

## Isotopic Exchange between 2,2-Dimethylbutane and Deuterium on Rhodium/Silica Gel Catalysts

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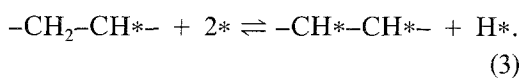
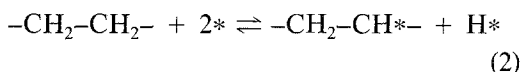
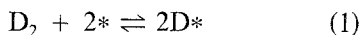
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Isotopic exchange between 2,2-dimethylbutane and deuterium has been investigated at 75°C on 10 rhodium on wide-pore silica gel catalysts with H(chemisorbed)/Rh ( $D_h$ ) ranging from 11 to 108% and subjected to a variety of pretreatment conditions. Some catalysts were prepared by ion exchange with  $\text{Rh}(\text{NH}_3)_5(\text{H}_2\text{O})^{3+}$  and some by impregnation to incipient wetness with  $\text{Rh}_4(\text{CO})_{12}$  or  $\text{Rh}_6(\text{CO})_{16}$ . The turnover frequency ( $N_t$ ) is affected both by  $D_h$  and by the conditions of pretreatment. The extreme variation was a factor of 330. Exchange into the ethyl group was about 10 times faster than into the *t*-butyl group. In general, the catalysts of largest  $D_h$  gave the largest  $N_t$  and the smallest degree of multiple exchange in the ethyl group. The pretreatment,  $\text{H}_2, 450^\circ$  gave the largest  $N_t$ . Mere removal of H\* from catalysts so treated by  $\text{He}, 300^\circ$  had little effect, but  $\text{He}, 450^\circ$  led to a substantial decrease in  $N_t$  except for 11-Rh/SiO<sub>2</sub>. The various coupled values of  $N_t$  and selectivity resulting from variations in  $D_h$  and pretreatment require a minimum of eight different sites.  $N_t$ 's and selectivities in the hydrogenolysis of methylcyclopropane on these same catalysts parallel those in the exchange of neohexane. © 1992 Academic Press, Inc.

### INTRODUCTION

It has been commonly considered that the fundamental processes in isotopic exchange between deuterium and alkanes are (1) dissociative adsorption of H<sub>2</sub> (HD or D<sub>2</sub>) and the reverse, (2) dissociative adsorption of alkane and the reverse, and (3) conversion of the monoadsorbed alkane formed in (2) to  $\alpha, \beta$ -diadsorbed alkane and the reverse (1, 2).

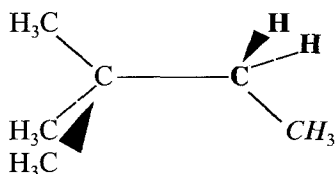


If the model is correct, exchange could

propagate past a  $-\text{C}(\text{CH}_3)_2-$  group only by the intermediacy of an  $\alpha, \gamma$ - or an  $\alpha, \delta$ -diadsorbed alkane since the quaternary carbon atom could not be involved in an  $\alpha, \beta$ -diadsorbed species. The minor extent of such  $\alpha, \beta$ - or  $\alpha, \gamma$ -propagation on Group VIII metals requires that monoadsorbed alkane convert to  $\alpha, \beta$ -diadsorbed alkane much more readily than to  $\alpha, \gamma$ - and  $\alpha, \delta$ -diadsorbed alkanes. The low values of the ratios,  $D_2/D_1$  and  $D_3/D_1$ , in exchanged neopentane require formation of  $\alpha, \alpha$ -diadsorbed alkanes also to be relatively slow. Here,  $D_i$  is the fraction or percent of alkane- $d_i$  in total exchanged alkane.

Neohexane (2,2-dimethylbutane) is a useful diagnostic molecule for the study of isotopic exchange between alkanes and deuterium (3). It contains three kinds of hydrogen atoms. If initial adsorption occurs by dissociative adsorption of one of the C–H bonds in the CH<sub>3</sub> groups in the *t*-butyl moiety (simple capitals in the formula below), the initial product

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will be primarily  $(\text{CH}_2\text{D})(\text{CH}_3)_2\text{C}-\text{CH}_2-\text{CH}_3$  since conversion of the  $\alpha$ -mono-adsorbed into any diadsorbed neohexane is slow. On the contrary, if initial adsorption is at the secondary position (cleavage of  $\text{C}-\text{H}$ ) or into the methyl group at the lower right (cleavage of  $\text{C}-\text{H}$ ), alternation between mono-adsorbed and  $\alpha,\beta$ -diadsorbed neohexane will lead to multiple exchange in the ethyl group up to  $(\text{CH}_3)_3\text{C}-\text{CD}_2-\text{CD}_3$ . The H and H atoms are located in neopentyl positions. This should lead to interesting data since steric hindrance accompanies substitution reactions at neopentyl positions in molecular  $\text{S}_{\text{N}}2$  reactions (4). As models show, neohexane mono-adsorbed into the *t*-butyl or methylene groups on relatively densely packed surface planes like (111) or (100) of cubic close-packed metals would suffer from somewhat similar surface-adsorbate hindrance, but no such steric hindrance accompanies adsorption into the  $\text{CH}_3$  group (3).

Previous papers in this series have reported studies of isotopic exchange of neohexane on  $\text{Pt}/\text{SiO}_2$  and  $\text{Pd}/\text{SiO}_2$  (3) and of hydrogenolysis of methylcyclopropane on sets of  $\text{Pt}/\text{SiO}_2$  (5),  $\text{Pt}/\text{Al}_2\text{O}_3$  (6),  $\text{Pd}/\text{SiO}_2$  (7), and on a set of  $\text{Rh}/\text{SiO}_2$  catalysts prepared by three different methods (8).

The information content of isotopic exchange runs with neohexane is potentially large and can be expressed as the turnover frequency,  $N_t$ , for total exchange, four of the five values  $D_1$ - $D_5$ , and *t*-bu/et, the ratio of the number of molecules exchanged into the *t*-butyl group to that of those exchanged into the ethyl group assuming that *t*-bu- $d_2$ /*t*-bu- $d_1$  is negligible.

Since heterogeneous catalysts are materials and not simple chemicals, can one speak of "the catalytic activity of rhodium," where "rhodium" comprises unsupported

Rh (single crystal, wire, powder, evaporated films),  $\text{Rh}/\text{SiO}_2$ ,  $\text{Rh}/\text{Al}_2\text{O}_3$ ,  $\text{Rh}/\text{TiO}_2$ , etc.? The answer is probably yes provided that Rh is metallic, that interactions between the support and Rh are not too large (9), and that the rhodium surface is uncontaminated. But even within these restrictions "the catalytic activity of rhodium" can be affected by the particle size (or percentage exposed) of the rhodium (structure sensitivity), the conditions of pretreatment, the method of catalyst preparation, and the identity of the support.

Controversy about the relative importance of these variables continues. In the extensive literature relating to this matter, most data involve the influence of the variables upon  $N_t$  for a single reaction. It was felt that the large information content of the present experiments coupled with the results of the hydrogenolysis of methylcyclopropane on the same set of catalysts would provide unusually detailed data as to the effect of the conditions of pretreatment particularly since the variety of pretreatment conditions was unusually large in parts of the present study. Further, the catalysts were prepared by three different methods. We hoped that the data from pretreatment and catalyst preparations conditions would provide information on the degree to which the  $\text{Rh}/\text{SiO}_2$  catalysts could be considered to be constituted of various proportions of a relatively small number of different kinds of sites. The only support employed in this work was silica gel, a support generally considered to be one of the most inert.

#### EXPERIMENTAL METHODS

##### Materials

Neohexane (2,2-dimethylbutane, Phillips Petroleum) was refluxed over sodium-potassium alloy for 1 h and distilled into a storage flask. All operations including storage were effected under argon. The purity of neohexane was found by gas chromatography to exceed 99.9%.

The catalysts employed in this work are listed in Table 1. Most had been prepared

TABLE 1  
Catalysts and Their Preparation

Catalyst <sup>a</sup>	Rh (wt%)	Calcination <sup>b</sup> (°C, h)	Reduction by H <sub>2</sub> <sup>c</sup> (°C, h)
11-SiO <sub>2</sub> -Rh <sub>6</sub>	0.50	60°, 0.75	60°, 0.5; 250°, 1
27-SiO <sub>2</sub> -Rh <sub>4</sub>	1.40	250°, 1	250°, 1
31-SiO <sub>2</sub> -Rh <sub>4</sub>	0.60	250°, 1	250°, 1
37-SiO <sub>2</sub> -Rh <sub>6</sub>	0.60	250°, 1	250°, 1
41-SiO <sub>2</sub> -Rh-IonX <sup>d</sup>	0.49	None	370°, 3
50-SiO <sub>2</sub> -Rh <sub>4</sub>	0.60	400°, 1	140°, 1
52-SiO <sub>2</sub> -Rh <sub>4</sub>	0.55	None	250°, 1.2
53-SiO <sub>2</sub> -Rh-IonX	0.78	None	450°, (H <sub>2</sub> O)1; 450°, 1 <sup>e</sup>
70-SiO <sub>2</sub> -Rh-IonX <sup>d</sup>	0.49	400°, 3	135°, 2
108-SiO <sub>2</sub> -Rh-IonX	0.78	400°, 3	135°, 2

<sup>a</sup> The catalyst code. The beginning number is the percentage exposed,  $D_h$ , as measured by hydrogen chemisorption; see Ref. (8). Rh<sub>6</sub> designates preparation from Rh<sub>6</sub>(CO)<sub>16</sub> and Rh<sub>4</sub>, from Rh<sub>4</sub>(CO)<sub>12</sub>. Rh-IonX designates preparation by ion exchange. Except for 41- and 70-SiO<sub>2</sub>-Rh-IonX, the data in the table are from Ref. (8).

<sup>b</sup> Treatment in flowing O<sub>2</sub> prior to reduction.

<sup>c</sup> Reduction in flowing H<sub>2</sub>.

<sup>d</sup> Measured by pretreating the reduced catalysts by O<sub>2</sub>, 300°, 0.5; H<sub>2</sub>, 300°, 1; Ar, 450°, 1, cool in Ar to 25° and then saturating with pulses of H<sub>2</sub> at 25°C. Seven min after the last pulse the catalyst was isolated and heated abruptly to 450°C. After 5 min, Ar flow was reestablished and the amount of hydrogen desorbed was measured (8).

<sup>e</sup> During warming to and treatment at 450°C for the first hour, the H<sub>2</sub> was saturated with H<sub>2</sub>O at 25°C.

by ion exchange of 80- to 100-mesh Davison grade 62 silica gel with [Rh(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]Cl<sub>3</sub> or by impregnation to incipient wetness with solutions of Rh<sub>6</sub>(CO)<sub>16</sub> or Rh<sub>4</sub>(CO)<sub>12</sub> (8). It may be noted that Rh<sub>4</sub>(CO)<sub>12</sub> has been reported to become converted to Rh<sub>6</sub>(CO)<sub>16</sub> upon chemisorption on silica gel (10). An additional batch of ion-exchanged silica gel was prepared to contain 0.49 wt% Rh by the techniques of Ref. (8). The rhodium content was measured by the Galbraith Laboratories (atomic adsorption spectroscopy) to be 0.42 wt%. One portion of the ion-exchanged material was exposed to flowing H<sub>2</sub> at a temperature rising from 25 to 370°C at 20°C min<sup>-1</sup> with a hold of 3 h at 370°C. The other portion was treated with flowing O<sub>2</sub> at a temperature rising at 1°C min<sup>-1</sup> from 25 to 400°C with a hold of 3 h at 400°C. Following cooling and flushing with He, it was heated

in flowing hydrogen at 0.5°C min<sup>-1</sup> to 135°C, at which temperature it was held for 2 h before cooling to 25°C. The catalyst was fluidized during treatment with O<sub>2</sub> but not with H<sub>2</sub>. The percentages exposed,  $D_h$ , of these two additional catalysts (41- and 70-SiO<sub>2</sub>-Rh-IonX) appear in Table 1. As with the other catalysts, values of  $D_h$  were determined by measurement of the amount of hydrogen desorbed from samples that had been saturated with hydrogen at 25°C. The values of turnover frequency ( $N_t$ ) for 70-SiO<sub>2</sub>-Rh-IonX and 41-SiO<sub>2</sub>-Rh-IonX do not depend upon which of the values of wt% Rh, 0.49 or 0.42, is used.

#### Catalyst Pretreatments

Since previous work in this laboratory had shown that the conditions of catalyst pretreatment often affect results as much as

$D_h$  (11), a number of different pretreatment conditions were investigated. All were started by exposing the catalyst to 99.999%  $O_2$  (less than 0.5 ppm C) at 300°C for 0.5 h to eliminate any carbonaceous adsorbates on the Rh that might have been formed despite attempts to minimize exposure to organic vapors. Then, while the catalyst was being purged with He for 20 min, the temperature was adjusted to 100, 300, or 450°C for the next step, exposure to  $H_2$  flowing at 50–60  $cm^3\ min^{-1}$  for 1 h. During the last 8 min the hydrogen was replaced by deuterium. In one series, the catalyst was cooled to reaction temperature in  $D_2$ . In the other series, after treatment in  $D_2$ , the catalyst was flushed with He, heated in flowing He for 1 h at 100, 300, or 450°C, and cooled in He to reaction temperature. When  $T_{He} > T_{H_2}$ , the catalyst was heated in flowing He from  $T_{H_2}$  to  $T_{He}$ . When  $T_{He} < T_{H_2}$ , the catalyst was cooled in  $H_2$  from  $T_{H_2}$  to  $T_{He}$ . Our codes for the two catalyst pretreatments are  $O_2, 300^\circ, 0.5; H_2, T, 1$  and  $O_2, 300^\circ, 0.5; H_2, T, 1; He, T', 1$ . However, since all pretreatments started with  $O_2, 300^\circ, 0.5$  and since the times for exposure to  $H_2$  and He were always 1 h, the pretreatments are usually given as  $H_2, T$  or  $H_2, T; He, T'$ . As in previous work  $O_2, 300^\circ, 0.5; H_2, 300^\circ, 1; He, 450^\circ, 1$  will be called the *standard pretreatment* because this pretreatment preceded measurement of  $D_h$ .

### Techniques

An apparatus patterned on that previously used for the study of isotopic exchange between neohexane and deuterium on Pd/SiO<sub>2</sub> and Pt/SiO<sub>2</sub> (3) was used in the present work. Great care was exercised in minimizing the content of oxygen and other impurities in the gas flows and to prevent leaks from one gas flow line into another. At the catalyst the content in  $O_2$  was less than 0.02 ppm.

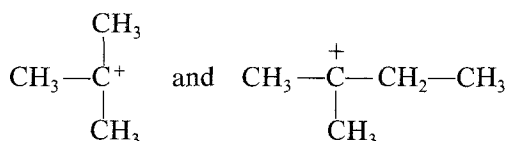
Deuterium, hydrogen, and helium entered the apparatus through traps of Davison Grade 62 silica gel cooled by liquid nitrogen, which reduces the contents in all

compounds, except these gases and neon, to very low levels. A Brooks mass flowmeter was followed by a MnO/SiO<sub>2</sub> trap to remove any adventitious  $O_2$ . Neohexane was introduced into flowing deuterium by passing deuterium through a bed of Filtros FS 140, the pores of which had been filled by the hydrocarbon under conditions that avoided admitting  $O_2$  (12). The Filtros was contained in a 1-cm-diameter glass tube 30 cm long wound into a helix. It was thermostated at -10°C with a slush bath of dodecane to give a saturated vapor pressure of 0.085 bar (8.8%). The  $D_2$ /alkane ratio in the exit stream from the saturator was determined by injecting a sample into helium carrier that passed through a Porapak Q chromatographic column and a catharometer. The calibration value for neohexane was calculated from that of hexane by use of the data of Dietz (13). The partial pressure of neohexane was independent of the flow rate of  $D_2$  between 10 and 60  $cm^3\ min^{-1}$ .

The reactor was a 6.35-mm Pyrex U-tube containing silica gel upstream of the catalyst to preheat the reactant gases. The amount of catalyst, chosen to give conversions of about 5%, ranged from 0.004 to 0.16 g depending upon the catalyst activity. To ensure that contents in  $O_2$  were kept very low, 2 cm lengths of MnO/SiO<sub>2</sub> were placed near each end of the reactor tube. During the  $H_2, T$  stage of the pretreatment, oxidized MnO sections were reduced by means of heating tapes and  $H_2$  flow. A Whitey four-way ball valve located above the reactor permitted the hydrogen flow to be directed so that water produced during the reduction of the oxidized MnO/SiO<sub>2</sub> did not pass through the catalyst bed. There were two sets of Swagelock fittings in parallel at the end of the apparatus to which traps in the form of U-tubes terminated with Teflon needle valves at both ends could be connected. Cooling the traps in liquid  $N_2$  effected the collection of hydrocarbons. The traps could be isolated and transferred to a quadrupole mass spec-

trometer for analysis. Before analysis,  $D_2$  was removed by evacuation of the trap while it was cooled in liquid  $N_2$ . Some analyses were performed on a Hewlett-Packard 5985 mass spectrometer in the Chemistry Department at Northwestern University, others on a Finnegan-Mat model 4500 at the Institute of Gas Technology in Chicago. The nominal ionizing voltages were 15 V. Agreement between the two instruments was good.

Mass spectrographic procedures were similar to those used previously (3). The primary data were the intensities of the masses associated with the *t*-butyl and the *t*-amyl fragments,



One wants the  $D_i$ 's, where  $D_i$  represents the fraction of the *exchanged* molecules  $C_xH_{2x+2}$  or of the exchanged fragments  $C_yH_{2y+1}$ , which contain  $i$  deuterium atoms. However, the mass spectrographic data represent the fractions of molecules with the same nominal mass, i.e.,  $^{12}\text{CD} = ^{13}\text{CH}$ . The mass fractions were converted to the  $D_i$ 's by an iterative computer program that used the normal value of  $^{13}\text{C}/^{12}\text{C}$  and the measured proportions of carbenium ion, carbenium ion  $-1$ , and carbenium ion  $-2$  for the perhydroalkane and assumed that a C—D bond breaks 85% as readily as a C—H bond. As a check, the previous exchange of neohexane at  $86.5^\circ$  on 21-SiO<sub>2</sub>-Pt-IonX-F given the standard pretreatment (3) was repeated. Agreement between the two runs was good.

Following catalyst pretreatment and with the saturator bypassed, the flow rate of  $D_2$  was adjusted. The flow was then directed through the saturator. Samples of exchanged neohexane were collected at about 10, 20, 30, and 50 min for periods of 2 to 8 min in either of two traps in parallel.

Fresh samples of catalyst and of MnO/SiO<sub>2</sub> were used for each experiment.

#### Turnover Frequencies and Percentages Exposed

The turnover frequency,  $N_t$ , was calculated by the relation

$$N_t = -L \ln(1 - \alpha)/(\text{mol Rh}_s),$$

where  $L$  is the flow rate of hydrocarbon in mol s<sup>-1</sup> and  $1 - \alpha$  is the fraction of the hydrocarbon that has not exchanged. Unlike  $D_i$ ,  $N_t$  so calculated is not perturbed by multiple periods of adsorption.

Even if one could precisely define a surface atom of Rh, it is not clear that H/Rh<sub>s</sub> would, in general, be unity at saturation (8, 11, 14). In particular, if H<sub>ads</sub> is located in three- or fourfold hollow sites as is probable (15), exact matching of H<sub>ads</sub> with Rh<sub>s</sub> becomes difficult and H<sub>ads</sub> is not likely to be precisely equal to Rh<sub>s</sub> for 2- or 3-nm particles of metal.<sup>2</sup>

In the case of 108-Rh-IonX, Rh<sub>s</sub> was taken to be equal to Rh although the "true" value of  $D_h$  might well be smaller than 100%. For a somewhat different view of  $D_h$  see Ref. (17). Despite what has just been written, the use of  $D_h$  measured by hydrogen chemisorption has been of major utility in heterogeneous catalysis even if it is basically an empirical quantity that needs calibration with more fundamental methods like X-ray line profile analysis or TEM (14).

#### RESULTS

All exchange runs with neohexane were made at  $75 \pm 0.2^\circ\text{C}$ . The activity of the

<sup>2</sup> Consider eight atoms of Rh at the vertices of a cube. Eight atoms of H would be adsorbed in atop positions, but only six in fourfold hollow sites, the cube being the regular hexahedron. However, if two hydrogen atoms can be associated with such coordinatively unsaturated Rh atoms, the number of adsorbed atoms would exceed the number of Rh<sub>s</sub> atoms. Two hydrogen atoms might well adsorb on highly coordinatively unsaturated atoms such as those at edges or vertices and rhodium appears to be particularly prone to this (16). It is well established that two molecules of CO can so adsorb at Rh<sub>s</sub>. Formation of Rh<sub>s</sub>(H)<sub>2</sub> is most likely on the smallest particles of metal.

empty reactor was zero at this temperature.  $N_t$  declined with time and at 50 min on stream its value was usually 75–85% of its value at 10 min, but with ethane the value was 90–95%. Listed  $N_t$  were at about 10 min time on stream.

Although rhodium is known to be an active hydrogenolysis catalyst, previous literature indicates that hydrogenolysis should be much slower than exchange at 75°C (9, 18). This was checked by passing a neohexane +  $D_2$  mixture over 0.246 g of 31-SiO<sub>2</sub>-Rh<sub>4</sub>, standard pretreatment, at 22 cm<sup>3</sup> min<sup>-1</sup> at 75°C. At 15 min on stream, the conversion in exchange was 30%,  $N_t = 0.08$  s<sup>-1</sup>. No hydrogenolysis products could be detected. After raising the temperature to 126°C, a trace of methane was detected. At 84 min on stream, 150°C, conversion to methane + neopentane was <1%,  $N_t$  (hydrogenolysis) < 0.003 s<sup>-1</sup>. At 200°C, conversion was 40% and, at 175°C, time on stream = 176 min, methane, isopentane, and neopentane were detected with neopentane/isopentane = 5 and  $N_t$  (hydrogenolysis) = 0.02 s<sup>-1</sup>. Deuterium exchange was remeasured at 75°C, time on stream = 235 min,  $N_t$  (exchange) was 0.08 s<sup>-1</sup>, the same value as that measured at 15 min time on stream. Thus, at 75°C, exchange is roughly 10<sup>4</sup> times more rapid than hydrogenolysis. This number is considerably smaller than would be observed with Pt or Pd, but it is large enough that hydrogenolysis does not directly confuse the results of exchange at 75°C. The fraction,  $\alpha$ , isomerized to methylpentanes of 2,3-dimethylbutane was  $0 \leq \alpha \leq 0.6\%$  in accord with the observations of Ref. (9).

After the standard pretreatment, the ratio of exchanged *t*-butyl groups to exchanged ethyl groups (*t*-bu/et) usually ranged from 0.05 to 0.10 and total exchange in the *t*-butyl group, from 0.2 to 0.8%. After H<sub>2</sub>, 450°, *t*-bu/et was smaller, about 0.02. However, since the concentration of mass 58 from <sup>13</sup>C<sup>12</sup>C<sub>3</sub>H<sub>9</sub><sup>+</sup> is 4% of that from mass 57 (<sup>12</sup>C<sub>4</sub>H<sub>9</sub>), in calculation of  $D_1$ , that part of mass 58 derived from <sup>12</sup>C<sub>4</sub>H<sub>8</sub>D, was subject

TABLE 2

Isotopic Exchange at 75°C between Neohexane and Deuterium, on 31-Rh<sub>4</sub>;H<sub>2</sub>,300°;He,300°<sup>a</sup>

Time <sup>b</sup>	$N_t^c$	$D_1$	$D_2$	$D_3$	$D_4$	$D_5$	$D_6$	<i>t</i> -bu/et
8	0.083	31.5	16.1	15.9	18.2	18.3	0	0.081
18	0.076	32.9	15.6	15.2	17.8	18.5	0	0.072
30	0.073	33.3	15.1	15.1	17.5	19.0	0	0.072
61	0.069	34.4	14.5	15.2	17.0	18.9	0	0.068
92	0.065	33.9	14.2	15.2	17.2	19.5	0	0.075
121	0.063	33.3	14.3	15.4	17.6	19.5	0	0.074
150	0.062	33.8	14.1	15.3	17.3	19.6	0	0.086
18 <sup>d</sup>	0.054	39.3	17.4	14.0	14.0	15.3	0	0.065

<sup>a</sup> Flow rate, 20.3 ± 0.3 cm<sup>3</sup> min<sup>-1</sup> (at 25°C), 0.0327 g of catalyst. The conversion declined from 4.1% at 8 min time on stream to 3.0% at 150 min.

<sup>b</sup> Time on stream in min.

<sup>c</sup> Turnover frequency in molecules exchanged per second per site for the chemisorption of H.

<sup>d</sup> On another sample of 31-Rh<sub>4</sub>;H<sub>2</sub>,300°;He,300°, 0.0374 g.

to substantial error, probably a factor of at least 2. The average value of  $D_2$ -*t*-bu/ $D_1$ -*t*-bu was 0.08, but concentrations of exchanged *t*-bu<sup>+</sup> were so small that one can say only that the ratio is small. Fractional errors in *t*-bu/et should be largest at the lowest conversions and since, in fact, our measured values tended to be largest for the lowest conversions, it is likely that the lower values of *t*-bu/et are closest to being correct. The exchanged ethyl groups contained all isotopic species,  $D_1$  to  $D_5$ . Values of  $N_t$  for formation of exchanged ethyl ranged from 0.01 to 2.5 s<sup>-1</sup> depending upon  $D_h$  and the pretreatment.

Table 2 exhibits the effect of deactivation by a run that was protracted to a time longer than usual. Deactivation is initially relatively fast, but it becomes slow after 60 min. The deactivation in the first 60 min is typical of that generally observed in the other runs which were usually limited to 60 min. As was also generally the case, the isotopic distribution pattern was independent of time on stream; i.e., deactivation eliminates sites but does not change their nature. The reproducibility in measuring  $D_3$ ,  $D_4$ , and  $D_5$  appears to be about ±0.5% units. Accuracy in  $D_1$  is lower than that in the other  $D_i$ 's. In the runs of Table 2, the amount of C<sub>5</sub>H<sub>10</sub>D<sup>+</sup> is about 1% that

TABLE 3

Isotopic Exchange at 75°C of Neohexane on Rh/SiO<sub>2</sub> Given the Standard Pretreatment<sup>a</sup>

Catalyst <sup>b</sup>	Type <sup>c</sup>	$N_1^0$ <sup>d</sup>	$D_1$	$D_2$	$D_3$	$D_4$	$D_5$	$D_6$	<i>t</i> -bu/et	$D_1/D_5$
11-Rh <sub>6</sub>	C-4	0.037	6.0	13.9	24.2	20.6	35.4	0	0.05	0.17
27-Rh <sub>4</sub>	C	0.057	11.8	14.1	17.9	23.6	32.7	0	0.10	0.36
31-Rh <sub>4</sub>	B-3	0.10	28.6	18.4	14.9	18.7	19.2	0.2	0.07	1.49
37-Rh <sub>6</sub>	B-2	0.027	17.7	12.9	15.5	19.8	33.7	0.4	0.17	0.52
41-IonX	B-3	0.055	23.6	14.8	13.8	17.9	29.9	0	0.14	0.79
50-Rh <sub>4</sub>	A-3	0.11	32.2	18.5	14.7	18.8	15.6	0	0.07	2.06
52-Rh <sub>4</sub>	B-2,3	0.14	18.6	17.6	17.7	26.1	20.0	0	0.05	0.93
53-IonX	C	0.075	13.4	17.1	17.0	22.7	29.8	0	0.09	0.45
70-IonX	A-3	0.14	40.5	19.6	13.1	14.8	12.0	0.1	0.07	3.38
108-IonX	A-3	0.24	41.7	21.1	13.5	14.6	9.1	0.1	0.06	4.58

<sup>a</sup> These data are the average of duplicate runs for each catalyst except there were four runs on 31-Rh<sub>4</sub>, three runs on 108-Rh-IonX, but only one run on 41-Rh-IonX. 0.01 to 0.15 g of catalyst were employed and the flow rate was about 22 cm<sup>3</sup> min<sup>-1</sup> for all catalysts except 108-Rh-IonX for which 40 cm<sup>3</sup> min<sup>-1</sup> was employed. Conversions ranged from 2 to 7%. At such conversions, correction for neohexane molecules being adsorbed and exchanging twice is negligible.

<sup>b</sup> The initial number is  $D_h$ , the following term identifies the catalyst; see Table 1.

<sup>c</sup> The type of distribution pattern; see Figs. 1-3.

<sup>d</sup> Turnover frequency in s<sup>-1</sup> per site for adsorption of hydrogen in the measurement of  $D_h$ .

of C<sub>5</sub>H<sub>11</sub><sup>+</sup> and the amount of <sup>13</sup>C<sup>12</sup>C<sub>4</sub>H<sub>11</sub><sup>+</sup> is 5% that of C<sub>5</sub>H<sub>11</sub><sup>+</sup>. Since determining C<sub>5</sub>H<sub>10</sub>D<sup>+</sup> from the mass 72 peak involves a large correction, all values of  $D_1$  for the 0.0327-g sample in Table 2 are probably the same within experimental error.

Table 2 also shows results of a run on another batch of 31-Rh<sub>4</sub> given the same pretreatment. Divergences between the two samples in  $N_1$  and in the  $D_i$ 's are somewhat larger than usual. The values of  $N_1$  and  $D_i$ 's reported in the tables are with few exceptions averages of two runs.

Table 3 presents results on all of the catalysts after the standard pretreatment. Distributions of the  $D_i$ 's can be classified as  $D_i$  generally rising with increasing  $i$  (Type C), declining with increasing  $i$  (Type A), or first declining and then rising (Type B). The presence of a minimum value of  $D_i$  can be shown by affixing a number to the letter. Thus, C-4 indicates the presence of a minimum in  $D_i$  at  $i = 4$  and a maximum at  $i = 3$ . Type B will necessarily have a minimum. Figure 1 exhibits examples of Types A and A-3 and Fig. 2, of Types B-2, B-3, C, and C-4.

A wide range of pretreatments was investigated with catalyst 31-Rh<sub>4</sub>. Results are presented in Fig. 3, which gives the distribution type,  $N_1$  and  $D_1/D_5$ , for various pretreatments. The pretreatment H<sub>2</sub>,300°;He,100° is anomalous as noted in the legends for Figs. 1 and 3. Reproducibility in runs on H<sub>2</sub>,300°;He,100° and H<sub>2</sub>,450°;He,300° or 100° were poorer than in other runs. A smaller number of pretreatments was investigated for catalysts 11-SiO<sub>2</sub>-Rh<sub>6</sub> and 108-SiO<sub>2</sub>-Rh-IonX, the only treatments with helium being none or He,450°,1. Results are shown in Table 4. Because of the very high activity of 108-Rh-IonX;H<sub>2</sub>,450° for isotopic exchange of neohexane, low conversions could not be obtained. Even with only 0.0052 g of catalyst (0.4 μmol Rh) and a flow rate of 56 cc min<sup>-1</sup>, the conversion was 36%. Therefore the  $D_i$ 's for 108-Rh-IonX;H<sub>2</sub>,450° in Table 4 are distorted by molecules having exchanged two or more times and by dilution of the D<sub>2</sub> by HD, 7% HD having been formed in the gas phase deuterium. The first effect shifts neohexane- $d_i$ 's from lower to higher

values of  $i$  and the second from higher to lower values of  $i$ .

### Mass Transport Limitations

Are mass transport limitations present in the experiment with 108-SiO<sub>2</sub>-Rh-IonX;H<sub>2</sub>,450° (Table 4), the rate of which is very large,  $N_t = 3.3 \text{ s}^{-1}$ ? Consider the case in which the rate is so fast that no unconverted reactant is present in the center of catalyst particles. Unlike usual cases, although neohexane- $d_0$  is absent from the center, neohexane is present and it will continue to react toward a statistical distribution of isotopic species. As comparison with the other runs with H<sub>2</sub>,450° shows, any such effect must be small in the present case. The run is nearly free of mass transport influences and, therefore, all other runs involve negligible such influences. This procedure provides a simple and powerful procedure for diagnosing intrusion of the mass transport effects.

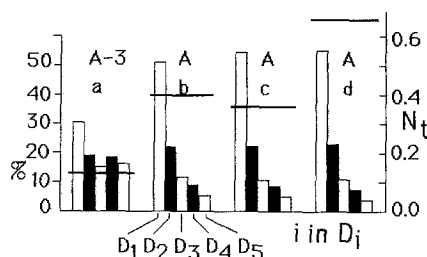


FIG. 1. Isotopic distribution patterns for single runs at about 9 min time on stream for exchange of neohexane at 75°C on 31-SiO<sub>2</sub>-Rh<sub>4</sub> catalysts of various pretreatments. The distribution type, A-3 or A (see text), is shown at the top of the graph.  $x$ -axis,  $i$  in  $D_i$ . The vertical bars give  $D_i$  in percentage on the left  $y$ -axis. The thin horizontal bars give  $N_t$  in  $\text{s}^{-1}$  on the right  $y$ -axis. Run number and pretreatment: (a) 26, H<sub>2</sub>,450°;He,450°. (b) 67, H<sub>2</sub>,450°,cool in H<sub>2</sub> to 300°;He,300°. (c) 77, H<sub>2</sub>,450°,cool in H<sub>2</sub> to 100°;He,100°. (d) 81, H<sub>2</sub>,450°,cool in H<sub>2</sub> to 75°;no He. (e) (not shown), 39, H<sub>2</sub>,450°;He,450°, $\frac{1}{6}$ ,cool to 100° in He, $N_t = 0.24 \text{ s}^{-1}$ .  $N_t$  and the isotopic distribution pattern were intermediate between (a), H<sub>2</sub>,450°;He,450° and (d), H<sub>2</sub>,450°.

TABLE 4

Effect of Pretreatment on the Isotopic Exchange of Neohexane on 11-SiO<sub>2</sub>-Rh<sub>6</sub> and on 108-SiO<sub>2</sub>-Rh-IonX

Pretreat. <sup>a</sup>	Deact. (%) <sup>b</sup>	$N_t$	$D_1$	$D_2$	$D_3$	$D_4$	$D_5$	Type
11-SiO <sub>2</sub> -Rh <sub>6</sub>								
100°;no He	3	0.053	9.8	10.4	20.6	19.1	40.1	C-4
100°;450°	3	0.043	14.2	12.7	22.7	19.3	31.1	C-4
300°;no He	7	0.014	12.6	10.7	22.9	18.5	34.8	C-4
300°;450°	0	0.037	6.0	13.9	24.2	20.6	35.4	C-4
450°;no He	10	0.0096	23.1	19.1	17.1	16.7	23.8	B-4
450°;450°	6	0.035	11.7	11.1	21.4	20.0	35.8	C-4
108-SiO <sub>2</sub> -Rh-IonX								
100°;no He	26	0.015	32.3	22.8	13.6	15.6	15.8	A-3
100°;450°	25	0.32	46.3	21.2	12.8	12.4	7.3	A
300°;no He	7	0.58	48.4	23.2	12.6	10.8	5.0	A
300°;450°	23	0.24	41.7	21.1	13.5	14.6	9.1	A-3
450°;no He <sup>c</sup>	7	3.3	44.4	26.1	14.6	10.4	4.6	A
450°;450°	16	0.33	41.1	22.2	14.2	14.4	8.0	A-3

<sup>a</sup> Pretreatment. The catalysts were first pretreated O<sub>2</sub>,300°;0.5 and then, after flushing with He, H<sub>2</sub>, $T$ ,1. The first number in the entry is  $T$ . The second number, if any, is the temperature,  $T'$  of a subsequent treatment in flowing He.

<sup>b</sup> The deactivation in percentage between about 10 and about 50 min on stream.

<sup>c</sup> The  $D_i$ 's are for just one run, conversion 36%.  $D_i$ 's are distorted from initial values. The conversion in the other run after H<sub>2</sub>,450° was 53%.



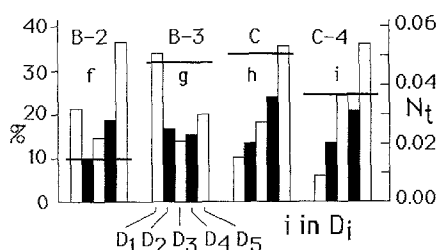


FIG. 2. Like Fig. 1, but (h) was on 27-SiO<sub>2</sub>-Rh<sub>4</sub> and (i) on 11-SiO<sub>2</sub>-Rh<sub>6</sub>, both at about 16 min on stream. Run number and pretreatment: (f), 24, H<sub>2</sub>, 100°; He, 100°. (g), 30, H<sub>2</sub>, 100°; He, 300°. (h), 12, H<sub>2</sub>, 300°; He, 450°. (i), 10, H<sub>2</sub>, 300°; He, 450°.

### Carbonaceous Deposits and Deactivation

Deactivation presumably results from deposition of slowly reacting carbonaceous residues. After catalytic exchange runs on Pd/SiO<sub>2</sub> and Pt/SiO<sub>2</sub>, the treatment H<sub>2</sub>, 450° restored the catalytic activity of catalysts that had been initially pretreated H<sub>2</sub>, 450°. Regeneration was accompanied by the liberation of neohexane at 100–200°C and of a small amount of methane at  $T > 300^\circ\text{C}$  (3). These matters were not investigated in the present work. However, Cogen and Maier (19) have shown that the carbonaceous deposit resulting from isotopic exchange of hexane on Rh black at 80°C is removed by H<sub>2</sub> almost exclusively as unaltered hexane. Cogen and Maier have also shown that surface metal sites rather than carbonaceous deposits are the sites for isotopic exchange, a conclusion analogous to findings for hydrogenation on Pt/SiO<sub>2</sub> (20).

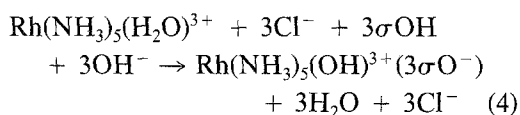
After a run on 31-SiO<sub>2</sub>-Rh<sub>4</sub>; O<sub>2</sub>; 300°; H<sub>2</sub>, 300°; He, 450°, the catalyst was exposed again to H<sub>2</sub>, 300°; He, 450°,  $D_h$  was measured and found to be unchanged. Thus, the catalytic run led to no coarsening of the metal particle size distribution.

### DISCUSSION

No temperature of reduction or pretreatment in this work exceeded 450°C, but several pretreatments terminated in H<sub>2</sub>, 450° or

He, 450° (meaning that the catalyst was treated in flowing H<sub>2</sub> or He for 1 h at 450°C and cooled in H<sub>2</sub> or He as indicated). The surface concentration of  $\sigma$ -OH (surface silanol groups) should be identical in all catalysts the pretreatments of which terminated at 450°C.

The Rh/SiO<sub>2</sub> catalysts employed in this work were prepared from wide-pore silica gels with the deliberate avoidance of chloride. Starting materials were silica gel impregnated with Rh<sub>4</sub>(CO)<sub>12</sub> or Rh<sub>6</sub>(CO)<sub>16</sub> or ion exchanged with [Rh(NH<sub>3</sub>)<sub>5</sub>(H<sub>2</sub>O)]Cl<sub>3</sub> (8). In the last, the chloride is removed on washing since it is never attached either to Rh or to SiO<sub>2</sub>.



There are rather varied reports of the ra-

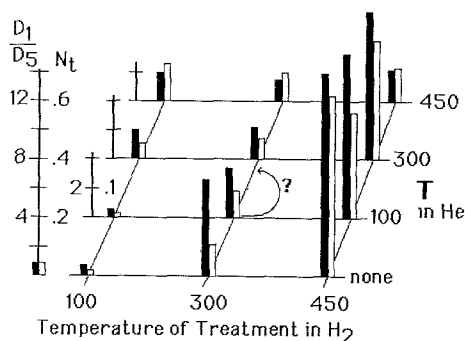


FIG. 3. Isotopic distribution patterns at about 9 min on stream of neohexane exchanged at 75°C on 31-SiO<sub>2</sub>-Rh<sub>4</sub> of various pretreatments. The temperature of pretreatment in H<sub>2</sub> is on the x-axis and that in He, if any, is on the y-axis. H<sub>2</sub>, 450°, 1, cool in H<sub>2</sub> to 300°; He, 300°, 1 and H<sub>2</sub>, 450°, 1, cool in H<sub>2</sub> to 100°; He, 100°, 1 represent single runs. Otherwise, the data presented are averages of at least two runs. H<sub>2</sub>, 300°; He, 100°, ? is actually H<sub>2</sub>, 300°, 1; He, 300°, 0.13, cool in He to 100°; He, 100°, 1. On the z-axis, hollow bars represents  $N_t$  in s<sup>-1</sup> and solid bars,  $D_1/D_5$ . For the temperatures of pretreatments in H<sub>2</sub> and He being respectively 300°; none, 450°; 300°, 450°; 100°; and 450°; none the isotopic distribution pattern was Type A. It was A-3 for 450°; 450°, 300°; 100°, 100°; 450°. It was B-3 for 300°; 450°, 300°; 300° and 100°; 300° and B-2 for 100°; 100° and 100°; none.

tios of  $N_t$ 's for Rh/SiO<sub>2</sub> prepared by impregnation with Rh(NO<sub>3</sub>)<sub>3</sub> vs that prepared with RhCl<sub>3</sub>: substantial in the hydrogenation of CO (21) and ethylene and propyne (22) and in the hydrogenolysis of esters (23); 3 in the hydrogenolysis of neopentane (9); slightly greater than unity in the dehydrogenation of cyclohexane (24); and about unity in the hydrogenolysis of ethane (25). Overall, it seems inadvisable to assume that all details of the results obtained with catalysts prepared from RhCl<sub>3</sub> would be identical to those of this paper.

A number of papers have compared physical or catalytic characteristics of rhodium on various supports. Rh–Rh coordination numbers were reported to be much larger on SiO<sub>2</sub> than on Al<sub>2</sub>O<sub>3</sub> (26) and Rh/Al<sub>2</sub>O<sub>3</sub> was reported to be 10 times as active as Rh/SiO<sub>2</sub> in the hydrogenation of CO (27), but these catalysts were prepared from RhCl<sub>3</sub>. The Figueras group found distinct differences between Rh/SiO<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> in the hydrogenation of benzene and in several hydrogenolytic reactions (28, 29). However, Rh/SiO<sub>2</sub> was prepared by ion exchange with [Rh(NH<sub>3</sub>)<sub>5</sub>Cl]Cl<sub>2</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> was prepared either by impregnation with RhCl<sub>3</sub> or with Rh(NH<sub>3</sub>)<sub>5</sub>ClCl<sub>2</sub>. In view of the well-known reaction of chloride with Al<sub>2</sub>O<sub>3</sub> to generate acidic surface species, caution should be exercised in comparing Rh/SiO<sub>2</sub> with Rh/Al<sub>2</sub>O<sub>3</sub> prepared by impregnation with chloride-containing compounds.

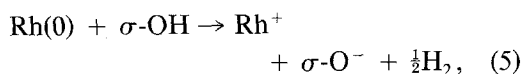
In our previous study of the hydrogenolysis of methylcyclopropane on these Rh/SiO<sub>2</sub> catalysts (8), it was found that the conditions of pretreatment had a large effect upon both total  $N_t$  and selectivity (taken as the ratio, isobutane/butane, in the products). Unfortunately, one can investigate only a limited set of the myriad of possible conditions of pretreatment. Since all of our pretreatments commence with O<sub>2</sub>, 300°; 0.5, it is not usually listed. This treatment removes any adventitious carbon that may have reached the catalyst despite strong countermeasures and it oxidizes 108-Rh-IonX nearly to Rh<sub>2</sub>O<sub>3</sub>/SiO<sub>2</sub> (8). After storage

of reduced 27-Rh<sub>4</sub> in air, the Rh(111) reflection in X-ray diffraction corresponded to an average particle diameter of 2.8 nm vs one of 3.8 nm after H<sub>2</sub>, 300°. After O<sub>2</sub>, 300°, no Rh core was detectable (8). Thus, O<sub>2</sub>, 300° must be followed by a reduction. We have employed only hydrogen as the reducing agent and have avoided CO and hydrocarbons on the view that they might lead to the formation of some kind of carbide. At 25°C, reduction by hydrogen was structure sensitive; that is, removal of \*-O from 108-IonX was only partial, but from 11-Rh<sub>4</sub> removal was complete. In the hydrogenolysis of methylcyclopropane, the pretreatments H<sub>2</sub>, 300° and H<sub>2</sub>, 300°; He, 450° gave catalytic activities that differed substantially both in  $N_t$  and in selectivity. In the present work, the effect of these variables was investigated for isotopic exchange, most exhaustively for 31-SiO<sub>2</sub>-Rh<sub>4</sub> (Fig. 3) and in somewhat less detail for 11-SiO<sub>2</sub>-Rh<sub>6</sub> and 108-SiO<sub>2</sub>-IonX (Table 4). As shown in Fig. 3, results were dramatic. Compare, for example, H<sub>2</sub>, 450° (very large  $N_t$ , extreme Type A distribution; see Fig. 1d); H<sub>2</sub>, 450°; He, 450° (medium  $N_t$ , Type A-3 distribution but nearly Type B; see Fig. 1a), and H<sub>2</sub>, 100°; He, 100° (very small  $N_t$ , Type B, see Fig. 2f).

As assayed by XPS, Rh/SiO<sub>2</sub>; H<sub>2</sub>, 300° is free of oxygen (21) as is Rh/SiO<sub>2</sub>; H<sub>2</sub>, 150° (30). Further, Kip *et al.* (31) found that in temperature-programed reduction of Rh(NO<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub>; O<sub>2</sub>, 450°; 3 consumption of H<sub>2</sub> occurred in a broad peak stretching from 298 to only 473 K. Here, removal of oxygen and desorption of hydrogen should have been complete by 200°C. However, Gorodetskii *et al.* (32) reported that TPD liberated a small amount of hydrogen at 600–800 K from a Rh filament that had been treated with hydrogen. This hydrogen was assigned tentatively to a subsurface species. Also, Rh/SiO<sub>2</sub> cooled in H<sub>2</sub> from higher temperatures contained more hydrogen than was adsorbed on clean catalyst at 25°C (8). Such extra sorbed H appeared to be neither spilled-over H nor ordinary \*H adsorbed on the surface. Similar excess sorbed H had

been observed on Pt/SiO<sub>2</sub> (14). Supported on Al<sub>2</sub>O<sub>3</sub>, Rh<sup>3+</sup> seems to be harder to reduce than on SiO<sub>2</sub> (33) and MgO (34).

*Pretreatment H<sub>2</sub>, T<sub>H<sub>2</sub></sub>; He, T<sub>He</sub>.* Although the catalyst should be free of oxygen after H<sub>2</sub>, 300°, the following reaction might occur during He, 450°,



a reaction that is general for nonnoble metals on supports containing  $\sigma\text{-OH}$  (35). H<sub>2</sub>O has been reported to oxidize Rh/SiO<sub>2</sub> at 250°C (30). However, the fugacity of H<sub>2</sub>O from SiO<sub>2</sub> would be very much smaller than that of added H<sub>2</sub>O vapor. Since a sweep by an inert gas must be used in measurement of  $D_h$  by chemisorption of H<sub>2</sub>, the results of the rather numerous measurements of  $D_h$  by hydrogen chemisorption indicate that the extent of any reaction (5) must be small. In a related experiment, Rh(NO<sub>3</sub>)<sub>3</sub>/SiO<sub>2</sub>; H<sub>2</sub>, 300°, cool H<sub>2</sub>; **CO, 20°**; He, 300°, cool in He to 20°, **CO, 20°**, the two measurements of adsorption of CO shown in boldface type agreed (22). Thus, here He, 300° negligibly promoted reaction (5). In an extreme case Rh/SiO<sub>2</sub> ex RhCl<sub>3</sub> was pretreated H<sub>2</sub>, 450°, 4; vac., 800°; H<sub>2</sub>, ~25°, 0.25 (36), conditions that should minimize content in chloride and promote reaction (5). In subsequent TPD, the main H<sub>2</sub> peak was near 307°C for the lowest coverage and near 127°C for the highest coverage. At lower coverages, the kinetics of desorption were very like that for unsupported Rh. Apparently, then, the extent of reaction (5) is small even at 800°C and a flow of helium for 1 h at 250°C would lead to full removal of adsorbed H<sub>2</sub> except for any like that of Ref. (32).

Exposure of 58-IonX to O<sub>2</sub>, 300°; H<sub>2</sub>, 25°; Ar, 450° led to the liberation of H<sub>2</sub> during the last step in amount corresponding to H/Rh = 0.48 (8). Thus, O/Rh was about 0.05 after H<sub>2</sub>, 25°, but this oxygen was removed by H\* during heating in Ar. 108-IonX similarly treated retained much more oxygen since no H<sub>2</sub> was liberated during Ar, 450°. It appeared that H<sub>2</sub>, 25° removed all oxygen from the

other catalysts. In the hydrogenolysis of methylcyclopropane at 0°C,  $N_t(\text{H}_2, 25^\circ)/N_t(\text{H}_2, 100^\circ)$  was only 0.1 on 108-IonX, but 0.3 on 58-IonX and nearly unity on 50-IonX. This accords with the conclusion that oxygen removal by H<sub>2</sub>, 25° is incomplete only for 108-IonX and 58-IonX. The very low values of  $N_t$  for isotopic exchange of neohexane after H<sub>2</sub>, 100° and H<sub>2</sub>, 100°, He, 100° on 31-SiO<sub>2</sub>-Rh<sub>4</sub> (Fig. 3) and 108-SiO<sub>2</sub>-IonX (Table 4) might be taken to indicate that these catalysts were incompletely reduced. However, the work just cited (8) indicates that oxygen removal from these catalysts was probably complete. Even were residual oxygen to remain after H<sub>2</sub>, 100°, the surface of the particles of Rh contained enough \*H to convert all residual surface oxygen to water since, as shown in Fig. 3, H<sub>2</sub>, 100°, H<sub>2</sub>, 300° and H<sub>2</sub>, 450° followed by He, 450° all gave nearly the same  $N_t$  and  $D_1/D_5$ . Rate and selectivity were also the same in the hydrogenolysis of methylcyclopropane on Rh/SiO<sub>2</sub> after the two pretreatments, H<sub>2</sub>, 25°; He, 450° and H<sub>2</sub>, 300°; He, 450° (8).

H<sub>2</sub>, 450° leads to the largest values of  $N_t$  and  $D_1/D_5$  in isotopic exchange of neohexane. Little change results from cooling H<sub>2</sub>, 450° in H<sub>2</sub> and exposing to He, 300°, a procedure that should remove surface H\*. However, He, 450° immediately following H<sub>2</sub>, 450° leads to a drastic reduction in activity and in  $D_1/D_5$  (Fig. 3). Thus, the H<sub>2</sub>, 450° catalyst is little changed by mere removal of surface H\*, but heating in He to 450°C leads to rearrangement of the catalyst surface. This process is accompanied and perhaps influenced by desorption of the "extra sorbed H<sub>2</sub>" mentioned earlier. Even at 450°C, the rearrangement is not very fast. Thus, H<sub>2</sub>, 450°; He, 450°, 0.17, cool in He generates a surface intermediate between H<sub>2</sub>, 450° and H<sub>2</sub>, 450°; He, 450°, 1 both in  $N_t$  and selectivity (Fig. 1e). H<sub>2</sub>, 300° gives a catalyst with  $N_t$  about half of that of H<sub>2</sub>, 450° but with  $D_1/D_5$  close to that of H<sub>2</sub>, 300°; He, 450°. Subsequent He, 300° has a much larger effect on H<sub>2</sub>, 300° than on H<sub>2</sub>, 450° and rates of

isotopic exchange of neohexane are the same on  $H_2, 100^\circ; He, 300^\circ$  and  $H_2, 300^\circ; He, 300^\circ$ , but quite different on  $H_2, 450^\circ; He, 300^\circ$ . The augmented values of  $N_t$  resulting from  $H_2, 450^\circ$  and  $H_2, 300^\circ$  are probably both associated with surface roughening, but the two surfaces appear to differ in nature.

*Catalysts 108-IonX and 11-Rh<sub>6</sub>*. The effect of pretreatment upon 108-IonX was similar in trend to that of 31-Rh<sub>4</sub> although  $N_t$ 's were distinctly larger (Table 4).  $He, 450^\circ$  led to nearly the same values of  $N_t$  and  $D_1/D_5$  whether preceded by  $H_2, 100^\circ$ ,  $H_2, 300^\circ$  or  $H_2, 450^\circ$ . However, 108-SiO<sub>2</sub>-IonX favors a strong A pattern (small  $D_5/D_1$ ) and except for  $H_2, 100^\circ$ , there was little difference in the  $D_i$  patterns. 11-SiO<sub>2</sub>-Rh<sub>6</sub> was different. Values of  $N_t$  were smaller.  $H_2, 100^\circ$  led to the most active surface for 11-Rh<sub>6</sub> (compare  $H_2, 100^\circ$  and  $H_2, 450^\circ$  for 11-SiO<sub>2</sub>-Rh<sub>6</sub> and 108-SiO<sub>2</sub>-IonX). Also, particularly strikingly,  $N_t$  after  $H_2, 450^\circ; He, 450^\circ$  was larger than that after  $H_2, 450^\circ$  (contrast 108-SiO<sub>2</sub>-IonX).

*Sites*. The catalytic sites will consist of one or more atoms of rhodium in a particular geometric arrangement. Since the Rh crystallites will expose different crystal planes and edges, each pretreatment condition is likely to produce a mixture of active sites and it is likely to be difficult to characterize the isotopic distribution patterns in terms of sites in fine detail. Nevertheless, the various site mixtures that result from the various pretreatments fit into a rather straightforward classification. From Fig. 3, the  $N_t, D_1/D_5$  pairs for 31-Rh<sub>4</sub> at the 12 values of  $H_2, T_{H_2}; He, T_{He}$  can be fitted into five categories:

(1)  $N_t$  in  $s^{-1}$  and  $D_1/D_5$  equal 0.6 and 14, respectively (sites generated by  $H_2, 450^\circ$ , alone, or followed by  $He, 100^\circ$  or  $He, 300^\circ$ )

(2)  $N_t$  and  $D_1/D_5$  equal 0.12 and 2 ( $H_2, 100-450^\circ; He, 450^\circ$ )

(3)  $N_t$  and  $D_1/D_5$  equal 0.12 and 6.5 ( $H_2, 300^\circ$ )

(4)  $N_t$  and  $D_1/D_5$  equal 0.07 and 2 ( $H_2, 100-300^\circ; He, 300^\circ$ )

(5) (probably)  $N_t$  and  $D_1/D_5$  equal 0.02 and 0.6 ( $H_2, 100^\circ$  alone or followed by  $He, 100^\circ$ ).

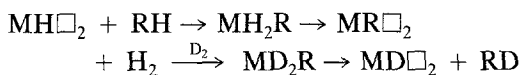
If site mixture (4) did not differ genuinely from site mixture (2), one would have to make the unlikely assumption that (2,4) was formed slowly from (1) by  $He, 450^\circ$ , but that it was formed readily from  $H_2, 300^\circ$  by  $He, 300^\circ$ . The other site mixtures must be independent. Catalyst 11-Rh<sub>6</sub> (Table 4), which combines rates and selectivities quite different from those of 31-Rh<sub>4</sub>, must add at least two or probably three site mixtures to the list. The very high activity of 108-IonX;  $H_2, 450^\circ$  would seem to require separate sites as would the combination of activity and selectivity of 108-IonX,  $100^\circ$ . The combination of selectivity and  $N_t^0$  of 52-Rh<sub>4</sub> would be difficult to generate by combination of the patterns enumerated above. It would be interesting to have data on the exchange of neohexane on several different crystal faces of rhodium single crystals.

The sites leading to isotopic exchange are on the rhodium particles, but NMR experiments on 5% RhCl<sub>3</sub>/SiO<sub>2</sub>;  $H_2, 200^\circ, 6; He, 200^\circ \rightarrow 22^\circ, H_2, 22^\circ$  showed that some  $H_{ads}$  on Rh interacted with  $\sigma O-H$  on the millisecond time scale (38). Thus, some  $H_{ads}$  and some  $\sigma OH$  were close and interacting. The proportion of such species should decrease with increasing particle size. Perhaps reactivity of the Rh-H species involved is blocked by  $\sigma OH$ , but on the contrary these Rh/H might be active and have unusual properties. It is conceivable if unlikely that these sites could contribute to the extreme activity of the  $H_2, 450^\circ$  pretreatment on 108-IonX and 31-Rh<sub>4</sub>.

Given only the solid bars in Fig. 3, one might have thought that their heights were proportional to the areal concentrations of single, uniformly active sites. However, as shown above, this cannot be so. When studying structure sensitivity it is a marked advantage to employ systems that simultaneously provide rate data and selectivity

data. In the present case, the surface must contain a complicated system of sites that may be interacting and appear to vary in activity and selectivity with the pretreatment conditions and the rhodium particle size. The data do not establish whether the conditions of preparation influence  $N_t$  and the selectivity.

Consider the proposal that binding sites in heterogeneous catalysis are monatomic like those in homogeneous catalysis and that all of the elementary processes in the catalytic cycle occur at one monatomic site which is necessarily coordinatively unsaturated to the extent of one, two, or three ligands according to the reaction catalyzed (39, 40). This model is very likely to apply to some reaction systems in heterogeneous catalysis (41) but not to the present one. Dissociative adsorption of an alkane would require a site of the type  $MH\Box_2$  (where  $\Box$  indicates a ligand vacancy) so that a sequence like the following can occur.



As shown above, this model would require eight or probably many more different tri-coordinatively unsaturated rhodium atoms. This seems unlikely. If the actual catalytic sites are polyatomic, matters are much simpler. Even if the sites involve only two atoms, four different kinds of adjacent atoms would generate 10 dimer sites.

*Effect of percentage exposed.* Table 3 lists  $N_t^0$  (the superscript designates the standard pretreatment) for all catalysts. In general,  $N_t^0$  increases with increasing  $D_h$ , but there is enough scatter from any averaged line of  $N_t$  vs  $D_h$  so that at one extreme one could say that  $N_t$  was low for 11-Rh<sub>6</sub> and 27-Rh<sub>4</sub>, high for 108-IonX, and without a clear trend between. In general, the selectivity also varied with  $D_h$ , from  $D_1/D_5$  being very small at the lowest  $D_h$  to being large for catalysts of large  $D_h$ , but again there is scatter. Thus, it could be said that  $N_t$  is mildly structure sensitive, but that  $D_1/D_5$  is strongly structure sensitive. However, this

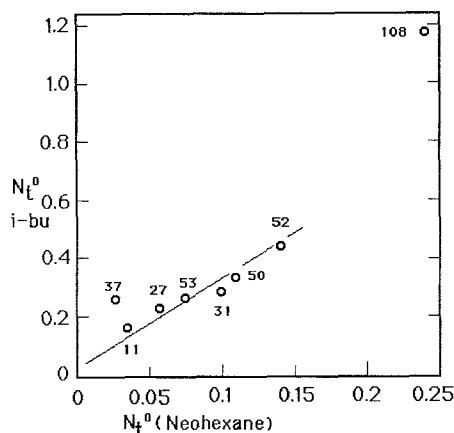


FIG. 4.  $N_t^0$  in  $s^{-1}$  for the hydrogenolysis of methylcyclopropane at  $0^\circ C$  ( $x$ -axis) from Ref. (8) vs  $N_t^0$  in  $s^{-1}$  for the isotopic exchange between  $D_2$  and neohexane at  $75^\circ C$  (this paper). The pretreatment conditions were  $H_2, 300^\circ; He, 450^\circ$  in both cases. Points are identified by their values of  $D_h$ .

statement would apply only to catalysts that had received the standard pretreatment. After  $H_2, 450^\circ$   $N_t$  is strongly structure sensitive since  $N_t$ 's for 11-Rh<sub>6</sub>, 31-Rh<sub>4</sub>, and 108-IonX were 0.01, 0.54, and  $3.3 s^{-1}$ , respectively.  $D_1/D_5$ , however, is less structure sensitive after  $H_2, 450^\circ$  than after the standard pretreatment. The exact nature of structure sensitivity in these Rh/SiO<sub>2</sub> catalysts depends upon the pretreatment as well as on  $D_h$  and one cannot make a general statement without considering pretreatment.

In the hydrogenolysis of methylcyclopropane (8) after  $H_2, 300^\circ; He, 450^\circ$ ,  $N_t^0$  also increases with increasing  $D_h$  but, again, because of scatter one could say only that there was no clear trend for intermediate values of  $D_h$ . However, as shown in Fig. 4, there is a rather good correlation after  $H_2, 300^\circ; He, 450^\circ$  between the values of  $N_t^0$  for the hydrogenolysis of methylcyclopropane and those for isotopic exchange of neohexane except for 37-Rh<sub>6</sub>.  $N_t^0$  for 108-IonX is so large for both reactions and so far removed from the other points that it is not clear that 108-IonX constitutes an anomaly.

Further,  $H_2, 25^\circ$  to  $H_2, 450^\circ$  followed by  $He, 450^\circ$  all gave nearly the same catalyst for both reactions. Butane/isobutane like  $D_1/D_5$  increases with increasing  $D_h$ . For example, 11-Rh<sub>6</sub> very strongly favors formation of isobutane and neohexane-*d*<sub>5</sub>. It then appears very probable that the isotopic exchange of neohexane and the hydrogenolysis of methylcyclopropane utilize the same or very similar sites on Rh/SiO<sub>2</sub> at least after the standard pretreatment.

It is often assumed that the tiny face-centered cubic metal particles of supported catalyst are bounded by regular (111) and (100) planes and that the major effect of increasing  $D_h$  is an increase in the ratio, [edge sites]/[face sites]. However, if the bounding planes are rough or incomplete, additional sites with the stereochemical properties of edge sites will be present and the effective ratio, [edge sites]/[face sites] will be larger than expected on larger particles. This matter is discussed in the following article.

That pretreatment has as large an effect upon rate and selectivity as particle size was noted in an earlier work with Pt, Pd, and Rh (3, 5–8). A complete explanation of these effects in any particular case is likely to require more information than is available, i.e., a detailed knowledge of the geometry of the crystallites and their interaction with the support, of the details of the mechanism of the reaction, and of the exact geometry of the transition states on all metallic sites (11). We suspect that the major determinant of rate and selectivity is the surface morphology as influenced by the temperature and the nature of the gases exposed to the catalyst during pretreatment. Despite evidence to the contrary, it might still be possible that small amounts of unremoved surface oxygen on Rh/SiO<sub>2</sub>;H<sub>2</sub>, 100° of larger  $D_h$  contributed to their lower catalyst activity.

One conceivable factor can be eliminated as influencing catalytic activity. The pretreatment conditions are too mild to result in the formation of metal silicides. Formation of palladium silicides requires more

drastic treatment than H<sub>2</sub>, 450° (42) as does that of platinum silicides (43). The formation of palladium carbide (PdC<sub>0.13</sub>) has been reported during the hydrogenation of acetylene (44) and upon heating Pd in C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, or CO (45). The C is located in octahedral holes and formation of the carbide suppresses formation of the interstitial hydride. Treatment with O<sub>2</sub> or H<sub>2</sub> at  $T > 150^\circ\text{C}$  destroys the carbide. The Rh/SiO<sub>2</sub> catalysts of the present paper were always initially free of carbide, but we cannot exclude the possibility that carbide was formed during reaction nor that formation of carbide is structure and pretreatment sensitive.

#### CONCLUSIONS

Both turnover frequency and the isotopic distribution pattern are affected by particle size and pretreatment conditions. The extreme variation in  $N_t$  is a factor of 330. The various  $N_t$  and selectivity couples resulting from variation in percentage exposed and pretreatment conditions appear to require a minimum of eight different sites. It seems likely that most of the sites involve more than one rhodium atom. Sites for exchange appear to be very similar to those for the hydrogenolysis of methylcyclopropane. On all Rh/SiO<sub>2</sub> except that with the largest particles (~10 nm) the pretreatment H<sub>2</sub>, 450° gives the largest  $N_t$  both for exchange and hydrogenolysis and the largest  $D_1/D_5$ . Mere removal of surface H\* from Rh/SiO<sub>2</sub>;H<sub>2</sub>, 450° does not affect  $N_t$  or selectivity, but He, 450° after H<sub>2</sub>, 450° reduces  $N_t$  apparently by promoting a surface reconstruction. After H<sub>2</sub>, 100–450°; He, 300 or 450°, the surface of Rh is clean and free of oxide.

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