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Isotopic Exchange between Alkanes and Deuterium on Rhodium/Silica Gel Catalysts

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Isotopic exchange between deuterium and cyclopentane and between pentane and ethane on the Rh/SiO_2 catalysts of the preceeding paper has been investigated after several different pretreatments. Although a more restricted number of catalysts was examined, as with 2,2-dimethylbutane, increased percentage exposed (D_h) appears to lead to increased turnover frequency (N_t). After the standard pretreatment, H_2,300°; He,450°, the rates in alkane(g) $\rightleftharpoons$ alkane(ads) increase only slowly as D_h increases, but the rates in monoadsorbed alkane $\rightleftharpoons$ diadsorbed alkane decline relatively rapidly. As with 2,2-dimethylbutane, the pretreatment H_2,450° leads to the largest values of N_t. He,450° following H_2, 450° removes surface hydrogen atoms and leads to reconstruction to a surface of much lower activity for exchange. Cyclopentane exchanges much faster than pentane on these catalysts. It appears that adsorption and desorption of cyclopentane involve single-step processes to and from diadsorbed cyclopentane + 2H*. Adsorption is faster than that with pentane because cyclopentane is essentially in the eclipsed conformation needed for this process. The rate of monoadsorbed $\rightleftharpoons$ diadsorbed cyclopentane is similarly augmented. Adsorbate-surface strain reduces the rate constant for adsorption of 2,2-dimethylbutane and increases that for desorption. When coverages by the unhindered hydrocarbon are large, the relative rate of exchange of the hindered hydrocarbon vs that of the unhindered hydrocarbon will be larger than one would conclude merely from the relative rate constants of adsorption.

INTRODUCTION

The preceding paper (*1*) was concerned primarily with the influence of percentage exposed and of conditions of pretreatment upon the isotopic exchange of neohexane on a set of Rh/SiO_2 catalysts. This paper adds data on the isotopic exchange of cyclopentane, pentane, and ethane and it considers the mechanism of isotopic exchange of alkanes in terms of these and previous data. It also compares results on the Rh/SiO_2 catalysts with those on Pt/SiO_2 and Pd/SiO_2 catalysts.

EXPERIMENTAL

Procedures

The apparatus and general procedures are given in the preceding paper (*1*). Cyclopentane (Chemical Samples) and pentane (Wiley Organics) were refluxed over sodium–potassium alloy for 1 h and distilled into a storage flask. All operations including storage were effected under argon. Ethane (Matheson grade 99.87%) was used without treatment. The purity of all hydrocarbons exceeded 99.9% as judged by gas chromatography.

Gas phase mixtures of hydrocarbon and deuterium were prepared by use of a saturator thermostated in the case of cyclopentane at 10°C with a slush bath of dodecane to give a saturated vapor pressure of 0.088 bar (8.5%) and in the case of pentane at −21.4°C with NaCl-ice to give a vapor pressure of pentane of 0.087 bar (8.7%). Ethane-D_2 mixtures were fed from a tank to which 0.882 bar of ethane and then deuterium had been added to bring the total pressure to 9.8 bar. The content in ethane was 9.0%. In catalytic

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TABLE 1

Isotopic Exchange of Cyclopentane on 31-SiO_2–Rh_4 and 108-SiO_2–Rh-IonX[a]

T[b]	Treat[c]	N_t[d]	D_1	D_2	D_3	D_4	D_5	D_6	D_7	D_8	D_9	D_{10}
					31-Rh_4							
30	Stand	2.7	20.6	36.4	15.4	10.4	12.9	1.2	1.1	0.7	0.6	0.7
55	Stand	7.5	10.6	25.6	16.0	14.4	22.2	3.3	3.1	1.9	1.4	1.4
75	Stand	13.9	7.4	20.9	14.8	14.5	26.9	4.1	3.6	2.7	2.4	3.0
30	H_2,450°	2.3	40.4	31.2	10.4	6.8	7.4	1.2	0.8	0.7	0.6	0.5
					108-Rh-IonX							
30	Stand	4.6	31.5	32.7	13.8	9.3	7.1	2.5	1.5	0.7	0.5	0.4
30	H_2,450°	11.2	28.2	25.0	15.8	11.6	8.9	4.7	2.8	1.6	0.9	0.5

[a] The data presented are the average of duplicate runs. Masses of catalyst ranged from 0.003 to 0.007 g and flow rates from 20 to 60 cm^3 min^{-1}. Conversions on 31-Rh_4 at 30°C were low enough so that the isotopic distribution patterns listed should be only slightly distorted from those that would be obtained with only one period of adsorption. However, at 75°C and even at 30°C on 108-IonX, conversions were so large the listed D_i's are distorted by multiple periods of adsorption. However, values of N_t would be unaffected by larger conversions.

[b] Temperature of reaction in °C.

[c] Conditions of pretreatment: stand, standard pretreatment, H_2,450° = H_2,450°; cool in H_2.

[d] Turnover frequency in s^{-1} per Rh_s.

runs, samples were collected for analysis at 10 and 50 min on stream.

Experimental Results

Cyclopentane. As shown in Table 1, isotopic exchange of cyclopentane was investigated on two catalysts, 31-Rh_4 and 108-Rh-IonX, and two pretreatments, H_2,450° and H_2,300°;He,450° (the "standard pretreatment"). Rates of exchange were exceptionally fast. Since conversions of cyclopentane at 75°C on 31-Rh_4; standard on any practicable amount of catalyst were so large that undistorted D_i's could not be obtained, runs were also made at 30 and 55°C. E_a was 32 kJ mol^{-1} for formation of exchanged cyclopentane. Uncertainty in E_a was augmented by uncertainty in the weight of the catalyst. Runs were made only at 30°C on 31-Rh_4; H_2,450° and on 108-Rh-IonX. In the runs on 31-Rh_4; standard at 75°C, since $(1 - D_0)$ was about 20%, there was some distortion in the distribution of D_i's. Of the molecules that had exchanged, 10% had undergone two periods of adsorption and exchange. Dilution of the D_2 pool with HD also resulted in distortion. However, it is clear that D_6–D_{10} increases with increasing temperature. Multiple periods of exchange do not affect values of N_t. Even at 30°, runs at low conversion could not be obtained with 108-IonX. In the runs of Table 1 at 30°C on 108-IonX; standard, conversions were about 35% and for H_2,450°, 60%. The D_i's entered in Table 1 for H_2,450° are for a catalyst at 47 min on stream, 56% conversion.

Pentane

Isotopic exchange between pentane and deuterium at 75°C on 31-Rh_4 and 108-Rh-IonX is shown in Table 2. The combination of D_h and pretreatment effects variation in N_t by a factor of 20. At 75°C, reaction on 108-Rh-IonX; H_2,450° was so fast that even with only 0.0029 g of catalyst and flow rates of 66 cm^3 min^{-1} conversions were 45%, N_t = 11.7 s^{-1}. D_i's for the other runs should be relatively undistorted.

Ethane

Table 3 exhibits the results of isotopic exchange between ethane and deuterium. Because of the slowness of exchange of ethane, runs were made at 125°C. However,

TABLE 2

Isotopic Exchange of Pentane at 75°C on 31-SiO_2–Rh_4 and 108-SiO_2–Rh-IonX[a]

Catalyst pretreatment	31-Rh_4 (standard)	31-Rh_4 (H_2,450°,1)	108-Rh-IonX (standard)	108-Rh-IonX (H_2,450°,1[b])	
N_t	0.46	1.24	1.21	11.1	(11.1)
D_1	23.8	40.7	29.8	24.0	(29.2)
D_2	14.9	16.3	17.5	14.8	(15.9)
D_3	10.2	8.9	9.3	10.3	(10.0)
D_4	7.0	6.4	7.8	8.4	(7.9)
D_5	5.0	4.9	5.6	7.1	(6.6)
D_6	4.2	4.2	4.6	6.5	(5.8)
D_7	3.8	3.8	4.0	5.9	(5.1)
D_8	3.4	3.1	3.4	5.3	(4.5)
D_9	3.0	2.5	3.3	4.7	(3.9)
D_{10}	2.6	1.9	2.6	4.5	(3.6)
D_{11}	5.2	2.4	3.8	4.9	(4.0)
D_{12}	17.0	5.0	8.5	3.6	(3.5)

[a] The data are averages of duplicate runs at times on stream of about 11 min. Flow rates varied from 26 to 66 cm^3 min^{-1} and catalyst masses between 0.003 and 0.014 g.

[b] The unparenthesized values are for the run with highest conversion, 57% at 10.5 min on stream. The parenthesized values are for the lowest conversion, 44% at 46 min time on stream. In this run, the highest flow rate was employed and the lowest amount of catalyst, 0.205 μmol Rh. In both runs, the isotopic distributions are distorted by isotopic dilution.

runs were also made at 100 and 75°C for 31-Rh_4;standard. E_a was 75 kJ mol^{-1}. The isotopic distribution pattern was nearly independent of temperature.

DISCUSSION

General Characteristics of Isotopic Exchange

With the exception discussed below, we interpret isotopic exchange primarily on the basis given in the previous paper, reaction among *D, *H, monoadsorbed alkanes, and α,β-diadsorbed alkanes (*1–3*).

$$H_2 + 2* \rightleftharpoons 2H* \tag{1}$$

$$\text{—CH}_2\text{—CH}_2\text{—} + 2* \rightleftharpoons \text{—CH}_2\text{—CH*—} + H* \tag{2}$$

$$\text{—CH}_2\text{—CH*—} + 2* \rightleftharpoons \text{—CH*—CH*—} + H* \tag{3}$$

This mechanism is closely related to the Horiuti–Polanyi mechanism for the hydrogenation of olefins (*3*), which proceeds by

$$\text{—CH=CH—} + 2* \rightarrow \text{—CH*—CH*—} \tag{4}$$

followed by (−3) and (−2) although Eq. (−2) is usually irreversible under hydrogenation conditions. Strong evidence indicates that the *—C bonds in —CH*—CH*— are *cis* and eclipsed (*3*). Some have argued fervently that —CH*—CH* is a π-complex (*4*) and others argued that the geometries of a π-complex and of a di-σ-adsorbed species differ little in geometry, serve equally well to accord with experimental results, and cannot be distinguished by isotopic exchange experiments alone (*3*, *5*). Infrared studies have identified both π- and di-σ-adsorbed ethylene on supported Group VIII metals, but the exact role of the two species in hydrogenation does not yet appear to be established (*6*). Perhaps

TABLE 3

Isotopic Exchange of Ethane on 31-SiO_2–Rh_4 and 108-SiO_2–Rh-IonX[a]

Catalyst	Pretreat	Temp. (°C)	N_t	D_1	D_2	D_3	D_4	D_5	D_6
31-Rh_4	Stand	75	0.0019	20.5	44.1	6.8	4.6	5.1	18.9
31-Rh_4	Stand	100	0.010	23.5	40.0	6.5	3.4	6.2	20.3
31-Rh_4	Stand	125	0.051	21.5	41.3	6.0	3.4	6.8	21.0
31-Rh_4	H_2,450°	125	0.092	35.0	35.3	7.4	4.9	5.8	11.7
108-IonX	Stand	125	0.083	30.5	38.8	6.4	3.8	5.7	14.9
108-IonX	H_2,450°	125	0.87	40.3	32.4	8.4	5.6	5.8	7.6

[a] Average of duplicate runs at times on steam of about 11 min. The flow rates were varied between 10 and 50 cm^3 min^{-1} and the catalyst masses between 0.004 and 0.45 g in order to keep the conversions below 8%. However, one run with 108-IonX; H_2,450° and one with 31-Rh_4; standard at 125°C exceeded 8%, but the averaged D_i's reported should not be seriously distorted.

both are involved. It has been variously proposed that adsorbed π-allyl species are involved in exchange, but such species are impossible in the exchange of neohexane.

Frennet and Gault have proposed a different mechanism for isotopic exchange, one that does not involve simple dissociative adsorption of alkane but proceeds in essence via the steps (*7*)

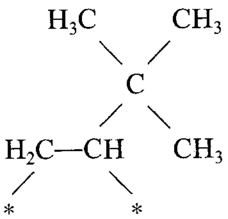
$$RH(g) + H* \rightleftharpoons R* + H_2(g) \quad (5)$$

$$R'CH_2CH_2* + H* \rightleftharpoons R'CH*CH_2* + H_2(g) \quad (6)$$

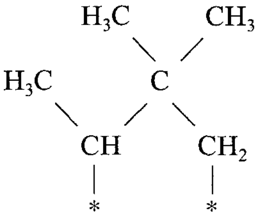
and is related to the Rideal–Eley mechanism for isotopic exchange between H_2 and D_2. Steps rather similar to those in the Frennet mechanism have been proposed to occur in the hydrogenation of olefins on some actinide and zirconium complexes supported on γ-alumina (*8*). However, homogeneous hydrogenations catalyzed by metal complexes of the later transition metals seem to proceed by an analog of the Horiuti–Polanyi mechanism, i.e., via "dissociative adsorption" of H_2 at the metal atom to form H*M*H, insertion of the olefin into an *M*—H bond, and reaction of R—*M*—H to liberate alkane, RH (*9*). Catalysts of Pt group metals might not, then, be the most likely place to find the Frennet mechanism. Further, olefin hydrogenation occurs at the surface of a palladium membrane that is fed with hydrogen from one side and with olefin from the other (*10*). Here, P_{H_2} in the vicinity of the mono- and diadsorbed alkanes is far too low to permit reactions (5) and (6) to occur at significant rates. Also, it is clear that dissociative adsorption of alkanes can occur on platinum group metals (*11*) in the absence of $H_2(g)$. An additional consideration is provided by isotopic exchange between D_2 and (+)-3-methylhexane on Ni/SiO_2 (*12*). Racemization and isotopic exchange paralleled one another and they were inhibited by $H_2(D_2)$ with n in $P_{H_2}^{-n}$ being about 0.6. In an experiment in which the pressure of alkane was constant but that of H_2 had been progressively decreased, P_{H_2} was abruptly reduced to zero. The rate of racemization rose immediately by a substantial factor but then decreased consequent to the formation of carbonaceous deposits. Here clearly, reactions (2) and (3) proceeded under conditions in which P_{H_2} was very low and reaction (−5) must have been very slow. None of these considerations constitutes a general disproof of the Frennet mechanism, but taken together they lead us to continue to use the conventional mechanism.

Exchange of Neohexane

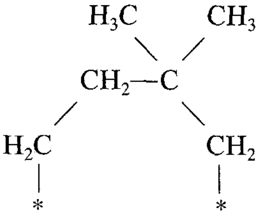
The substantial values of neohexane-d_5 shows that neohexane monoadsorbed in the ethyl group reacts to form α,β-diadsorbed neohexane much faster than it desorbs. At low conversions (% neohexane-d_6)/(% neohexane-d_5) was zero to within experimental error (*1*). It follows that a species monoadsorbed in the ethyl group of neohexane desorbs much more rapidly than it is converted either to an α,γ- or the α,δ diadsorbed form.



α,β-diadsorbed



one α,γ-diadsorbed



α,δ-diadsorbed

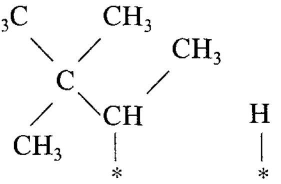
Since (% *t*-butyl-d_2)/(% *t*-butyl-d_1) was small or zero, $*CH_2C(CH_3)_2(C_2H_5)$ reacts with H* to form desorbed neohexane-d_1 much more rapidly than it reacts to form an α,α-, an α,γ-, or an α,δ-diadsorbed species. Presumably the rate of formation of an α,α-diadsorbed species is nonzero, but since *t*-butyl-d_1 was small we can say only that *t*-butyl-d_2/*t*-butyl-d_1 was small. Similar results with rhodium catalysts have been reported in the past (*3, 13, 14*).

However, on a 1% Rh/SiO$_2$;H$_2$,400°,1; vac.,400°, 0.5 at 120°C and 15% conversion, the *t*-butyl carbenium ion from exchanged neopentane had D_1 = 67%, D_2 = 14.1%, D_3 = 9.3%, D_4 = 3.4%, D_5 = 1.7%, D_6 = 1.3%, and D_7, D_8, and D_9 = 1.0% each (*15*). The very low values of D_6 in the *t*-amyl carbenium ions from exchanged neohexane (*1*) might appear to be incompatible with the results of Ref. (*15*), but the temperature of catalytic runs with neohexane was 50°C lower and pressures about 10 times larger than those with neopentane. Alternatively, the Rh/SiO$_2$ of Ref. (*15*) may have had sites that lead either to a different mechanism of exchange or to relatively rapid interconversion between monoadsorbed and α,γ-diadsorbed species.

On the basis of the discussion above, isotopic exchange between deuterium and neohexane would, in general, involve the following reactions.

$$D_2 + 2* \rightleftharpoons 2D* \tag{7}$$

t—bu—CH$_2$—CH$_3$(g) + 2* ⇌



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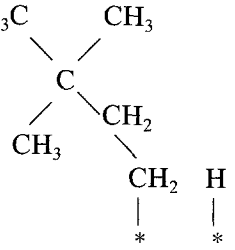
I

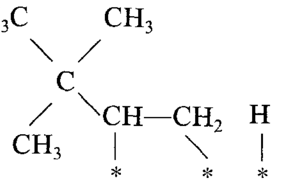
t—bu—CH$_2$—CH$_3$(g) + 2* ⇌



(8p)

II

t—bu—CH$_2$—CH$_2$* + 2* ⇌



(9s)

III

TABLE 4

Rates of Isotopic Exchange of Neohexane and Cyclopentane after the Standard Pretreatment[a]

	T (°C)	Rh/SiO$_2$	Pd/SiO$_2$	Pt/SiO$_2$
t-bu/et in neohexane	75	0.05–0.14[b]	~0.6[b,c]	~1.9[b,d]
N_t^0 (neohexane) (s^{-1})	75	0.09 ± 0.05[b]	~0.0003[b,e]	~0.008[b]
N_t^0 (cyclopentane) (s^{-1})	55	7.2[e]	0.004[f,g]	0.015[b]

[a] From this paper, Ref. (*16*) and V. Eskinazi (*40*), except cyclopentane on Pd/SiO$_2$ and Pt/SiO$_2$ are from Pitchai *et al.* (*41*).

[b] For 30% < D_h < 70%.

[c] Value at 105°C.

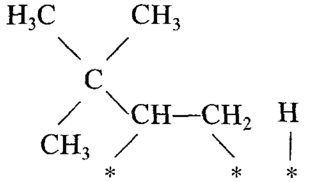
[d] Value at 86.5–110°C.

[e] For 31-Rh/SiO$_2$.

[f] For D_h ~ 50%.

[g] N_t^0 for cyclopentane at 75°C extrapolated from 55°C was 0.010 s^{-1}.

t—bu—CH*—CH$_3$ + 2* ⇌



(9p)

III

where here H* represents H* or D* as appropriate. The very small ratio t-bu/et (Table 4) shows that on Rh/SiO$_2$ the rate ratio, (adsorption into the t-butyl group)/(adsorption into the ethyl group) is small. Because of less steric hindrance adsorption into the methyl group of ethyl (—CH$_2$**CH$_3$**) is likely to be faster than into a methyl group of t-butyl.

At steady state on a set of uniform sites, the rate of exchange, r_{ex}, would be given by that of either reaction (8s) or reaction (−8s),

$$r_{ex} = k_{g\to I}\theta_*^2 P = k_{I\to g}\theta_I\theta_H, \quad (10)$$

where $k_{g\to I}$ is the rate constant in dissociative adsorption to form **I**, P is the pressure of neohexane in the gas phase, and θ_*, θ_I, θ_H are the fractions of sites that are vacant and are **I** and *H, respectively. It is assumed that reactions (8s) and (8p) parallel one another.

The ratio of rates on equal numbers of face and edge sites is given by

$$r_f/r_e = (k_{g\to I}\theta_*^2)_{face}/(k_{g\to I}\theta_*^2)_{edge}. \quad (11)$$

Because of the reduced adsorbate-surface strain with edge sites and their greater coordinative unsaturation, $k_{g\to I}$ will be larger on edge than on face sites, but for the same reason, $k_{I\to g}$ will be larger on face sites.

When θ_* is near unity,

$$r_f/r_e = (k_{g\to I})_{face}/(k_{g\to I})_{edge}$$

depends only upon the rate constant ratio. However, when θ_* is small and edge sites are nearly completely covered by hydrocarbon residues that react slowly by Eq. (−2), exchange at the unhindered edge sites can become slower than at hindered face sites. An intermediate situation could exist in which r_f/r_e is unity because $(k_{g\to I})_{face}/(k_{g\to I})_{edge}$ just cancels $(\theta_*^2)_f/(\theta_*^2)_e$. Since experimentally N_t^0 is larger at large D_h, one would conclude that N_t^0 is larger at edge sites and that the $k_{g\to I}$ term in $k_{g\to I}\theta_*^2$ dominates. However, since after H$_2$,450°, N_t's for 11-, 31-, and 108-Rh/SiO$_2$ are 0.0096, 0.61, and 3.3 s^{-1}, respectively, the edge site/face site ratio would have to be much larger after H$_2$,450° than after H$_2$,300°; He,450° if one were to ascribe the entire augmentation of rate to the edge/face ratio. This matter was previously analyzed on the basis of $k_{g\to I}$ alone (*16*), but properly the θ_* term should be considered.

Formation of neohexane-d_5 requires that the rates of (9s), (−9s), (9p), and (−9p) all be significant. D_1/D_5 is determined by the ratio $r_{\mathrm{I}\rightarrow\mathrm{g}}/r_{\mathrm{I}\rightarrow\mathrm{III}} = r_{\mathrm{ex}}/r_{\mathrm{I}\rightarrow\mathrm{III}}$. When $r_{\mathrm{I}\rightarrow\mathrm{g}}/r_{\mathrm{I}\rightarrow\mathrm{III}}$ is large, D_1/D_5 is large. Recalling that $r_{\mathrm{I}\rightarrow\mathrm{g}} = r_{\mathrm{g}\rightarrow\mathrm{I}}$ and $r_{\mathrm{I}\rightarrow\mathrm{III}} = r_{\mathrm{III}\rightarrow\mathrm{I}}$ and assuming that $r_{\mathrm{III}\rightarrow\mathrm{II}}$ and $r_{\mathrm{III}\rightarrow\mathrm{I}}$ parallel one another, one finds that

$$\begin{aligned} r_{\mathrm{I}\rightarrow\mathrm{g}}/r_{\mathrm{I}\rightarrow\mathrm{III}} &= [k_{\mathrm{g}\rightarrow\mathrm{I}}/k_{\mathrm{I}\rightarrow\mathrm{III}}][(\theta_*{}^2P)/(\theta_*{}^2\theta_{\mathrm{I}})] \\ &= [k_{\mathrm{g}\rightarrow\mathrm{I}}/k_{\mathrm{I}\rightarrow\mathrm{III}}][P/\theta_{\mathrm{I}}]. \quad (12) \end{aligned}$$

Since the coordinative unsaturation of the sites (the asterisks) in Eq. (9b) increases in going from face to edge sites, $k_{\mathrm{g}\rightarrow\mathrm{I}}$, $k_{\mathrm{I}\rightarrow\mathrm{III}}$, and θ_{I} in the rightmost expression in Eq. (12) all increase in going from face to edge sites. The increase in θ_{I} will result from augmentation of $-\Delta H$ of reaction (9b) consequent to an increase in coordinative unsaturation and a decrease in steric hindrance. Thus, the simple model above cannot provide a qualitative prediction as to the effect of edge vs face sites upon the D_i's. Experimentally, $r_{\mathrm{I}\rightarrow\mathrm{g}}/r_{\mathrm{I}\rightarrow\mathrm{III}}$ increases as D_{h} increases, as the average particle diameter decreases, or, on the usual assumption, as the edge/face ratio increases. Thus, under the conditions investigated here, $k_{\mathrm{g}\rightarrow\mathrm{I}}$ dominates over $k_{\mathrm{I}\rightarrow\mathrm{III}}\theta_{\mathrm{I}}$.

The elementary steps in Eqs. (8) have been expressed as proceeding from the gas phase directly to the adsorbed phase. However, the van der Waals adsorbed phase may well be intermediate (*17*). If this were the case, no significant changes would be necessary in the treatment given above.

Although lumped with $r_{\mathrm{I}\rightarrow\mathrm{III}}$ above, the term, $r_{\mathrm{II}\rightarrow\mathrm{III}}$, is always significant since D_5 is always finite. If $r_{\mathrm{III}\rightarrow\mathrm{II}}$ were zero, exchange in one period of adsorption (i.e., at low conversions) would be limited to neohexane-d_4, *t*-bu-$CHDCD_3$, a situation seen in none of the isotopic distribution patterns. Similarly, if $r_{\mathrm{III}\rightarrow\mathrm{I}}$ were zero, exchange would be limited to *t*-bu-CD_2CH_2D. Although the general trend of increase in D_1/D_5 with increasing D_{h} and rough equality in $r_{\mathrm{III}\rightarrow\mathrm{II}}$ and $r_{\mathrm{III}\rightarrow\mathrm{I}}$ is clear, it would not be easy to interpret the isotopic distribution patterns in fine detail since the surfaces of the catalyst must contain more than one kind of site.

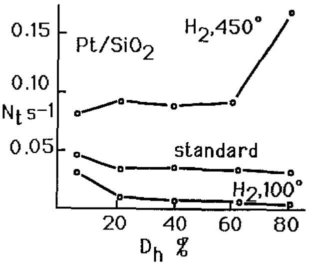


FIG. 1. Rates of exchange between deuterium and neohexane on Pt/SiO_2 at 100°C (*16*), turnover frequency vs percentage exposed after the three pretreatments, H_2,450° (upper line), He,300°; He,450° (middle line), and H_2,100° (lowest line).

Comparison with Pt/SiO₂ and Pd/SiO₂. As noted above (Table 4), *t*-bu/et is very small on Rh/SiO_2 (*1*), considerably smaller, in fact, than on Pt/SiO_2 and Pd/SiO_2 (*16*). The isotopic exchange of neohexane is more sensitive to the effects of particle size and pretreatment on Rh/SiO_2 than on Pd/SiO_2 and Pt/SiO_2. As shown in Fig. 1, N_{t}^0 for Pt/SiO_2;H_2,300°;He,450° is nearly independent of D_{h} and of whether the catalyst was prepared by impregnation with H_2PtCl_4 or by ion exchange with $Pt(NH_4)_4^{2+}$. In most cases at 100°C, $N_{\mathrm{t}}(H_2, 450°)/N_{\mathrm{t}}^0$ was ~3 and $N_{\mathrm{t}}(H_2, 100°)/N_{\mathrm{t}}^0$ was $\sim\frac{1}{6}$. However, after H_2,450°, $D_{\mathrm{h}} = 81\%$, and after H_2,100°, $D_{\mathrm{h}} = 6.3\%$, N_{t} was anomalously large.

D_1-ethyl is measured by D_1-$(CH_3)_2C(C_2H_5)^+ - \frac{2}{3}D_1$-$(CH_3)_3C^+$. With Pt/SiO_2, the large value of D_1-*t*-bu/D_1-ethyl causes the calculation of D_1-ethyl to be attended by rather large errors. After H_2,300°; He, 450° or H_2,100°, D_1-ethyl was about 23 ± 10% for the smallest values of D_{h} and 43 ± 10% for the largest where the ±10% is the possible error. In consequence, values of D_1-et were usually omitted. The isotopic distribution patterns were all characterized by a maximum at D_3. The distribution I in Fig. 2 was that with the largest value of D_3,

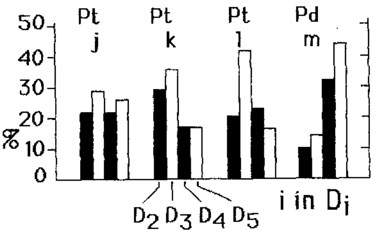


FIG. 2. Isotopic distribution patterns for single runs at about 9 min time on stream for the exchange of neohexane on Pt/SiO_2 at 100°C and on Pd/SiO_2 at 105°C (*16*). Run **j** is on 40-PtCl; H_2,300°; He,450°, $N_t = 0.035$ s^{-1}. Run **k** is on 40-PtCl; H_2,100°, $N_t = 0.005$ s^{-1}. Run **l** is on 6.3-PtCl; H_2,100°, $N_t = 0.048$ s^{-1}. Run **m** is on 29.3-Pd-IV;H_2,300°,He,450°, $N_t = 0.0033$ s^{-1}.

whereas **j** represents one with one of the smaller values of D_3. In general, variation in the isotopic distribution patterns was not large.

The Pd/SiO_2 catalysts were prepared by ion exchange with $Pd(NH_3)_4^{2+}$. Since *t*-bu/et was about 0.5, D_1-ethyl was not usually given. Plots of N_t vs D_h paralleled one another after all three pretreatments except for the low value for 96.7-Pd/SiO_2;H_2,450° (Fig. 3). N_t's were nearly the same for 13.8-, 29.3-, 49.8-, and 65.5-Pd/SiO_2 but 2.5–3 times larger for D_h = 79.1 and 96.7%. N_t's were nearly the same for H_2,300°; He,450 and H_2,450° but N_t was only one-third as large for H_2,100°. The isotopic distribution patterns were all of Type C as exemplified by **m**, 29.3-Pd–SiO_2, in Fig. 2. No anomalies at D_3 were detected in any run. After all pretreatments D_5 was larger for 49.8 and 65.5% than for the others and at all values of D_h, D_5 was a little larger after H_2, 100° and a little smaller after H_2,450° than after H_2,300°;He,450°. After H_2,300°; He,450° a catalyst prepared from Pd(acetylacetonate)$_2$, D_h = 22.5, exhibited about the same N_t as 29.5-Pd/SiO_2, but the value of D_1/D_5 was the smallest of any, 3/78, vs 5/62 for 49.8-$PdSiO_2$.

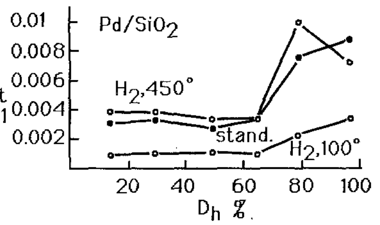


FIG. 3. Rates of exchange between deuterium and neohexane on Pd/SiO_2 at 105°C (*16*), turnover frequency vs percentage exposed after three pretreatments, H_2,450° (upper line), He,300°; He,450° (middle line), and H_2,100° (lowest line).

Exchange of cyclopentane, pentane, and ethane

Previous work had shown that (i) The exchange of cyclopentane is much faster on Rh than on Pt and that D_6–D_{10} on Rh is relatively small (*13*); (ii) on Rh the rate of dissociative adsorption of an acyclic alkane at a secondary position is much greater than at a primary position (*18*); and (iii) adsorption at a secondary position is much less dominant on Pt and Pd (*18*).

The increase in N_t^0 on Rh/SiO_2 by a factor of 230 in the sequence ethane, neohexane, pentane (Table 5) accords with item (ii). The small value of *t*-bu/et for Rh/SiO_2, ~0.08 (Table 4), indicates that the rate ratio (8p)/(8s) is small and this also accords with item (ii). The much larger values of *t*-bu/et on $PdSiO_2$ and Pt/SiO_2 accord with item (iii). However, per C–H, reaction (8s) is faster than (8p) on all three metals. The data in Table 4 accord with item (i). In addition, compared with Pt/SiO_2, N_t^0 (cyclopentane)/N^0 (neohexane) on Rh/SiO_2 was anomalously large. Thus, on 31-Rh/SiO_2, standard pretreatment, 75°C, cyclopentane exchanged 30 times faster than pentane and 140 times faster than neohexane (Table 5). On 40-Pt/SiO_2 at 81°C, cyclopentane exchanged only about 10 times faster than neohexane but about 23 times faster than the ethyl group of neohexane (*16*). On 29.8-Pd/SiO_2 at 90°C, cyclopentane exchange was about 48 times faster than that of the ethyl group of neohexane.

Replacing *t*-butyl with *n*-butyl in reactions (8) and (9) permits alternation among

TABLE 5

Rates of Isotopic Exchange of Various Hydrocarbons

Hydrocarbon	N_t^0/N_t^0(neohex) on 31-Rh/SiO$_2$, 75°C[a]	N_t(Rh/SiO$_2$)/N_t(Pt/SiO$_2$)
CH_4	—	0.2 (190°C)[b]
C_2H_6	0.02	—
C_3H_8	—	20 (38°C)[b]
n-C_4H_{10}	—	33 (38°C)[b]
Neopentane	—	0.61 (50°C)[b]
Neohexane	(1.0)	10 (86.5°C)[c]
Pentane	4.6	—
Cyclopentane	140	580 (55°C)[d]

[a] Standard pretreatment.

[b] 0.1 mmol metal per g of SiO$_2$. Pretreatment: H$_2$,400°,1; vac.,400°,0.5. The parenthetical figures give the reaction temperatures. From Ref. (*18*).

[c] N_t^0(Rh)/N_t^0(Pt), medium values of D_h for Rh/SiO$_2$ and Pt/SiO$_2$ from Ref. (*16*).

[d] N_t^0(Rh)/N_t^0(Pt). 31-Rh/SiO$_2$ and an average at medium values of D_h for Pt/SiO$_2$ from Ref. (*32*). Because of the large difference in E_a between the two catalysts (32 and 71 kcal mol^{-1}, respectively), this ratio changes rather rapidly with temperature; at 75°C the ratio would be 240.

mono- and diadsorbed species, which leads to migration of the position of adsorption along the carbon chain and, thus, to exchange of all hydrogen atoms. Since $D_{12} > D_{11} > D_{10}$ in exchanged pentane (Table 2), there is a process (process A) in which $r_{-1} \gg r_{-3} \gg r_{-2}$ (where 1, 2, and 3 refer to the equations at the beginning of the Discussion); that is, $D*/H* \gg 1$ and alternation between mono- and diadsorbed is fast vs associative desorption (*2, 3*). However, most of the exchange results from process B in which $r_3/r_{-2} \approx 1$ and $r_{-1}/r_2 \gg 1$, or alternatively r_3/r_{-2}, could be larger if r_{-1}/r_2 is relatively small, that is, if, for example, $D*/H* \approx 1$.

Isotopic distributions resembling those in Table 2 are common on Rh, Pt, Pd, and Ni and it has long been considered that such U-shaped distributions result from the presence of two or more different sites with different values of r_1, r_2, and r_3 (*19, 20*). However, Hegarty and Rooney have recently proposed that the U-shaped distribution results from the following scheme exemplified by ethane (*21*).

$$\begin{tikzcd}
 & C_2H_6(g) \arrow[d, shift left, "a"] & \\
\mathbf{X} & CH_3{-}CH_2{*} \arrow[u, shift left] \arrow[r, shift left, "b"] \arrow[d, "c"] & CH_2{*}{-}CH_2{*} \arrow[l, shift left] \\
\mathbf{Y} & CH_3{-}CH_2{*} \arrow[r, shift left, "d"] \arrow[d, "e"] & CH_2{*}{-}CH_2{*} \arrow[l, shift left] \\
 & C_2H_6(g) &
\end{tikzcd}$$

Here, **X** and **Y** are different sets of sites between which $CH_3{-}CH_2{-}$ can transfer by step (c). A U-shaped distribution (large D_1 and D_6, small D_2 D_3, D_4, and D_5) results from the following assumptions: step (b) is relatively slow so that CH_3CH_2* on **X** is but slightly exchanged whereas step (d) is relatively fast so that CH_3CH_2* on **Y** is heavily exchanged; and *steps (c) and (e) are essentially irreversible; i.e., exchanged ethane desorbs from sites **Y** but ethane does not adsorb on these sites, ethyl moves from sites **X** to sites **Y** but not from **Y** to **X**.*

The italicized phrases above violate the principle of microscopic reversibility as may readily be seen by the following. Let C_2H_6 + H_2 pass over the catalyst. The gas phase will come to equilibrium with respect to the adsorbates and the rates of the forward and reverse reactions will become equal in each step including (c) and (e). Now replace H_2 by D_2. Steps (e) and (−e) will continue to be equal. Mere replacement of H_2 by D_2 cannot change the rate of adsorption of ethane on sites **Y**, small kinetic isotope effects excepted. Furthermore, steps (c) and (−c) will remain unchanged and equal. Ordinarily, the principle of microscopic reversibility applies exactly only at chemical equilibrium, and the detailed mechanism of reaction between O_2 and CH_4 at very low conversion may not be the same as at very high conversions. An advantage of isotopic exchange experiments and isotopic tracing in general is that the involvement of an isotopic species does not alter the basic mechanism. Thus, the mechanism of Hegarty and Rooney in its present form must be rejected.

The isotopic distribution pattern of cyclopentane is unusual in that D_2 is anomalously large, in most case larger than D_1. We associate these anomalies with the fact that most of the *cis*-α,β pairs of hydrogen atom in cyclopentane are in eclipsed conformations. In pentane the fraction is very small since the enthalpy of such a conformation is at least 3.4 kcal mol^{-1} above that of the staggered (*22*). The prevalence of *cis*-eclipsed conformations in cyclopentane may potentiate the concerted adsorption of cyclopentane as 2H* (or conceivably, adsorbed H_2) plus diadsorbed cyclopentane as a reaction faster than simple dissociative adsorption, reaction (2).

$$\text{—CH}_2\text{—CH}_2\text{— } + 4* \rightarrow \text{—*CH—*CH— } + 2\text{H}* \text{ or } \text{H}_2* \quad (13)$$

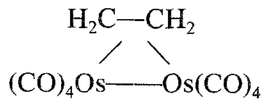
or

$$\text{—CH}_2\text{—CH}_2\text{— } + 3* \rightarrow \pi\text{—(—CH=CH—)}* + 2\text{H}* \text{ or } \text{H}_2* \quad (14)$$

The transition state in (13) or (14) would be stabilized by some contribution from ethylene, a contribution not available in reaction (2). If adsorption occurs by Eqs. (13) or (14), desorption must occur by the reverse to generate cyclopentane-d_2. By similar arguments, the rate of step (3) should also be much faster with cyclopentane than pentane since only those monoadsorbed species with —*CH—CH_2— in eclipsed conformations can react directly. The rates of both Eqs. (3) and (13) must be similarly augmented if the usual shape of an isotopic distribution pattern is to result. As before, two types of sites would be needed.

The requirement of four empty sites in Eq. (13) is large and would lead to different kinetics for the exchange of pentane and cyclopentane, but (13) with H_2* would be less demanding. An alternative less concerted mechanism would involve adsorption by Eq. (2) in which cyclopentane exchanged faster than pentane because the transition state for cyclopentane would involve some release of eclipsing enthalpy which would not occur with pentane. Therefore, a lower activation energy would result although one may doubt that it would be low enough to make the exchange of cyclopentane so much faster than that of pentane.

Adsorption of cyclopentane on Pt(111) (*23*) at 90 K forms an agostic-like bond-softened species. At 200 K, some desorbs and some (20%) reacts to form di-σ-adsorbed cyclopentane as in Eq. (13), perhaps in a concerted process, although there is no proof that the reaction does not proceed via a monoadsorbed cyclopentane. C_2–C_6 alkanes adsorbed on Pt(111) exhibit no detectable bond softening (*24*). Adsorbed cyclohexane also exhibits bond softening on Pd(111), Pd(110), Pt(111), and Ru(001) and reacts to form adsorbed benzene at 200–300 K without desorbing (*25*). It has been shown that ethylene dissociates from the di-σ bound species



in a concerted step (*26*). This process has some resemblance to that in Eq. (13).

If initial adsorption of cyclopentene occurs by step (13) and if as usual D*/H* is large, D_1 would be zero. In fact, D_1 is large. The following model accords with these rate and selectivity results.

Cyclopentane. A process S (analogous to process B) is needed in which D*/H* is in the vicinity of unity and r_3/r_{-13} is somewhat larger than unity. Most of the exchange occurs by this process although its proportion decreases with increasing temperature. Since isotopic exchange of cyclopentane is so fast, the occurrence of such a relatively low value of D*/H* on some sites is not unreasonable although it is probably rare in acyclic alkanes. In this interpretation, at least two hydrogen atoms in cyclopentane-d_1 have actually been exchanged but, because of the low value of D*/H*, only one atom of D has been substituted. In addition, process S is needed to give a maximum at D_5, i.e., $r_{-1} \gg r_{-3} \gg r_{-13}$. Formation of substantial amounts of d_5 via only mono- and diadsorbed cyclopentane requires a large value of D*/H* (*2, 3*). For example, even if D*/H* were 9.0, only 59% of the molecules in which five positions had been equilibrated with the D/H pool would be d_5. A further process is required that will generate d_6–d_{10} (*3*).

The presence of a maximum at D_2 in cyclopentane exchanged on rhodium catalysts has been noted before and involvement of a reaction like Eq. (13) was suggested (*5, 14*), but the role of eclipsing energy and of the identity in rates of adsorption and desorption were not elaborated. In addition, the direct, one-step reaction,

$$\text{alkane} + 4* \rightarrow \text{allyl}* + 3\text{H}*$$

has been proposed for isotopic exchange of propane on Ni/Al_2O_3 on the basis of fitting to isotopic distribution data assuming a uniform set of sites (*27*). Desorption would necessarily go by the reverse of this reaction. The entropy of activation needed for reaction (−13) would be negative enough to be somewhat worrisome but that for the reaction involving allyl* + 3H* would be even more unfavorable.

There are particularly strong interrelations between the present paper and that of Cogen and Maier (*14*) which deal with the exchange of hexane and some other hydrocarbons on metallic rhodium and Rh/Al_2O_3–Cl prepared from $RhCl_3$. In both investigations, increased D_h led to a lesser proportion of multiple exchange. They report the important finding that the two atoms of deuterium in hexane-d_2 are in α,β positions. Some differences between the two papers, however, need to be mentioned. Unlike Cogen and Maier we find maxima at D_5 in neohexane exchanged on Rh/SiO_2 with $D_h < 40\%$. Thus, α,β-diadsorbed alkane is formed readily. In general our data provide no compelling evidence for participation of the π-allylic intermediate favored by Cogen and Maier for other hydrocarbons. We doubt the utility of considering the initial adsorption of hydrocarbon as the rate-determining step since one could as well consider the rate-determining step to be desorption. In fact we doubt the utility of talking about a rate-determining step in this reaction.

Cogen and Maier pretreated their catalysts in H_2 for 4 h at 120°C, a temperature that we did not test. However, 100°C, which we did test, might be expected to give fairly similar results. Except for our Rh/SiO_2 catalyst with the lowest D_h (11%), H_2,100° led to low N_t; see Fig. 3 and Table 4 of Ref. (*1*). N_t for the exchange of neohexane on 31-Rh/SiO_2; H_2,120°, 4 at 75°C would be $>0.02\ s^{-1}$ (Fig. 3 of Ref. (*1*)). N_t for pentane would be four to five times larger or $>0.1\ s^{-1}$. For the exchange of hexane at the same D_h, Cogen and Maier report 0.0025 at 60°C and 0.014 s^{-1} at 120°C. Their hydrocarbons were subjected to no purification and it is likely that their runs were subject to considerable poisoning. In addition, as they noted, their H_2 and D_2 probably contained some O_2 to which they ascribed the relatively rapid deactivation of the catalyst that occurred at 0°C in the absence of hydrocarbon. However, as did we, they observed that the isotopic distribution patterns were unaltered by deactivation. In our work, the treatment H_2,100° was anomalous in that rates were much smaller than after treatment with H_2 at 350 and 450°C (for example, with 108-Rh/SiO_2, smaller by a factor of over 200 vs H_2, 450°) except for 11-Rh/SiO_2. Values of N_t for the exchange of hexane reported by Cogen and Maier declined rapidly with D_h. In our work, this was also true for Rh/SiO_2 after H_2,100° although the degree of decline was smaller, but, after the other pretreatments, N_t increased with D_h.

Ethane. As shown in Table 5, N_t^0 of pentane on 31-Rh_4 is 250 times that of ethane. This large difference is assigned to the small value of r_2 for methyl groups on Rh/SiO_2. Slow reaction of ethane is general on Group VIII metals. However, like the more rapidly exchanging cyclopentane, D_2 after the standard pretreatment is large for ethane and larger even than D_1. Probably then, the very low value of r_2 with ethane results in r_{13} being faster than r_2. Consequently, the D_i pattern resembles that of cyclopentane.

Effects of Particle Size and Conditions of Pretreatment

In the exchange of neohexane after the standard pretreatment, small D_h tends to favor process A (extensive multiple exchange), high D_h favors process B (restricted multiple exchange), and intermediate D_h leads to a mixture of A and B (*1*). Similar effects appear in the exchange of the other alkanes as shown in Tables 1, 2, and 3 but differences among patterns are smaller than with neohexane. Larger crystallites of Rh have previously been reported relatively to favor process A (*13*). H_2,450° leads to a considerably higher proportion of process B than does the standard pretreatment with all hydrocarbons of this paper.

TABLE 6

N_t in s^{-1} for Isotopic Exchange of Alkanes

Catalyst	Stand. Pretreat.	H_2,450°
	Neohexane at 75°C	
N_t(31-Rh_4)	0.10	0.61
N_t(108)/N_t(31)[a]	2.4	5.4
	Cyclopentane at 30°C	
31-Rh_4	2.7	2.3
N_t(108)/N_t(31)[a]	1.7	4.9
	Pentane at 75°C	
31-Rh_4	0.46	1.24
N_t(108)/N_t(31)[a]	2.6	9.0
	Ethane at 125°C	
31-Rh_4	0.051	0.092
N_t(108)/N_t(31)[a]	1.6	9.5

[a] Ratio of turnover frequencies for catalysts 108-IonX and 31-Rh_4 after the standard pretreatment and after H_2,450°.

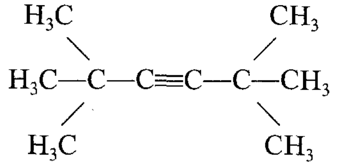
If the initial product of adsorption is monoadsorbed alkane (Eq. (2)), r_{ex} for pentane and neohexane would be given by Eq. (10), but if the initial product is diadsorbed alkane (Eq. (13)) as with cyclopentane, r_{ex} is given by

$$r_{ex} = k_{g\rightarrow \mathbf{III}} P\theta *^4 = k_{\mathbf{III}\rightarrow g}\theta_{\mathbf{III}}\theta_H^2 \qquad (15)$$

One might, then, expect that variation in D_h and pretreatment would lead to considerable variation in the ratio N_t(108-IonX)/N_t(31-Rh_4) for the three alkanes. Such a comparison is provided in Table 6. In fact, variation in the ratio after the standard pretreatment, although definite, is rather small. Variation in the ratio after H_2,450° is also rather small, but larger than after the standard pretreatment. If, as appears likely, each catalyst contains multiple sets of sites of different activity, it will be difficult to interpret these ratios quantitatively.

Origin of Structure Sensitivity

In competitive hydrogenation in the liquid phase on a set of Pt/SiO_2 catalysts (*28*), cyclopentene was favored over the hindered acetylene,



but was heavily disfavored vs the unhindered diethylacetylene. Further, the competitive rates of cyclopentene/di-*t*-butylacetylene hydrogenation increased substantially with increasing particle size (decreasing D_h). The approach of the triple bond of di-*t*-butylacetylene to flat (111) and (100) planes of cubic close-packed metals and thus adsorption on these faces should be highly hindered. However, adsorption at edge atoms should be much less hindered. Thus, on the view that the metallic crystallites of supported metal catalysts are bounded only by (111) and (100) planes (*29*), di-*t*-butylacetylene should be increasingly disfavored competitively as particle size increases as was indeed observed. However, surprisingly, the rate of hydrogenation of dimethylacetylene alone was almost independent of D_h. What can compensate for the expected increase in the edge/face ratio as D_h increases? Roughness of the surface planes in larger crystals and extractive chemisorption of the acetylene (raising the metal atom(s) to which the acetylene is bound above the plane of the metal surface) may be possibilities (*16, 28*). However, the rate of hydrogenation of di-*t*-butylacetylene may well be equal simply to the rate of adsorption of H_2 at gaps in the hydrocarbon layer (rate proportional to $P_{H_2}^1 P_{acet}^0$) (*30*) and the concentration of gaps may be approximately the same on all surfaces.

In the isotopic exchange of alkane, reactions (1) and (−1) are ordinarily fast and the rate of exchange is not that of the rate of adsorption of H_2. The origin of the relatively small variation in N_t^0(neohexane) with D_h must be different. The explanation for this at the beginning of the section, Exchange of Neohexane, can at least partly explain why pentane containing three methylene groups exchanges only about four times faster than neohexane (Table 5).

Mention has been made (Ref. (*38*) of Ref. (*1*)) of the possibility that interaction between surface silanol groups and metal sites might affect exchange on smaller metal crystallites. However, effects of surface morphology on catalytic behavior are probably more common.

The proposal that the surfaces of metal particles in supported catalysts are bounded only by low index planes like (111) and (100) (*29*) is unlikely always to be true (*28, 31*) and some surfaces must be rough. For example, the effect of pretreatment upon 11-Rh_6 was different from the other catalysts. O_2,300°; H_2,100° led to a rate of exchange larger than that of the standard pretreatment (Table 4 of (*1*)), whereas it was smaller on other catalysts. A similar phenomenon was observed in the Pt/SiO_2 set of catalysts (*32*). H_2,100° in reducing the oxide overlayer on the catalyst particles of 6.3-Pt-SiO_2 generated a larger surface area than the standard pretreatment. Heating Pt/SiO_2;H_2,100° to 450°C in Ar reduced the area to a normal value. Probably, then, H_2,100° also leads to an enhanced and rougher surface in 11-Rh_6 but not in Rh/SiO_2 of larger D_h. In addition, on 11-Rh_6, $N_t^{H_2,450°}/N_t^0$ was 0.25, whereas the ratio was 5.8 on 31-Rh_4 and 10 on 108-IonX. Since smooth, densely packed faces are unlikely to be the origin of the very high activities of catalysts treated H_2,450° (Table 6), it appears that H_2,450° smooths the surface of 11-Rh_6 but that it roughens or produces special morphologies on the surface of smaller particles.

Occurrence of reconstruction as a consequence of the gas environment is well attested (*33*), although available data permit few generalizations. On the basis of IR spectra of adsorbed NO, exposure of Pt/SiO_2 to H_2 at 400°C was reported to result in smoothing of the Pt crystallites (*34*). However, exposure to H_2 at 500°C has been reported to convert ordered very fine particles of Pt on γ-Al_2O_3 to disordered ones (*35*). O_2, 550°;H_2,300° has been reported to roughen the surfaces of Pt in Pt/γ-Al_2O_3, but CO,25°; H_2,300° to smooth them (*36*). H_2,627° produces cube shapes with (100) faces from Pt crystallites on a smooth silica film, but rounded shapes result from N_2,627°C (*37*). In previous work, the rounded-cubic transition was reported to be reversible even at 500°C (*38*).

Roughness may have another effect. Minot *et al.* (*39*) have made extended Hückel calculations on a system involving a plane of 49 atoms in a (100) monolayer upon which planar islands of 1, 2, 3, 4 . . . atoms are placed. Some adjacent *M–M* bonds in the monolayer are strongly affected and to degrees that vary with the size of the island. Some bonds are strengthened and therefore shortened, whereas others are weakened and therefore lengthened. If these conclusions apply to real surfaces, they would have substantial catalytic consequences, certainly for crystallites large enough to have larger planes, but in smaller crystallites edge atoms might produce significant effects.

CONCLUSIONS

On Rh/SiO_2, secondary hydrogen atoms exchange much faster than primary ones; in particular, with neohexane the exchange ratio *t*-bu/et is much smaller than unity. This behavior separates Rh/SiO_2 from Pt/SiO_2 and Pd/SiO_2. Another separating feature is the much faster exchange of cyclopentane than pentane on Rh/SiO_2. At least some of the exchange on Rh/SiO_2 proceeds via adsorption and desorption of cyclopentane to and from 2H* (or H_2*) + *CH—*CH_2— or ((—CH=CH—)*).

The rate of exchange ratio, N_t^0(108-IonX)/N_t^0(31-Rh_6), is near 2 for all hydrocarbons, but $N_t^{H_2,450^\circ}$(108-IonX)/$N_t^{H_2,450^\circ}$(31-Rh_6) is several times larger. Small D_h favors proportionately more extensive multiple exchange and large D_h favors less for all hydrocarbons. Thus, although the rate monoadsorbed ⇌ (g) for a particular pretreatment and hydrocarbon does not change much as D_h increases, the rate monoadsorbed ⇌ diadsorbed decreases substantially.

H_2,450° generates the most active catalysts. Mere removal of adsorbed hydrogen, He,300° after H_2,450°, does not change N_t for the exchange of neohexane, but He,450° causes surface reconstruction to a surface giving a much lower N_t for exchange, i.e., for $RH + 2* \rightleftharpoons R* + H*$. 11-$Rh_6$ is an exception; He,450° increases N_t for 11-Rh_6; H_2,450° presumably consequent to the larger planes present on this catalyst.

As judged by exchange of neohexane, the pretreatments H_2,100°;He,450°;H_2,300°; He,450°, and H_2,450°;He,450° operating on a particular catalyst produce very nearly the same final catalyst.

Adsorbate-surface strain reduces the rate constant for adsorption and increases that for desorption. Particularly for higher coverages by hydrocarbon, the rate of exchange of a hindered hydrocarbon will be faster than one would conclude from the rate constant of adsorption alone.

Rh/SiO_2 is generally more sensitive to pretreatment than Pt and Pd/SiO_2. Particularly after H_2,450°, Rh/SiO_2 is more sensitive to D_h.

REFERENCES

1. Takehara, D. K., Butt, J. B., and Burwell, R. L., *J. Catal.* **133** (1991).
2. Kemball, C., *in* "Advances in Catalysis" (D. D. Eley, P. W. Selwood, and P. B. Weisz, Eds.), Vol. II, p. 223. Academic Press, New York, 1959; *Chem. Soc. Rev.* **13**, 375 (1984); Ozaki, A., "Isotopic Studies in Heterogeneous Catalysis." Kodansha, Tokyo, 1977.
3. Burwell, R. L., Jr., *Acc. Chem. Res.* **2**, 289 (1969); *Catal. Rev.* **7**, 25 (1972).
4. Rooney, J. J., *J. Mol. Catal.* **31**, 147 (1985).
5. Faro, A. C., Jr., and Kemball, C., *J. Chem. Res. Synop.* 348 (1984).
6. Sheppard, N., *Annu. Rev. Phys. Chem.* **39**, 589 (1988).
7. Garin, F., and Gault, F. G., *J. Am. Chem. Soc.* **97**, 4466 (1975); Parayre, P., Amir-Ebrahimi, V., Gault, F. G., and Frennet, A., *J. Chem. Soc. Faraday Trans. 1* **76**, 1704 (1980); Frennet, A., *in* "Hydrogen Effects in Catalysis" (Z. Paál and P. G.

Menon, Eds.), p. 399. Dekker, New York, 1988; Garin, F., and Maire, G., *Acc. Chem. Res.* **22,** 100 (1989).

8. He, M.-Y., Xiong, G., Toscano, P. J., Burwell, R. L., Jr., and Marks, T. J., *J. Am. Chem. Soc.* **107,** 641 (1985); Dahmen, K.-H., Hedden, D., Burwell, R. L. Jr., and Marks, T. J., *Langmuir* **4,** 1212 (1988).

9. James, B. R., *Adv. Organomet. Chem.* **17,** 319 (1979); Cotton, F. A., and Wilkinson, G., "Advanced Inorganic Chemistry," 5th ed., pp. 1249–1254. Wiley, New York, 1988.

10. Gryaznov, V. M., Smirnov, V. S., and Slin'ko, M. G., *in* "Proceedings, 7th International Congress on Catalysis, Tokyo, 1980" (T. Seiyama and K. Tanabe, Eds.), Part A, p. 224. Elsevier, Amsterdam, 1981.

11. Ceyer, S. T., *Annu. Rev. Phys. Chem.* **39,** 479 (1988); Brass, S. G., and Ehrlich, G., *Surf. Sci.* **191,** L819 (1987).

12. Burwell, R. L., Jr., and Briggs, W. S., *J. Am. Chem. Soc.* **74,** 5096 (1952).

13. Roth, J. A., Geller, B., and Burwell, R. L., Jr. *J. Res. Inst. Catal. Hokkaido Univ.* **16,** 221 (1968).

14. Cogen, J. M., and Maier, W. F., *J. Am. Chem. Soc.* **108,** 7752 (1986).

15. Kemball, C., and Brown, R., *Chem. Soc. Chem. Commun.,* 771 (1987). See also, Brown, R., and Kemball, C., *J. Chem. Soc. Faraday Trans. 1* **85,** 2159 (1989).

16. Eskinazi, V., and Burwell, R. L., Jr., *J. Catal.* **79,** 118 (1983).

17. Cogen, J. M., and Maier, W. F., *Langmuir* **3,** 830 (1987).

18. Oliver, J. A., Kemball, C., Brown, R., and Jamieson, E. W., *J. Chem. Soc. Faraday Trans. 1* **81,** 1871 (1985).

19. Anderson, J. R., and Kemball, C., *Proc. R. Soc. (London) A* **223,** 361 (1954).

20. Rowlinson, H. C., Burwell, R. L., Jr., and Tuxworth, R. H., *J. Phys. Chem.* **59,** 225 (1954).

21. Hegarty, B. F., and Rooney, J. J., *J. Chem. Soc. Faraday Trans. 1* **85,** 1861 (1989).

22. March, J., "Advanced Organic Chemistry," 3rd ed., pp. 121–122. Wiley, New York, 1985.

23. Avery, N. R., *Surf. Sci.* **163,** 357 (1985).

24. Chesters, M. A., Gardner, P., and McCash, E. M., *Surf. Sci.* **209,** 89 (1989).

25. Raval, R., and Chesters, M. A., *Surf. Sci.* **219,** L505 (1989).

26. Hembe, R. T., Scott, C. P., and Norton, J. R., *J. Am. Chem. Soc.* **109,** 3468 (1987).

27. Öz, H., and Gäumann, T., *J. Catal.* **126,** 115 (1990).

28. Kung, H. H., Pellet, R. J., and Burwell, R. L. Jr., *J. Am. Chem. Soc.* **98** 5603 (1976); Burwell, R. L. Jr., Kung, H. H., and Pellet, R. J., *in* "Proceedings, 6th International Congress on Catalysis, London, 1976" (G. C. Bond, P. B. Wells, and F. C. Tompkins, Eds.), p. 108. The Chemical Society, London, 1977.

29. van'Hardeveld, R., and Hartog, F., *Surf. Sci.* **15,** 189 (1969).

30. Kung, H., and Burwell, R. L., Jr., *J. Catal.* **62,** 11 (1980).

31. Burwell, R. L. Jr., *Langmuir* **2,** 2 (1986).

32. Uchijima, T., Herrmann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50,** 464 (1977); Inoue, Y., Herrmann, J. M., Schmidt, H., Burwell, R. L. Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **53,** 401 (1978).

33. Somorjai, G. A., *J. Phys. Chem.* **94,** 1013 (1990).

34. Sarkany, J., Bartok, M., and Gonzalez, R. D., *J. Phys. Chem.* **91,** 4301 (1987).

35. Robota, H. J., Cohn, M. J., Ringwelski, A. Z., and Eades, R. A. *Mater. Res. Soc. Symp. Proc.* **111,** 201 (1988).

36. Hicks, R. F., Qi, H., Kooh, A. B., and Fischel, L. B. *J. Catal.* **124,** 488 (1990).

37. Shi, A.-C., and Masel, R. I., *J. Catal.* **120,** 421 (1989).

38. Wang, T., Lee, C., and Schmidt, L. D., *Surf. Sci.* **163,** 181 (1985).

39. Minot, C., Lowe, J. P., and Salem, L., *Catal. Lett.* **4,** 195 (1990).

40. Eskinazi, V., Doctoral dissertation, Northwestern University, 1979.

41. Pitchai, R., Wong, S. S., Takahashi, N., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **94,** 478 (1985).