SiO$_2$ and Pd/SiO$_2$; standard pretreatment.

Values of turnover frequencies were calculated separately for butane and isobutane. The selectivity is expressed as $S = N_t(\text{i-C}_4)/N_t(n\text{-C}_4)$. The approximate order of the reaction with respect to MCP was measured by measuring rates at different values of H$_2$/MCP obtained by varying the temperature of the Filtros saturator. The order was 0.2–0.3, except for the catalyst of lowest D_h (11-SiO$_2$-Rh$_6$), which had the value 0.7. These results are in general agreement with those of Bond and Newham (*32*). Measured values of N_t were adjusted to H$_2$/MCP = 16 using the kinetic order in MCP to be 0.7 for 11-Rh$_6$ and 0.25 for the other catalysts. Change in the partial pressure of hydrogen was always small, and it was ignored. Pure SiO$_2$ support had no activity under the conditions employed.

Two granule sizes of silica gel had been used in the study of MCP hydrogenolysis on Pt/SiO$_2$: 70–80 and 120–140 mesh (*7*). Since the two mesh sizes led to equivalent rates, diffusional gradients in the catalyst pores must have been absent. Rates in the present experiments are roughly the same as those found with Pt/SiO$_2$, so that serious concentration gradients also were absent in this work, which employed 80- to 100-mesh granules of the same silica gel.

The extent of deactivation with time-on-stream varied with D_h, from zero deactivation over a 1-h period with 11-Rh$_6$ to 25% deactivation for 108-IonX over a period of 30 min. In all cases, the rate of deactivation was essentially constant, and reported values of N_t were obtained by linear extrapolation to zero time.

Effect of Percentage Exposed on Catalytic Activity

Values of N_t (i-butane) and of the corresponding S are shown in Figs. 1 and 2 for reaction conditions H$_2$/MCP = 16, 0°C and standard pretreatment. The points indicate the average values of typically four or more experiments, with the range showing maximum and minimum values. Exceptions were D_h = 27 and 37%, where only two experiments were run. Data for Pt/SiO$_2$ and Pd/SiO$_2$ under the same conditions of pretreatment and reaction are also included for comparison. The value of N_t (i-butane) increases by a factor of 9 with increasing percentage exposed, so the reaction is clearly moderately structure sensitive over the Rh/SiO$_2$ series. The pattern for N_t (i-butane) is

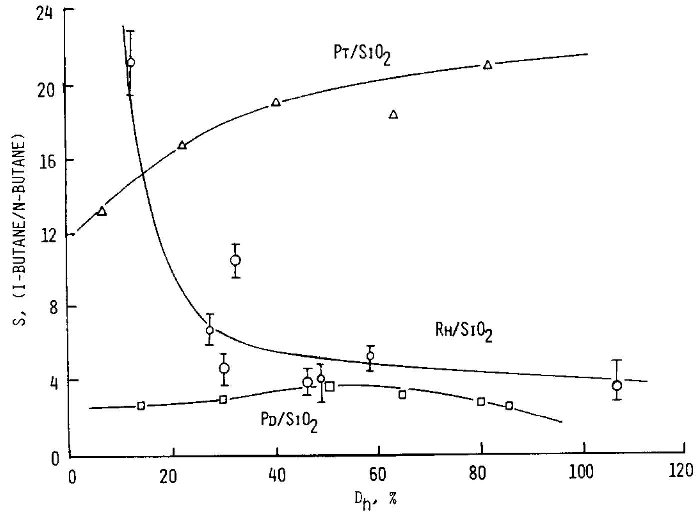

FIG. 2. Selectivity vs D_h for Rh/SiO$_2$ and comparison with Pt/SiO$_2$ and Pd/SiO$_2$; standard pretreatment.

similar to that for Pt/SiO$_2$; however, for $D_h > 40\%$, the activity of Rh/SiO$_2$ is greater by a factor of 2–3; in comparison to Pd/SiO$_2$, this factor increases to ca. 10. This activity order for these metals in MCP hydrogenolysis is in agreement with the results for cyclopropane (CP) hydrogenolysis reported by Bond (*32*).

The values of N_t (*n*-butane) are not shown but generally parallel those for N_t (i-butane) at $D_h > 45\%$. However, activities of low D_h catalysts for *n*-butane formation are very low, and there is an apparent substantial decrease in selectivity going from 11-Rh$_6$ to 50-Rh$_4$ shown in Fig. 2. For $D_h > 40\%$, the selectivity of Rh/SiO$_2$ is a little above that for Pd/SiO$_2$.

Unlike Pt/SiO$_2$ and Pd/SiO$_2$, a small amount of double hydrogenolysis to produce propane was observed on Rh/SiO$_2$. Although this activity could not be determined precisely, it was in general at least two orders of magnitude less than the primary hydrogenolysis reaction ($N_t \simeq 0.0015\ s^{-1}$, structure insensitive) and is not an important factor in determining product distribution. Verma and Ruthven (*33*) also have reported a similar result for CP hydrogenolysis over supported Rh.

Effect of Temperature

Values of N_t were evaluated at four reaction temperatures between −20 to 33°C after the standard pretreatment. The experiments were run with no patterned sequence of temperatures. The apparent activation energies are independent of D_h, with the exception of 11-Rh$_6$ and 27-Rh$_4$ for isobutane, and possibly *n*-butane. Results are summarized in Table 3. In general, these activation energies appear slightly lower

TABLE 3

Summary of Apparent Activation Energies for Reaction after Standard Pretreatment

Catalyst	E_a,*i-b*[a]	E_a,*n-b*	$E_{a,p}$[b]
Rh/SiO$_2$[c]	32.8 ± 4.3	35.8 ± 5.5	45
Pt/SiO$_2$[d]	38.3 ± 1.3	43.7 ± 4.2	—
Pd/SiO$_2$[e]	37.0 ± 2.8	42.8 ± 3.7	—
11-SiO$_2$-Rh$_6$	39.4 ± 1.9	40.9 ± 2.5	48
27-SiO$_2$-Rh	37.8 ± 1.2	38.7 ± 1.7	48

[a] kJ/mol.

[b] Approximate value of E_a for the formation of propane, estimate ±7 kJ/mol.

[c] Average of determinations for 31-SiO$_2$-Rh$_4$ through 108-SiO$_2$-Rh-IonX.

[d] Data of Otero-Schipper *et al.* (*7*).

[e] Data of Wong and co-workers (*3*).

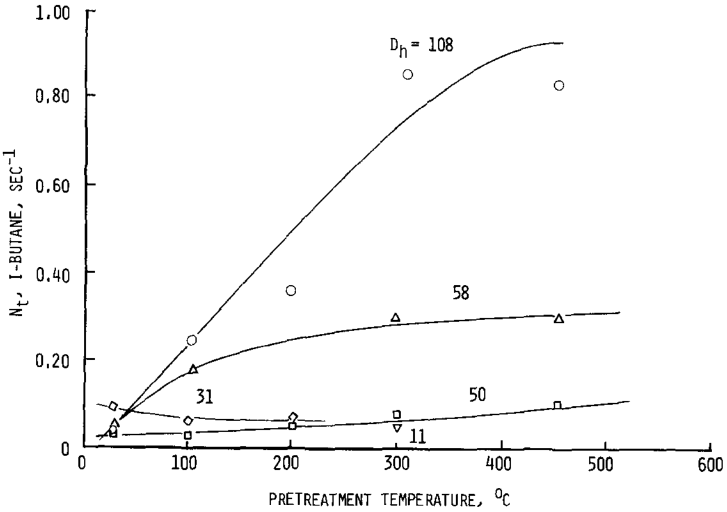

FIG. 3. N_t for i-butane on Rh/SiO$_2$ at different pretreatment temperatures in H$_2$.

than those for both the Pt/SiO$_2$ and Pd/SiO$_2$ series, although experimental uncertainty is sufficiently large to preclude a definite conclusion in this regard. The average apparent activation energies obtained here are in good agreement with the results of Addy and Bond (*34*) for Rh/pumice, and Dalla Betta *et al.* (*35*) for Rh/SiO$_2$ for CP hydrogenolysis. The values given for the apparent activation energy of the double hydrogenolysis reaction to form propane, $E_{a,p}$, are only approximate due to analytical imprecision at the low conversions involved. However, they agree with those reported by Dalla Betta *et al.* (*35*) for CP hydrogenolysis on Rh/SiO$_2$ and Os/SiO$_2$.

Effect of Catalyst Pretreatment Conditions

In previous studies the conditions of pretreatment in hydrogen were found to have large effects on the activity and selectivity patterns of Pt/SiO$_2$ and Pt/Al$_2$O$_3$ for MCP hydrogenolysis. On Pt there was an interchange of the pattern of N_t vs D_h for catalysts reduced below ca. 150°C and those reduced above 200°C (change from N_t decreasing with D_h to N_t increasing with D_h). A minimum in activity, with N_t nearly structure insensitive, occurred for pretreatment in the range 150–200°C. For Pd/SiO$_2$, while there was some modification of activity levels with varying pretreatment conditions, changes in the pattern of structure sensitivity were not observed. In view of these differing results, a similar systematic investigation of hydrogen pretreatment effects was undertaken for the present Rh/SiO$_2$.

Catalyst samples were subjected to an initial O$_2$,300°,0.5, then flushed with He for 0.25 h. These samples then were pretreated H$_2$,T_H,1 for $25 \leq T_H \leq 450$°C and cooled, H$_2$ to reaction temperature. The N_t (i-butane) as a function of H$_2$ pretreatment is illustrated in Fig. 3. The patterns do not exhibit the pronounced minima with respect to T found with supported Pt. In general, N_t(i-butane)/N_t(n-butane) for the various pretreatments was the same as for the standard pretreatment. In particular, S was large for 11-Rh$_6$.

Finally, there is a depression in activity for catalysts heated H$_2$,300°,1;cool H$_2$ (column 6, Table 4) vs those given the standard pretreatment (column 4). This might be due to the formation of a strongly bound hydrogen species that He,450°,1 is able to remove but which cannot be displaced by MCP at 0°C. However, it also might result from differing catalyst morphologies formed by the two pretreatments (*36*).

TABLE 4

Turnover Frequencies for MCP Hydrogenolysis on Rh/SiO_2[a]: Effect of Pretreatment Temperature

Catalyst	O_2,300°,0.5 H_2,25°,1	O_2,300°,0.5 H_2,25°,1 He,450°,1	*S*	O_2,300°,0.5 H_2,300°,1 He,450°,1	*S*	O_2,300°,0.5 H_2,300°,1 Cool H_2	*S*
11-SiO_2-Rh_6	0.25[b]	0.10	19.5	0.11	20.9	0.03	—
31-SiO_2-Rh_4	0.10[b]	0.08	4.6	0.24	4.4	—	—
50-SiO_2-Rh_4	0.03	0.44	2.8	0.28	3.3	0.07	6.8
58-SiO_2-Rh,IonX	0.06	0.69	4.3	0.53	4.8	0.29	8.9
108-SiO_2-Rh-IonX	0.02	1.31	3.0	0.99	3.5	1.85	2.8

[a] N_t(i-butane), s^{-1}, at 0°C, 16 : 1/H_2 : MCP.

[b] Reduction at 25°C without prior oxidation.

DISCUSSION

Rh/SiO₂ Catalysts

Catalysts 108-SiO_2-Rh-IonX and, to a lesser extent, 58-SiO_2-Rh-IonX were somewhat unstable, as judged by the fact that values of H/Rh measured by hydrogen chemisorption at 25°C from pulses were lower after the pretreatment which terminated in Ar,450°C than after that which terminated in Ar,375°C (see section Percentage Exposed of Rhodium). Further, H_2,550°;Ar,450° led to a value of H/Rh which was 43% less than that after H_2,300°; Ar,450°. 58-IonX behaved similarly, but the decline was only 15%.

Some of the catalysts also were measured by X-ray line profile analysis. Checks were excellent for 11-Rh_6 and 27-Rh_4, fair for 37-Rh_6, and poor for 31-Rh_4 and for unclarified reasons. There may be some uncertainty in the exact values of the percentage exposed of Rh, D_h, but this should not affect the relative ordering of the catalysts in Table 2 with respect to D_h, except possibly for the three catalysts of D_h near 50%, where it would make no difference.

H/Rh also was measured after exposure of clean catalysts to H_2,25°,1 followed by desorption to 375°C in Ar (D_{25} in Table 2). D_{25} was about 10% larger than D_h. Similar treatment by H_2,375°,1 (D_{375}) led to values about 16% larger than those of D_{25}. There apparently is some slow adsorption on Rh at 25°C and some form of sorbed hydrogen that appears at higher temperatures. We doubt that the extra sorbed hydrogen results from "spillover" onto the surface of silica gel. If the areal concentration of H were to become uniform on the silica gel, D_{375}/D_{25} should decrease as the moles of Rh_s per gram increased. However, although Rh_s per gram varies from 5 to 76 μmol g^{-1} in the catalysts of Table 2, D_{375}/D_{25} is nearly independent of D_h.

Chemisorption of oxygen at 25°C, measured by the pulse method on clean (i.e., after the standard pretreatment) 108-IonX, led to a value for O/Rh of 143%, which corresponds nearly to formation of Rh_2O_3. Subsequent pulse titration with hydrogen at 25°C, followed by Ar,450°, led to evolution of H_2 equal to H/Rh = 27%. Thus, the pulses of hydrogen had led to only partial removal of O(ads), since, had reduction been complete, H/Rh would have been 108%. Repetition of the sequence led to O/Rh of only 130%. This result again indicates that the very highly dispersed 108-IonX was somewhat unstable. 58-IonX behaved similarly, but O/Rh was only 104%.

H_2,25°,1 left still more oxygen on 108-IonX pretreated O_2,300°,0.5. The degree of removal of oxygen was larger on 58-IonX. Thus, the catalysts given O_2,300°,0.5;H_2,25°,1 used in the experiments with methylcyclopropane were initially incompletely reduced. Catalysts of smaller D_h were not examined, but presumably the extent of their reduction by H_2,25°,1 following O_2,300°,0.5 would be larger. Storage in air must substantially convert the Rh(0) of freshly prepared catalysts to oxide as indicated by X-ray line profile analysis of 27-Rh_4. The average particle diameter in the (111) direction after storage in air for several months was 2.8 nm. After O_2,300°,0.5 no (111) diffraction was detectable. After H_2,300°,1, the average diameter was 3.8 nm and the relative intensity of the (111) line was twice that of the initial value.

The group of Prins at Leiden has reported extensive investigations of the textural and chemisorptive characteristics of Rh/Al_2O_3 (*28, 37, 38*). In general, our results on the reduction of Rh-IonX catalysts and the reaction of the reduced catalysts with oxygen and, in particular, formation of Rh_2O_3 in the case of catalysts of large D_h resemble those reported by the Prins group. However, Rh/Al_2O_3 catalysts may be harder to reduce than Rh/SiO_2.

In the chemisorption of CO at 25°C, CO/Rh was close to that of H/Rh for $D_h < 52\%$. However, (CO/Rh)/(H/Rh) was larger than unity for the catalysts of largest D_h, as shown in Table 2. Formation of surface $Rh(CO)_2$ units, probably with a charge of +1, may well have resulted from treating these catalysts with CO (see section Chemisorption of CO). Such species also appear to be formed by the oxidative fragmentation of $Rh_4(CO)_{12}$ and $Rh_6(CO)_{16}$ on silica gel (*39*).

Surface Morphology and Catalytic Activity

Interpretations of the type of structure sensitivity exhibited in Fig. 1 often have involved the assumption that the metal crystallites of metal/support catalysts are bounded by perfect, densely packed crystal planes like the (111) and (100) planes of fcc crystals. In this model, the ratio, edge/face atoms, decreases monotonically with increasing particle size. It then is assumed that it is the ratio LC/HC (surface metal atoms of lower coordination number/surface metal atoms of higher coordination number) which results in the observed structure sensitivity. Although one might expect some correlation between LC/HC and particle size, it is doubtful that the model of perfect planes is generally correct (*36, 40, 41*). Further, pretreatment conditions such as varying T_H in O_2,300°, 0.5;H_2,T_H,1;cool in H_2 and cooling in He rather than H_2 well may result in different surface morphologies in analogy with results of surface chemical physics (*36*).

Electronic factors also might be invoked in the interpretation of structure sensitivity; however, it is well known that geometric and electronic factors are not easily separately identified. Studies by Sinfelt (*42*) and Boudart and Ptak (*43*) have proposed relationships of hydrogenolysis activity with percentage *d*-character, but recently attempts have been made to utilize L_{III} absorption edge resonance spectra for characterization and correlation of catalytic activity of metals. Such resonance is interpreted as an electronic transition from a core $2P_{3/2}$ to vacant *d*-states of the absorbing atom; thus the transition probably is related to empty *d*-states, and the threshold resonance area should be correlated with *d*-band vacancies. This has been demonstrated for metallic Au, Pt, Ir, and Ta (*44*) and in the characterization of Pt/SiO_2 (*45*). A correlation with the catalytic properties of Pt/SiO_2 for propene hydrogenation has been proposed by Rorris *et al.* (*46*), on the basis that vacancies in the *d*-band increase with increasing D_h. A similar view has been proposed by Lornston (*47*) for Pt/Al_2O_3. Analogous effects might be expected for Rh. Koningsberger *et al.* (*38*) report evidence for the existence of some Rh^{n+} in highly dispersed Rh/Al_2O_3 that are in close contact with Rh. An increase in vacancies in the *d*-band could be due to the existence of these metal ions in higher dispersion catalysts. Presumption that increased activity is correlated with *d*-band vancancies, how-

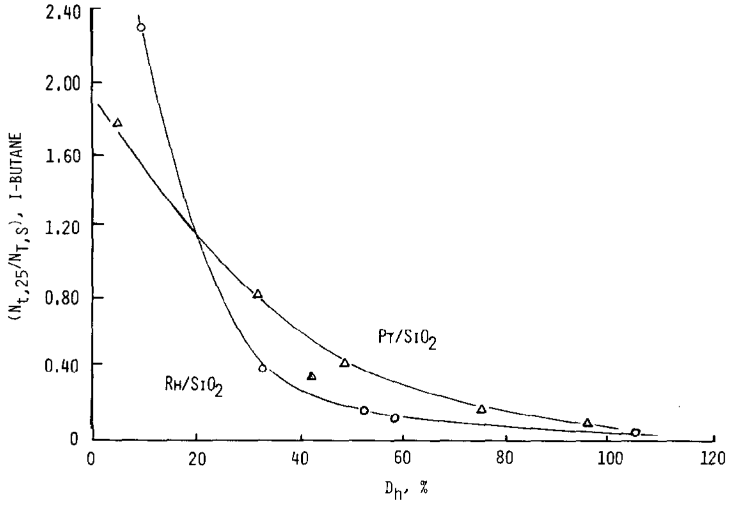

FIG. 4. Depression in activity resulting from low pretreatment temperature as a function of D_h for Rh/SiO_2 and Pt/SiO_2.

ever, rests upon the tacit assumption that one is on the ascending portion of the volcano correlation between catalytic activity and strength of surface bonding. While the increase in activity with decreasing particle size is reasonable in light of the discussion above (given correctness of the tacit assumption), specific absorption edge measurements remain to be done for supported Rh.

Effect of Pretreatment on Catalytic Activity

The present results correspond in some respects, particularly in the depression of activity at lower pretreatment temperatures, to prior results on Pt/SiO_2 and Pt/Al_2O_3 both for MCP hydrogenolysis (*7*) and for deuterium exchange with neohexane (*40*).

As shown in Table 4 and Fig. 4, the standard pretreatment (O_2,300°,0.5;H_2,300°,1; He,450°,1) gave much higher rates for the hydrogenolysis of methylcyclopropane than the pretreatment O_2,300°,0.5;H_2,25°,1 for $D_h > 31\%$, but lower rates for $D_h = 11\%$. As reported in the section Chemisorption of Oxygen, H_2,25°,1 left considerable oxygen on the surface of 108-SiO_2-Rh-IonX pretreated O_2,300°,0.5, and somewhat less on 58-IonX. Although only these two catalysts were examined in this way, it appears reasonable to assume that the ease of removal of oxygen would steadily increase as D_h decreases, as was observed on Pt/SiO_2 (*1*). Accordingly, the low activity of catalysts of larger D_h resulted from residual surface oxygen atoms. On the contrary, catalyst 11-Rh_6 was apparently nearly fully reduced, and its augmented activity probably was caused by surface roughness or faceting resulting from reduction by H_2,25° after oxidation by O_2,300°,1. It has been noted previously that redution of platinum catalysts at low temperatures results in an augmented surface area that is removed by exposure to higher temperatures (*1*).

Although O_2,300°,0.5;H_2,25°,1 left considerable oxygen on the rhodium of 58-IonX, H_{ads}/O_{ads} was greater than 2, and heating to 450° in helium led to complete reaction of O_{ads} to form water and the liberation of excess H_{ads} as H_2. Similar reactions between H_{ads} and O_{ads} were observed on Pt/SiO_2 and Pt/Al_2O_3 (*2*). With 108-IonX, H_{ads}/O_{ads} was less than 2, no H_2 desorbed upon heating to 450°C in helium, and oxygen remained upon the Rh. However, the residual oxygen was small and in a state such that it reacted rapidly with H_2 at 25°C. Therefore, the surface of 108-IonX pretreated O_2,300°,0.5;H_2,25°,1;He,450°,1 would rapidly become free of O_{ads} upon exposure to H_2 + MCP at 25°C. Thus, O_2,300°,0.5;H_2,25°,1;He,450°,1 and O_2,300°,0.5;H_2,300°,1;He,450°,1 should lead to catalysts of nearly the same activity. Table 4 shows that this was indeed the case.

Another factor may influence the data of Fig. 4. Water made by reduction of O_{ads} at 25°C should migrate from Rh to the silica surface immediately adjacent to the particles of Rh and be strongly adsorbed there by hydrogen bonding. Water so adsorbed might block those Rh atoms that are nearest to the silica surface and thus lead to reduced rates. This reduction in rates should be structure sensitive and relatively more prominent for smaller Rh particles than for larger ones. Such adsorbed water would desorb during He,450°. Since this effect and that resulting from incomplete removal of oxygen by H_2,25° would be structure sensitive in the same way, we cannot rigorously separate these two possibilities.

Although $N_{t,25}/N_{t,s}$ ($N_{t,25}$ for O_2,300°,0.5; H_2,25°,1 and $N_{t,s}$ for the standard pretreatment) declined from 2.3 for D_h = 11% to 0.02 for D_h = 108% (Fig. 4), an inverted trend appeared in the ratio $N_{t,300}/N_{t,s}$. As shown in Table 4, $N_{t,300}/N_{t,s}$ increased from 0.3 to 1.9 over the same range of D_h. In the absence of definite information as to surface morphologies, one can only speculate that the standard pretreatment and O_2,300°,0.5;H_2,300°,1;cool in H_2 lead to different surface morphologies (*36*). The excess hydrogen adsorbed at 300°C may perhaps also be involved, but since D_{375}/D_{25} is nearly constant, it is not apparent why the excess hydrogen should generate structure sensitivity.

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