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Isotopic Exchange between Deuterium and 2,2-Dimethylbutane on Platinum/Silica and Palladium/Silica

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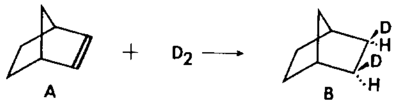
Isotopic exchange between deuterium and 2,2-dimethylbutane (neohexane) has been investigated on a series of Pt/SiO_2 (percentage exposed of metal, D_h = 6.3–81%) and Pd/SiO_2 (D_h = 13.8–96.7%) catalysts at temperatures in the vicinity of 100°C. Catalysts were investigated after three different pretreatments: *standard:* O_2,300°; H_2,300°; He,450° and *H_2,450°*: O_2,300°; H_2,450° and *H_2,100°*: O_2, 300°; H_2,100°. One might expect exchange into the methylene group to be subject to substantial steric hindrance from the adjacent t-butyl group and the degree of steric hindrance to be less at edge atoms than at atoms in (100) and (111) faces, i.e., relatively less on small crystallites than on larger ones. In general, the effect of D_h upon the relative yield of ethyl-d_5 in neohexane did not accord with this expectation. A possible explanation is that the bounding faces of the crystallites are defective and contain many vacancies which generate sites about equivalent to edge sites in the degree of hindrance. If so, usual tests of structure sensitivity could be seriously affected.

INTRODUCTION

This paper is concerned with the characterization of the surface of the metal particles in Pt/SiO_2 and Pd/SiO_2 by study of the structure sensitivity of isotopic exchange between deuterium and neohexane. It is expected that there would be substantial adsorbate–surface hindrance in cleaving the CH bond in the CH_2 group of neohexane.

Steric interactions between adsorbates and the surfaces of heterogeneous catalysts might be expected to be at least as important to heterogeneous catalysis as are analogous steric interactions to other areas of chemistry, because the steric bulk of a surface is apt to be at least as large as that of any molecular species. Such information as we have on this matter derives primarily from studies of hydrogenation reactions where the effect of adsorbate–surface strain on selectivities can be major (*1*). For example, in the hydrogenation with deuterium of bicycloheptene on platinum (*2*, *3*), the methylene bridge offers less hindrance to the adsorption of the double bond than does the ethylene bridge. Accordingly, the bicycloheptene adsorbs so that the methylene bridge faces the surface, deuterium adds from the methylene side, and the product is heavily *exo*-dideuterobicycloheptane.



As a second example, in competitive hydrogenations of mixtures of cyclopentene and *cis*-di-t-butylethylene (*4*), cyclopentene is hydrogenated with high preference because the t-butyl groups in *cis*-di-t-butylethylene introduce substantial adsorbate–surface strain in the adsorbed olefin. Such strain is so severe in adsorbed *trans*-di-t-butylethylene that the olefin alone is hydrogenated very slowly unlike the case with the *cis* compound.

On the other hand, steric effects in isotopic exchange between alkanes and deuterium have received little attention except for occasional speculation about the possible occurrence of such an effect (*5*) and the report (*3*) that bicycloheptane exchanges on palladium at 200°C to give predominantly

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the same *exo*-bicycloheptane-d_2, species **B**, as formed in addition of deuterium to **A.**

It is clear from much work by several groups on many hydrocarbons (see, for example, Ref. (*6*)) that isotopic exchange between deuterium and hydrocarbons on metal catalysts involves a number of processes. The turnover frequency per surface metal atom for the formation of all exchanged species plus the isotopic distribution pattern (the relative yields of d_1, d_2, d_3, . . .) have a large information content from which one may hope to extract important mechanistic information, and in suitable cases, information of a steric nature.

The fundamental processes in alkane exchange have usually been taken to be: (1) dissociative adsorption of hydrogen, (2) dissociative adsorption and associative desorption of alkane, and (3) interconversion of monoadsorbed and 1,2-diadsorbed alkane. These are illustrated below for an ethyl group.

$$D_2 + * \rightleftharpoons 2D*, \tag{1}$$

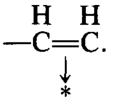
$$\text{R-CH}_2\text{-CH}_3 + 2* \rightleftharpoons \text{R-CH}_2\text{-CH}_2* + \text{H}*, \tag{2p}$$

$$\text{R-CH}_2\text{-CH}_3 + 2* \rightleftharpoons \text{R-CH}*\text{-CH}_3 + \text{H}*, \tag{2s}$$

$$\text{R-CH}_2\text{-CH}_2* + 2* \rightleftharpoons \text{R-CH}*\text{-CH}_2* + \text{H}*, \tag{3s}$$

$$\text{R-CH}*\text{-CH}_3 + 2* \rightleftharpoons \text{R-CH}*\text{-CH}_2* + \text{H}*. \tag{3p}$$

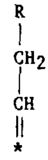
The diadsorbed alkane could also be written as a π-adsorbed alkene,



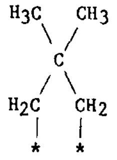
$$\overset{\text{H}}{\text{—C}}=\overset{\text{H}}{\text{C}}.$$

The correct electronic representation of diadsorbed alkane is uncertain as is whether binding is to one or several atoms of metal. However, all representations involve similar geometries for the adsorbate and in the present paper it will make little difference as to which is closer to the correct formulation.

If reactions (3) are fast vs reactions (2), the ethyl group can be converted to $-CD_2CD_3$ in the initial product, i.e., in one period of adsorption, provided that desorption of HD is fast so that the ratio, D*/H*, is kept large. This is generally the case in isotopic exchange between deuterium and alkanes (*6*). It is also assumed that rotation about the CH_2–CH_3 bond is fast. If (3) is slow vs (−2), the initial product would be largely RCH_2CH_2D or $RCHDCH_3$. At temperatures in the vicinity of 50–100°C, 1,1- and 1,3-diadsorbed alkanes contribute much less to isotopic exchange than do 1,2-diadsorbed alkanes (*6*).



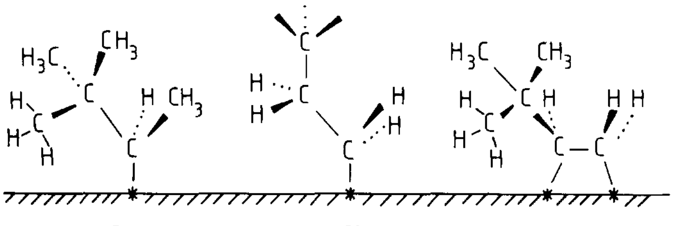
1,1-diadsorbed



1,3-diadsorbed

Thus in the initial products of the exchange of neohexane, one expects to find CH_2D–$C(CH_3)_2$–C_2H_5 and $(CH_3)_3C$–C_2H_4D · · · $(CH_3)_3C$–C_2D_5 but no $C_6H_8D_6$. However, exchange of neohexane involves a feature absent in simpler alkanes. The hydrogen atoms in the methylene group are adjacent to the bulky t-butyl group, i.e., the hydrogen atoms are at a neopentyl position, and significant steric hindrance should lead to slower rates in reactions (2s) and (3s). If slow enough the only exchanged ethyl group in the initial product would be $-CH_2CH_2D$. That is, the t-butyl group should disfavor **I** vs **II.** The diadsorbed alkane **III** should form less readily than from unbranched alkanes like butane and cyclopentane. The adsorbate–surface strain in **III** would be like that in adsorbed *cis*-di-t-butylethylene although smaller.

One might expect that rates and selectivities in heterogeneous catalytic reactions would depend upon the surface morphology of the catalytic component of supported metallic catalysts and, in particular, upon the distribution of M_s (surface atoms



of metal) among various C.N. (coordination numbers). In the absence of methods to determine surface morphologies, one has assumed that the metal crystallites are bounded by more densely packed planes like (100) and (111) of fcc (we shall later advance doubts regarding this assumption). On this assumption, the ratio of edge atoms (low C.N.) to face atoms (larger C.N.) would decrease with increasing particle diameter which can be measured by X-ray diffraction, electron microscopy, or chemisorption. At larger crystallite diameters, even at 4 nm, most M_s would be assumed to be located in planes of high C.N., whereas the contrary would be true at ~1.4 nm. A structure-sensitive (insensitive) reaction on a particular type of catalyst is then one in which the rate or the selectivity varies (does not vary) significantly with particle size or percentage exposed of the metallic component. Thus, in structure-insensitive reactions, and most reactions at lower temperatures have been reported to belong to this class, M_s of both low and high C.N. lead to nearly the same rates and selectivities.

Since the steric bulk at an atom in an edge should be much less than that at one in a face (*4*), formation of **I** from neohexane (g) or from **III** would be relatively more favored on small than on large platinum crystallites. Therefore, the initial product of exchange should contain more extensively exchanged neohexane on smaller than on larger crystallites of platinum. In competitive hydrogenation of cyclopentene and di-t-butylacetylene on supported platinum catalysts (*4*), the degree of inhibition by cyclopentene of the hydrogenation of the acetylene steadily decreased (although always large) as the particle size decreased.

We had available a set of Pt/SiO_2 catalysts (*7*) of a wide range of particle sizes which had been rather extensively characterized by physical methods and upon which a number of reactions had been studied (*8–11*). It appeared, therefore, of interest to study isotopic exchange between deuterium and neohexane on these catalysts. This work was extended to a set of Pd/SiO_2 catalysts. Because previous work had indicated that variation in the conditions of pretreatment of Pt/SiO_2 catalysts could lead to larger effects than variation in D_h (percentage exposed of metal), we investigated all of the catalysts after exposure to three pretreatments: *standard,* i.e., O_2,300°,0.5; He,300°,0.25; H_2,300°,1; He or Ar,450°,1; cool in He or Ar, *H_2,100°*, i.e., O_2,300°, 0.5;He, 300°,0.25;H_2,100°,1, and *H_2*,450°, i.e., O_2,300°,0.5;He,300°,0.25; H_2,450°,1; cool in H_2. In the pretreatment code, O_2,300°, 0.5; He,300°,0.25 means that the catalyst was exposed to flowing O_2 at 300°C for 0.5 hr and then to He at 300°C for 0.25 hr. The first pretreatment is called standard because this is the pretreatment which must precede measurement of D_h by hydrogen chemisorption. The exchange reactions were investigated at temperatures near 100°C and with D_2/neohexane ≈10.

EXPERIMENTAL METHODS

Catalysts

The catalyst support was the wide-pore Davison grade 62 (*7*). Its iron content was 48 ± 15 ppm as determined by neutron activation analysis on the Triga Mark I reactor at Reed College, Portland, Oregon and 40 ppm as determined by atomic adsorption spectroscopy on a solution of the gel in hydrofluoric acid. To illustrate the meaning of the catalyst code, 81-Pt-IonX had a percentage exposed of Pt of 81% and it was made by ion exchange of $Pt(NH_3)_4^{2+}$ with silica gel. PtCl rather than IonX indicates preparation by impregnation with H_2PtCl_6. These catalysts had been characterized by hydrogen chemisorption at 25°C, X-ray line profile analysis, and transmission electron microscopy (*7*, *12*).

Some of the Pd/SiO_2 catalysts were prepared by ion exchange at 25°C with a solution which contained a known quantity of $Pd(NH_3)_4(NO_3)_2$ and which was brought to a pH of 9.5 by the addition of ammonia aq. The catalysts were then washed thoroughly with redistilled water. In 49.8-Pd-IV, the percentage exposed is 49.8% and IV designates the method of preparation just described. Method II was the same but it used $Pd(NH_3)_4Cl_2$.

In method I, ion exchange was effected by exposing silica gel to a solution of $PdCl_2$ in concd ammonium hydroxide at 70°C for 1 hr (*13*). Extracting the Pd^{2+} from several catalysts with 0.1 M HNO_3 followed by analysis for Pd(II) polarographically gave good checks for content in Pd with that obtained by assuming complete ion exchange of the added Pd(II). In addition, analysis by uv absorption spectroscopy always showed that the supernatant solution from ion exchange was free of Pd.

In method III, silica gel was impregnated to incipient wetness with a benzene solution of $Pd(acetylacetonate)_2$ followed by drying in a mechanically rotated beaker illuminated with an infrared lamp (*7*). The low solubility of the $Pd(acac)_2$ in benzene necessitated several successive impregnations to attain the desired content in Pd.

To ensure that the surface of the silica gels in the various catalysts should all be as similar as possible, i.e., to have the same degree of dehydroxylation, catalyst reduction and pretreatment should not involve steps with temperatures exceeding 450°C. In catalysts prepared by methods I and II, calcination at 400–450°C before reduction did not lead to lower percentages exposed (D_h) as had been the case with Pt/SiO_2 catalysts and a variety of procedures for reduction all led to large D_h. It was then found that the presence of water vapor during reduction led to lower D_h. In method IV, catalysts were reduced in a fluidized bed and, in some cases, the hydrogen used for reduction was saturated with water (*14*).

Percentage exposed of Pd was measured with hydrogen at 60°C using a pulse technique (*7*, *14*). Values of D_h for catalysts I and II were determined before the technique for measurement of D_h for Pd/SiO_2 had been standardized and may be of lower accuracy.

Table 1 presents data regarding preparation and values of D_h for the Pd/SiO_2 catalysts employed in this paper. Values of D_h are given to more significant figures than are warranted so as to serve in the catalyst code. Some water was added to 13.8- and 29.3-Pd-IV before starting the reduction procedure (*14*).

Isotopic Exchange Procedures

Exchange runs were made in a grease-free apparatus of the type previously described (*9*). Deuterium was purified by passage through a Deoxo unit, 5A sieve, and grade 62 silica gel at −196°C. H_2 passed through a Deoxo unit, 5A sieve at −196°C, and $Cr(II)/SiO_2$ (*7*). Helium was similarly purified except that $CaCl_2$ replaced the Deoxo unit. All gases also passed through a $Mn(II)/SiO_2$ trap located immediately before the saturator. The $Cr(II)/SiO_2$ was periodically regenerated with H_2 at 500°C and the $Mn(II)/SiO_2$ trap at 350°C.

Neohexane (Chemical Samples Co., 99.9% purity) was refluxed and then distilled from a sodium–potassium alloy under nitrogen and stored under nitrogen. A mixture of deuterium (684 Torr) and neohexane

TABLE 1

Palladium Catalysts

Catalyst	Pd (wt%)	Reduction procedure[a]
13.8-Pd-IV	2.09	[H_2 + H_2O(25°)], 25°,0.5; H_2,300°,[b]; H_2,450°,[c]1[d]
29.3-Pd-IV	2.09	[H_2 + H_2O(25°)], 25°,0.5; H_2,250°,[b]; H_2,450°,[c]1[d]
49.8-Pd-IV	1.56	[(H_2 + H_2)(40°)], 40°,0.5; H_2,450°,[b]1
65.5-Pd-IV	2.09	[He + H_2O(25°)], 25°,1; H_2,450°,[c]1[d]
79.1-Pd-IV	0.49	He,300°,[c]1; cool to 50° in He; H_2,450°,[c]1[d]
18.8-Pd-I	0.38	Air,650°,6; H_2,300°,11; H_2,650°,5[d]
31-Pd-I	0.17	H_2,650°,4; He,650°,2; air,650°, cool to 25°; H_2,300°,2
54.4-Pd-I	0.17	Air,120°,12; H_2,300°,11; He,300°,4[d]
79.2-Pd-I	0.17	H_2,300°,[e]2; cool to 25° *in vacuo;* H_2,400°,1.5
94.7-Pd-I	0.17	H_2,300°,[e]2; cool to 25° *in vacuo*
96.7-Pd-II	0.38	Vacuum, 25°,2; O_2,25°,0.5; O_2,400°,[b]3; H_2,25°,2; H_2,135°,[b]2
22.5-Pd-III	1.52	Air,300°,[c]2; He,cool to 50°,H_2,300°,[c]3

[a] The treatment code is the same as the pretreatment code. [H_2 + H_2O(25°)] means treatment with hydrogen saturated with water at 25°C.

[b] The rate of temperature rise was 0.5–1°C/min.

[c] The rate of temperature rise was 4°C/min.

[d] Cooled after the last hydrogen treatment in helium, otherwise in hydrogen.

[e] The rate of temperature rise was 30°C/min.

(66 Torr) was prepared by passing deuterium through a tube of Filtros FS-140 (14–40 mesh) (*9*) maintained at −9.6°C by a slush bath of dodecane.

We tried to keep conversions in isotopic exchange large enough to get reliable measurement of the yields of the various exchanged species but small enough so that distortion of the initial isotopic distribution patterns by further adsorption and exchange of already exchanged molecules was small. If x is the fraction of molecules of neohexane exchanged, then, at lower conversions, the ratio of doubly to singly reacted molecules is $x/2$ (*15*). We attempted to keep total conversions near 6% where $x/2$ is 0.03, but some runs with conversions of ~10% were employed. Conversions were controlled by adjustment of the amount of catalyst (0.036–0.24 g for Pt/SiO_2 and 0.18–1.2 g for Pd/SiO_2) and by the flow rate of D_2 (3–60 cm^3 min^{-1}). The catalyst was near the bottom of one arm of a U-tube of $\frac{1}{4}$-in. fused silica and it was preceded and followed by small layers of Mn(II)/SiO_2 which prevented access of oxygen to the catalyst. In the standard pretreatment, the Mn(II)/SiO_2 layers which were near the top of the U-tube were regenerated during the H_2,300°,1 period. In the H_2,100° and H_2,450° pretreatments, the layers were regenerated by the use of auxiliary heating of the layers to ~350° during the H_2,100°,1 and H_2,450°,1 periods. The layers were exposed to O_2 only at 25°C in all cases. Before isotopic exchange runs, the catalysts were pretreated *in situ* in one of the three ways given in the Introduction, standard, H_2,100°, or H_2,450°.

During exchange runs, the catalyst temperature was controlled to ±0.2°C. At the start of a run, D_2 was passed over the catalyst for some minutes and then diverted through the saturator with the effluent mixture bypassing the catalyst. After 5–6 min during which a steady state was reached, flow of D_2–neohexane over the catalyst was started. Four to five successive samples of exchanged neohexane were collected for 1 to 5 min periods in traps kept at −196°C. The samples were analyzed by mass spectroscopy on a CEC-10-240 mass spectrometer using a nominal ionizing voltage of 20 V.

Preliminary experiments indicated that

TABLE 2

Reproducibility of Mass Spectroscopic Analysis

	m/e					
	71	72	73	74	75	76
	Run 1[a]					
Intensity	(100)	9.01	0.85	0.52	0.32	0.31
	Run 2[b]					
	(100)	8.89	0.81	0.50	0.30	0.29

[a] On fresh catalyst given the standard pretreatment; 0.0726 g of 40-Pt-PtCl-Large, 100°C, flow rate of D_2 = 15 cm^3 min^{-1}. This is not the same catalyst as 40-Pt-PtCl-Small of Table 3.

[b] On catalyst of run 1 reexposed to the standard pretreatment and run under the same conditions as in footnote *a*.

the temperature which appeared to give the most information as to differences among isotopic distribution patterns of the various catalysts lay near 100°C. Runs were made at 86.5, 100, and 110°C for Pt/SiO_2 and at 90 and 105°C (and occasionally at 115 and 125°C) for Pd/SiO_2.

Mass spectrometry. Since neohexene gives only trace intensity at the parent peak, isotopic analyses depended upon the t-butyl and the t-amyl carbonium ion peaks. Table 2 provides data which typify the reproducibility of runs. The initial content in H of the D_2, 0.3%, was increased by isotopic exchange between D_2 and neohexane. Correction for the small isotopic dilution was made as previously described (*16*).

The analysis of the t-butyl ion peak gave directly the isotopic yields in the $(CH_3)_3C$— group. The isotopic yields for the ethyl group were obtained by subtracting two-thirds of D_1, D_2, and D_3 of the t-butyl group from the isotopic yields in the t-amyl group. This calculation assumes that there is no isotope effect in the fragmentation of neohexane and that all deuterium atoms in the t-butyl group are on the same methyl. Because of the small values of D_2/D_1 and D_3/D_1 in t-butyl, errors resulting from the latter assumption must be very small. It was further assumed that no isotopic rearrangement accompanied formation of $(CH_3)_3C\text{-}d_i$ and $(CH_3)_2(C_2H_5)C\text{-}d_i^+$. Since such rearrangement could lead to substantial error, $(CH_3)_3(C_2D_5)C$ was prepared and examined mass spectrometrically. Five cubic centimeters of 3,3-dimethyl-1-butyne (Chemical Samples Co., 99% purity) was isotopically exchanged twice with 6 cm^3 of D_2O (in which 0.02 g of sodium had been dissolved) to give $(CH_3)_3C—C{\equiv}CD$ of 98.9% isotopic purity (NMR). This was hydrogenated with D_2 using 81-Pt-IonX as the catalyst to give a product which exhibited a single peak in NMR, that due to the nine methyl protons. Mass spectrometric analysis of the t-butyl ion revealed the presence of small amounts of d_1 and d_2 and small amounts of deuterium appeared to have been lost from the t-amyl ion. We conclude that isotopic rearrangement occurred in fewer than 5% of the $(CH_3)_3(C_2D_5)C^+$ ions. Errors introduced by such a degree of isotopic rearrangement are not serious.

EXPERIMENTAL RESULTS

Isomerization and Deactivation

Samples isotopically exchanged on 40-Pt-PtCl-S at 100°C and on 11.7-Pd-IonX-III at 125°C were examined by gas chromatography using a flame ionization detector. Since no isomerized hexanes could be detected, the exchange reaction was at least 20 times faster than any isomerization reaction. Platinum is known to catalyze the isomerization of neopentane at ~275°C, much above the temperature range employed in the present work (*17*). Palladium is usually much less effective (*17*).

The activity of catalysts declined with time on stream, approximately linearly for the first ~6 min and then more slowly. At 10 min, declines in activity were ~15%. The listed rates in this paper are initial rates obtained by extrapolating to zero time. The isotopic distributions were independent of time on stream.

Scatter in D_1-ethyl (see below) was rather large because D_1-(ethyl) = D_1-(t-amyl)-$\frac{2}{3}$ D_1-

(t-butyl) and both of the quantities on the right are somewhat uncertain because of substantial corrections for ^{13}C. Therefore, we usually exclude d_1-(ethyl) from the isotopic distribution patterns. We define D_i to mean the percentage of t-butyl-d_i or t-amyl-d_i in the isotopically exchanged ion, i.e.,

$$D_i = d_i \Big/ \sum_{i=1}^{n} d_i.$$

For ethyl we usually give D_i',

$$D_i' = d_i \Big/ \sum_{i=2}^{5} d_i.$$

TABLE 3

Isotopic Exchange between D_2 and Neohexane on Pt/SiO_2

Catalyst[a]	T (°C)	D_2'	D_3'	D_4'	D_5'	t-bu/et[b]	N_t[c] × 10^2
			Standard pretreatment				
6.3-Pt-PtCl-S	86.5	26	39	19	16	1.3	1.4
21.5-Pt-IonX-F		22	38	19	21	1.2	1.5
40-Pt-PtCl-F		24	28	20	28	2.0	1.6
63-Pt-IonX-F		27	28	21	24	2.0	1.8
81-Pt-IonX-F		27	28	21	24	2.3	1.3
40-Pt-PtCl-F[d]	81	9	11	6	74	—	9.0
6.3-Pt-PtCl-S,S	100	22	38	21	20	1.5	3.0
21.5-Pt-IonX-S		21	33	21	24	1.5	3.4
40-Pt-PtCl-S		22	29	22	26	2.0	3.5
63-Pt-IonX-S		25	29	22	24	1.9	3.2
63-Pt-IonX-F[e]		24	27	23	27	1.9	3.1
81-Pt-IonX-F		21	28	23	28	2.3	3.1
81-Pt-IonX-S,S,S[e]		24	26	22	28	2.2	3.1
6.3-Pt-PtCl-S,S,S	110	17	36	23	24	1.5	6.5
21.5-Pt-IonX-S,S		20	31	24	26	1.4	6.9
40-Pt-PtCl-F		18	27	23	32	2.0	6.9
63-Pt-IonX-S,S		22	26	22	30	1.9	7.6
81-Pt-IonX-F		21	25	23	31	1.9	8.0
			H_2,100° pretreatment				
6.3-Pt-PtCl-S	100	20	42	23	16	1.3	4.8
21.5-Pt-IonX-F		24	35	24	18	1.8	0.9
40-Pt-PtCl-F		30	36	17	17	1.8	0.5
63-Pt-IonX-F		32	32	21	15	1.8	0.4
81-Pt-IonX-F		26	33	20	21	1.8	0.5
			H_2,450° pretreatment				
6.3-Pt-PtCl-F	100	26	24	22	28	2.1	8.0
21.5-Pt-IonX-L,L		24	28	23	25	1.9	9.1
40-Pt-PtCl-L		28	26	20	27	2.1	8.8
63-Pt-IonX-S,S		25	29	19	27	2.2	9.0
81-Pt-IonX-H		24	29	20	28	2.1	17.0

[a] F at the end of the code indicates a fresh catalyst, S indicates that the catalyst had been exposed to the standard pretreatment and repretreated, L indicates a catalyst previously treated H_2,100°, and H indicates one previously treated H_2,450°.

[b] Ratio of exchanged t-butyl groups to exchanged ethyl groups.

[c] Turnover frequency per Pt_s for exchange into t-amyl in sec^{-1}.

[d] D_i' for isotopic exchange between cyclopentane and D_2 (9). D_1 was 6.5, D_6 6.0, D_7 4.2, D_8 3.7, D_9 2.6, and D_{10} 20.1%.

[e] These runs are included to show typical degrees of reproducibility.

TABLE 4

Isotopic Exchange between D_2 and Neohexane on Pd/SiO_2 at 105°C

Catalyst	D'_2	D'_3	D'_4	D'_5	t-bu/et	$N_t \times 10^3$
Standard pretreatment						
13.8-Pd-IV-S	10	11	37	42	0.39	3.0
29.3-Pd-IV-S	10	14	32	44	0.32	3.3
49.8-Pd-IV-L	5	8	25	62	0.69	2.8
65.5-Pd-IV-S	9	12	29	50	0.56	3.3
79.1-Pd-IV-S	9	13	32	46	0.29	7.6
96.7-Pd-II-S,S	8	10	35	47	0.35	8.9
18.8-Pd-I-S	4	8	12	76	1.0	0.7
32-Pd-I-S	3	7	17	73	0.9	1.2
54.4-Pd-I-L	7	9	29	55	0.5	3.4
79.2-Pd-I-S	8	12	35	45	0.4	3.8
94.7-Pd-I-S	9	13	35	43	0.4	3.0
22.5-Pd-III-S	3	5	14	78	0.5	2.9
H_2,100° pretreatment						
13.8-Pd-IV-S,S,S	9	12	28	50	0.43	0.9
29.3-Pd-IV-S,S,S	7	11	28	54	0.49	1.0
49.8-Pd-IV-F	4	6	18	71	0.80	1.1
65.5-Pd-IV-S,S,S	5	9	22	64	0.43	0.9
79.1-Pd-IV-F	9	11	30	50	0.37	2.2
96.7-Pd-II-S,S,S,S	8	11	29	52	0.42	3.4
H_2,450° pretreatment						
13.8-Pd-IV-S,S,S,L	14	21	36	29	0.26	3.9
29.3-Pd-IV-S,S,S,L	9	12	34	46	0.38	4.0
49.8-Pd-IV-S,L	8	9	31	53	0.47	3.4
65.5-Pd-IV-S,S,S,L	6	11	32	51	0.43	3.3
79.1-Pd-IV-S,S,L	11	15	31	43	0.28	10.0
96.7-Pd-II-F	12	14	35	40	0.27	7.2

Tables 3 and 4 present values of D'_i for the catalysts. Table 3 includes duplicate runs on 63.5- and 81-Pt-IonX at 100°C, standard pretreatment, which typify the reproducibility of runs. In general, values of D'_i are subject to errors of about ±2 percentage units.

Pt/SiO_2

For the standard pretreatment, D_1-(ethyl) was 23±10% for catalysts of the smallest D_h and it increased to 42±10% for those of the largest D_h. H_2,100° led to similar results, but H_2,450° led to about the same value of D_1 for all D_h, about 40%.

As expected, D_2-(t-butyl) was small and D_3-(t-butyl), very small. After correction for double adsorption, D_1-(t-butyl) was 92–97% following the standard pretreatment, but slightly larger, 95–99%, following H_2,100°, and H_2,450°. D_6-(t-amyl) was essentially zero (no $(CH_3)_2(CH_2D)C(C_2D_5)$) whence there were negligible concentration gradients of exchanged hydrocarbon in the catalyst pores (*21*).

Catalysts which had been used in runs after any of the pretreatments and then treated H_2,450° gave results indistinguishable from those with a fresh catalyst. H_2,100° gave the same results on a fresh catalyst as on one previously given the standard or the H_2,100° pretreatment. However, the standard pretreatment following H_2,450° gave values of N_t about 50% higher than those on a fresh catalyst given the standard pretreatment and D'_5 was a little

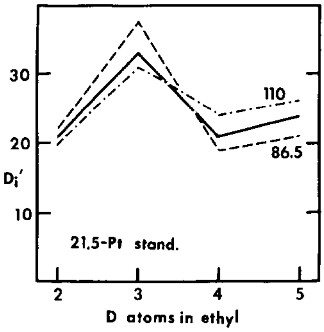


FIG. 1. D_i' vs i in ethyl-d_i for isotopic exchange on 21.5-Pt-IonX after standard pretreatment. At 110°C doubly dashed line; at 100°C solid line; at 86.5°C singly dashed line.

higher. However, this matter was only casually investigated.

Increasing the temperature of exchange runs led to an increase in D_4'- and D_5'-(ethyl), particularly the latter, at the expense of D_3' and D_2', particularly the former. This is shown in Fig. 1 for 21.5-Pt-IonX after the standard pretreatment. Increase in the relative yield of more highly exchanged alkanes with increasing temperature is common in isotopic exchange on metals. Similar effects of temperature were found in runs after H_2, 100° and H_2,450° although the increase was only about one-half as large after H_2,450° as in the other cases. In general, then, r_3/r_{-2} increases with increasing temperature.

Pd/SiO₂

13.8- and 29.3-Pd-IV have been characterized by X-ray line profile analysis (*18*). The crystallites are approximately equiaxed, i.e., they could be approximately inscribed in a sphere, and they have a microstrain density which is equivalent to about 4×10^{11} dislocations cm^{-2}, whereas only 6.3-Pt-PtCl had detectable strain density in the Pt/SiO_2 catalysts. The distribution of particle sizes is rather broad. The calculated particle sizes were in good agreement with D_h. This is also true for 49.8- and 65.6-Pd-IV although, because of the small particle size, the X-ray data are less complete (*19*).

D_1-(t-butyl) was 94–98% after correction for double reaction, and it appeared to be larger for runs in which D_5' was larger. D_6-(t-amyl) was negligible.

The ratio, t-bu/et, averaged about 0.5 and appeared to be larger on 49.8-Pd-IV than on the other catalysts. No effect of temperature upon t-bu/et could be detected. The effect was investigated in more detail on 49.8-Pd-IV than on any other catalyst. With three samples of catalyst and between 90 and 125°C, t-bu/et was 0.65 ± 0.10 without trend. D_1-(ethyl) was 9 ± 5% with no clear effect on D_1 of D_h, the temperature of the run, or the pretreatment.

For all catalysts given the standard pretreatment, D_5' increased with increasing temperature at the expense of D_2', D_3', and D_4' as illustrated for 65.5-Pd-IV in Fig. 2. In general, elevation of the temperature of runs from 90 to 115°C led to an increase in D_5' of about 8 percentage units. Catalysts given the pretreatments, H_2,100° and H_2,450° were investigated only at 105°C.

The effect upon the D_i's occasioned by changing from the standard to the H_2,100° pretreatment was the same for preparations I, II, and III as for IV, that is, D_5' increased ~8 percentage units. 22.5-Pd-III which had a very large D_5' (78%) was an exception; the

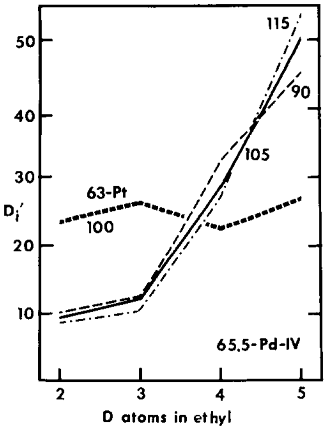


FIG. 2. D_i' vs i in ethyl-d_i for isotopic exchange on 65.5-Pd-IV after standard pretreatment. At 115°C doubly dashed line; at 105°C solid line; at 90°C singly dashed line. 63-Pt-IonX at 100°C after standard pretreatment is shown for comparison.

effect was negligible. Compared to the standard, the pretreatment H_2,450° led D'_5 to be lower by about 8–10 percentage units except for 94.7- and 79.2-Pd-I, in which case the change was negligible.

DISCUSSION

As has long been known, there are at least two classes of hydrocarbon species on the surfaces of metal catalysts during catalytic reactions between hydrocarbons and hydrogen at lower temperatures: one kind reacts with hydrogen and desorbs rapidly to give the observed products of the catalytic reaction; the other reacts and desorbs much more slowly. In reactions in the vicinity of 0°C, the more slowly reacting species are liberated in flowing hydrogen at a temperature slightly above the temperature of the catalytic reaction without change in the number of carbon atoms of the reactant, for example, in the hydrogenation of ethylene on Pt/SiO_2 at −31°C (liberated as ethane) and in the hydrogenolysis of cyclopropane at 0°C (liberated as propane) (*20*). In reactions at higher temperatures, fragmented alkane products are liberated in addition but only at $T \simeq 300$°C or above. For example, in isotopic exchange between deuterium and cyclopentane and pentane at 81°C, 90% of the residue is liberated as the original alkane at 100°C but 10% appears as methane at about 300°C (*9*). Presumably, at 50–125°C there is slow formation of those hydrocarbon species which are involved in hydrogenolysis at ~300°C. There was no indication that slowly reacting residues behave as catalytic sites in any of these reactions.

In cyclopentane exchange, the decline in N_t from its initial value was rather small compared to the value of C/Pt_s and the isotopic distribution patterns were independent of time on stream. The catalyst was regenerated by the standard pretreatment during which residues were oxidized to CO_2 (*9*). Similar statements apply to isotopic exchange of neohexane. In particular, after runs at about 100°C on both Pt/SiO_2 and Pd/SiO_2, most of the slowly reacting residues were liberated at 100–200°C as neohexane and methane appeared only at 300°C. The rate of formation of exchanged neohexane was at least 100 times that of the slowly reacting species. We do not know whether the slowly reacting residues consist of special species adsorbed at any point on the surface of the metal or of more common species, for example, a 1,2-diadsorbed alkane, adsorbed on special sites, nor do we know what fraction, if any, of the residue has been transferred to the silica support.

Isotopic Exchange of Neohexane on Pt/SiO_2

Some of the results accord with the expectations presented in the Introduction, but, in general, the expected effects of change in D_h were not found.

In the first category, there is the relatively low value of neohexane-d_5 vs cyclopentane-d_5 as shown near the top of Table 3. The hydrogen atoms on one side of a cyclopentane ring constitute a model for the exchange of five atoms in unhindered positions, because distortion of the isotopic distribution pattern occasioned by the formation of d_6–d_{10} by rollover should be rather small. This low value of neohexane-d_5 is support for the presence of steric hindrance in forming **I** and **III**.

Hindrance to formation of **I** and **III** is also evidenced in the low rate of initial adsorption into the $-CH_2-$ group of $(CH_3)_3C-CH_2-CH_3$. The relative rate of adsorption into the CH_3 of ethyl can hardly be less than that into each CH_3 of t-butyl, but it could be larger. Let us assume that the relative rates are the same. Then, t-bu/et = 1.5 if exchange into $-CH_2-$ is the same as that into CH_3 and 2.0 if that into $-CH_2-$ is 0.5 that into CH_3. From Table 3, t-bu/et = 1.5 for D_h = 6.3–21.5%, 2.0 for 40–63%, and 2.2 for 81%. Thus, as an upper limit, exchange into $-CH_2-$ is as fast as that into CH_3, but exchange into secondary positions is usually much faster than that into primary positions (*22*). Seen in another way,

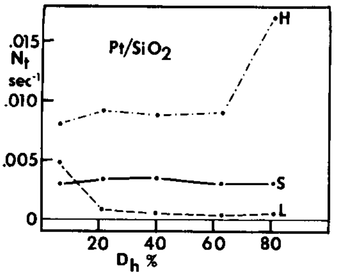


FIG. 3. $N_t \times 10^2$ in sec^{-1} at 100°C vs D_h for Pt/SiO$_2$ after standard pretreatment (solid line, S), H$_2$,450° (doubly dashed line, H), and H$_2$,100° (singly dashed line, L).

at 86.5°C, N_t^0 (turnover frequency after the standard pretreatment) for exchange into the five methylene groups of cyclopentane is 40–80 times larger than that into the single methylene of neohexane (0.16 vs 0.002–003 sec^{-1}) using the assumptions employed above. However, exchange into –CH$_2$– should be relatively favored by an increase in the proportion of edge atoms, i.e., by increasing D_h. The opposite trend was found.

As shown in Fig. 3 and Table 5, N_t^0 for t-amyl was nearly independent of D_h as were the E_a's, all about 70 kJ mol^{-1}. One might have expected the increasing proportion of edge sites of lower hindrance to lead to an increased rate of adsorption at methylene and, thus, to some increase in N_t^0 with increasing D_h. H$_2$,450° led to larger values of N_t with that for D_h = 81% being considerably larger than the others and H$_2$,110° led to much smaller values of N_t except that N_t for 6.3% was 10 times as large as the others. What can cause the differences between the standard pretreatment and H$_2$,450°? If the platinum crystallites were all bound by close-packed planes, if the crystallites were equiaxed, i.e., roughly inscribable in a sphere (*12*), and if surfaces were fully reduced, values of N_t should be determined only by D_h.

As shown in Table 5, rather similar effects of D_h and pretreatment have been noted for isotopic exchange between deuterium and cyclopentane on these same Pt/SiO$_2$ catalysts. Further, similar effects were noted for the hydrogenolysis of methylcyclopropane at 0°C (*8*): after H$_2$,300°, N_t was nearly structure insensitive; after H$_2$,100°, N_t declined considerably with increasing D_h; and after H$_2$,450°, N_t increased considerably with increasing D_h and to an extent greater than that noted in the isotopic exchange of neohexane. Previous discussion of possible effects of pretreatment appears in Refs. (*8, 9*).

TABLE 5

Isotopic Exchange on Pt/SiO$_2$

	Cyclopentane exchange at 81°C			Neohexane exchange at 100°C		
D_h (%)	6.3	40-S	81	6.3	40-S	81
N_t^{0a}	0.14	0.087	0.113	0.030	0.035	0.031
N_t(H$_2$,100°)/N_t^0	2.9	1.0	0.23	1.6	0.14	0.16
N_t(H$_2$,450°)/N_t^0	1.0	0.86	1.35	2.7	2.5	5.5

[a] Turnover frequency in sec^{-1} per Pt$_s$ after the standard pretreatment.

As shown in Table 3 and Figs. 1 and 4, the isotopic distribution patterns usually exhibited maxima at D'_3 and D'_5. On the model for structure sensitivity of the Introduction, D'_5 should increase with increasing D_h since edge atoms would provide sites for adsorption with lower steric hindrance to the formation of **I** and **III**. This is indeed observed for the standard pretreatment as shown in Fig. 4 for the two extreme catalysts of D_h = 6.3 and 81%. However, after H$_2$,450°, the isotopic distributions including

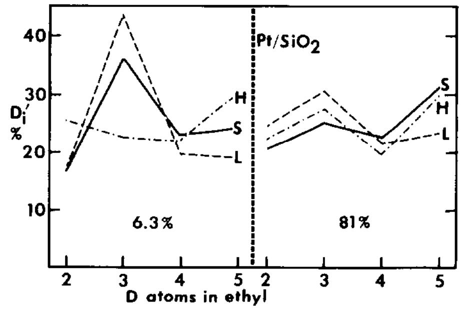


FIG. 4. D_i' vs i in ethyl-d_i at 110°C for 6.3-Pt-PtCl (left) and for 81-Pt-IonX (right) after standard pretreatment (solid line, S), H$_2$,450° (doubly dashed line, H), and H$_2$,100° (singly dashed line, L).

TABLE 6

N_t^0 of Isotopic Exchange; Pd/SiO_2 vs Pt/SiO_2 at 90°C

	t-Amyl[a] (sec^{-1})	$-CH_2-$[b] (sec^{-1})	Cyclopentane[c] (sec^{-1})	E_a[d] (kJ)
40-Pt-S	0.019	0.003	0.19	70
49.8-Pd	0.0010	0.0006	0.10	90

[a] N_t^0 of t-amyl in neohexane.

[b] N_t^0 for adsorption into the methylene group of neohexane, i.e., for reaction (2s).

[c] N_t^0 for exchange of cyclopentane extrapolated from 81°C for 40-Pt-S and from 70°C for 49.8-Pd from Refs. (9) and (23), respectively.

[d] These activation energies are applicable to all three exchanges on all catalysts.

D_1-ethyl were nearly structure insensitive (except for 6.3-Pt-PtCl) and rather like 81-Pt-IonX given the standard pretreatment.

Pd/SiO₂

We consider first the results with Pd-SiO_2-IV and -II. Table 6 and Fig. 2 exhibit some of the differences between the catalytic characteristics of Pd/SiO_2 and Pt/SiO_2.

The rate of exchange of cyclopentane at 90°C is only about 2 times larger on Pt/SiO_2 than on Pd/SiO_2, but that of neohexane is 19 times larger. This difference is primarily associated with the ratio,

(adsorption into CH_3)/(adsorption into CH_2 of cyclopentane),

being considerably larger on platinum. Given that t-bu/et was ~0.5 for Pd/SiO_2, the assumptions used with Pt/SiO_2 lead to a lower limit for the ratio for neohexane,

(adsorption into CH_3)/(adsorption into hindered CH_2),

of ~0.2, whereas the limiting ratio of 40-Pt-S was 2. Initial adsorption into the five methylene groups of cyclopentane is, then, ~160 times faster than that into the methylene group of neohexane. Thus, as with Pt/SiO_2, formation of species I on Pd/SiO_2 appears to involve considerable steric hindrance. However, as exemplified in Fig. 2, D_5-(t-amyl) is much larger for Pd than for Pt. This indicates that r_{-3s}/r_{-3p} is roughly unity and **III** is relatively stable so that r_3/r_{-2} is large. In Pt/SiO_2, r_{-3s}/r_{-3p} is probably large.

As shown in Fig. 5, N_t^0-(t-amyl) at 105°C was about 0.0030 sec^{-1} for all Pd-SiO_2-IV and -II except that it was larger for 79.1-Pd-IV and 96.7-Pd-II, 0.0076 and 0.0085, respectively. For comparison, N_t^0 for cyclopentane at 55°C increased steadily with D_h, from 0.0015 sec^{-1} for 29.3-Pd-IV to 0.0088 for 79.1-Pd-IV (*23*). H_2,100° led to values of N_t about one-third those of N_t^0, but 79.1-Pd-IV and 96.7-Pd-II were relatively more active. H_2,450° led to values of N_t slightly larger than those of N_t^0.

The values of D_i' increased steadily from D_2' to D_5'. For catalysts IV and I, D_5' maximized at D_h = 49.8 as shown in Fig. 5. This was true for all pretreatments. All D_5' were larger after H_2,100°, but after H_2,450° isotopic distributions were very similar to those after the standard pretreatment except that D_5' was low on 13.8- and 49.8-Pd-IV.

Unlike the case of Pt/SiO_2, the standard pretreatment and H_2,450° led to very similar behavior. In general, the effect of pretreatment appears to be larger for Pt/SiO_2 than Pd/SiO_2. It should be noted that one

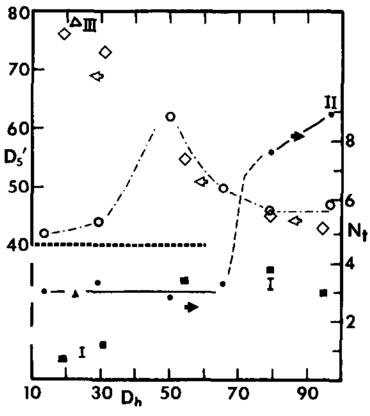


FIG. 5. Isotopic exchange at 105°C on Pd/SiO_2 after the standard pretreatment. D_5' on left axis, open symbols; N_t^0 in $ksec^{-1}$ on right axis, solid symbols; vs D_h on x axis. Circles: Pd-II (extreme right only) and Pd-IV. Squares and diamonds: Pd-I. Triangles: Pd-III.

would not expect to form β-PdH with these catalysts at the temperatures employed (*19*).

H_2,100° and H_2,450° were examined only at 105°C. Consequently there are many fewer data for each catalyst than after the standard pretreatment.

Catalysts I and III suffer from the possible disadvantage that they were reduced in a fixed rather than in a fluidized bed. Thus, the concentration of water could have increased in going through the bed with a consequent accompanying decrease in D_h. It is difficult to see how such nonuniformity could have led 22.5-Pd-III (ex $Pd(acac)_2$) to have exhibited the largest D'_5 of any catalyst. The isotopic distribution for 22.5-Pd-III, but not N_t^0-(t-amyl) or t-bu/et, is incompatible with catalysts IV and II.

The use of a fixed rather than a fluidized bed should not have led to significant nonuniformity in the highly dispersed 94.7-Pd-I and probably not in 79.2-Pd-I. However, all Pd-I were exposed to rather strong base during initial preparation which may have led to redistribution of silica so as to encapsulate Pd crystallites in such a way that some Pd surface was accessible to H_2 but not to neohexane. In addition, 18.8- and 31-Pd-I were heated at 650°C in air and in hydrogen. However, it is difficult to see why 54.5-Pd-I accords with the IV + II series both in N_t^0 and in D'_5, whereas the two Pd-I of larger D_h accord in D'_5 but not in N_t^0 and the lowest two with neither. In sum, whereas one expects on the conventional interpretation of structure sensitivity that D'_5 should increase steadily as D_h increases, the data of Fig. 5 exhibit no accord with such an expectation. Further, catalysts of different preparation but the same D_h have given substantially different results.

The Apparently Anomalous Effect of Percentage Exposed

In sum, there was clearly evident steric hindrance in forming species **I** and **III** on both Pd/SiO_2 and Pt/SiO_2. However, the expected effects of D_h upon D'_5 were not observed. Three explanations could be considered.

(1) The conventional mechanism for isotopic exchange of alkanes is wrong, but even so, could one find a mechanism in which substitution at a neopentyl position was not less hindered at an edge than at an atom in a complete surface plane?

(2) Extractive chemisorption. In a previous study, we found that N_t for hydrogenation of di-t-butylacetylene on platinum catalysts was nearly the same on large and small particles of platinum, and, thus, on the conventional interpretation, one must conclude that the acetylene was adsorbed and underwent hydrogenation on flat (100) or (111) faces. Since adsorption on a flat, closely or nearly closely packed face should be difficult, we suggested tentatively (*4*) that in chemisorption of the acetylene, one or two atoms of platinum were pulled above the initial level of the plane. This would reduce adsorbate–surface hindrance.

(3) Absence of really flat surfaces. We do know that the platinum atoms of the crystallites in 21.5- and 27-Pt-IonX and 40-Pt-PtCl are at correct lattice points in the fcc lattice (*12*), but there is no direct evidence anywhere in the scientific literature that such crystallites are bounded by *complete* (111) or (100) planes. Indeed, there is evidence primarily but not exclusively from field ionization microscopy that surfaces become increasingly defective above room temperature (*24, 25*).

Incomplete (100) or (111) bounding surfaces would provide degrees of steric hindrance which depended upon the steric demands of the reactant molecule and upon the concentration and distribution of the surface vacancies. The X-ray structure of $Pt(bicycloheptene)_3$ shows that the *exo* side of the double bond faces the Pt atom (*26*) just as in bicycloheptene adsorbed on platinum (see Introduction). Here then, even one atom provides substantial steric hindrance and the hydrogenation of bicycloheptene at atoms, at edges, in defective surfaces, and in complete surfaces would probably all lead to the same stereochemical result. On the other hand results with a long nearly linear molecule like *trans*-di-t-butylethylene would probably vary with the nature of the surface imperfections.

Neohexane with but one t-butyl group would probably fall between the above two examples. Two adjacent vacancies or perhaps even one would generate a site for adsorption as species **I** and **III** with about the same degree of hindrance as at edge atoms.

Should the surfaces of supported noble metal catalysts indeed prove to have a substantial concentration of vacancies or other defects which would have behaviors simulating those of edges, then one could expect that different concentrations and pretreatments could lead to different fractions and kinds of defects. This idea in a general sense is, of course, ancient.

Further work to test explanation (3) is desirable because, should it prove to be correct, the basis for investigating structure sensitivity would need to be altered.

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