Pt/SiO₂

IV. Isotopic Exchange between Cyclopentane and Deuterium

YASUNOBU INOUE, JEAN M. HERRMANN,[1] HELMUT SCHMIDT,[2] ROBERT L. BURWELL, JR.,[3] JOHN B. BUTT, AND JEROME B. COHEN

Ipatieff Laboratory, Department of Chemistry, Northwestern University, Evanston, Illinois 60201

Isotopic exchange between cyclopentane and deuterium, mostly at 81°C, has been investigated on a set of 10 Pt/SiO₂ catalysts whose percentages exposed ranged from 6.3 to 81%. The standard pretreatment, O₂, 300°C; H₂, 300°C; He 450°C with cooling in helium, leads to turnover numbers for formation of exchanged cyclopentanes, which decline by a factor of less than 2 as the percentage exposed increases from 6.3 to 63.5% and then at 81% rise to about the value for 6.3%. Selectivity to various exchanged species varies with percentage exposed and, in particular, D_6/D_{10} (the ratio of initial yields of d_6 and d_{10}) decreases substantially as the percentage exposed increases. This suggests that exchange of the hydrogen atoms on both sides of the cyclopentane ring proceeds mainly via formation of α,α-diadsorbed cyclopentane on catalysts with a smaller percentage exposed and by rollover on catalysts with a large percentage exposed. Other pretreatment conditions such as O₂, 300°C; H₂, 100°C and O₂, 300°C; H₂, 450°C with cooling in hydrogen give larger structure sensitivities for activity and different selectivities. Catalysts deactivate rather rapidly but with little change in selectivity. Deactivation is accompanied by the formation of carbonaceous residues. C/Pt_s becomes approximately 0.5 and the activity declines 10% in about 10 min on stream. Ninety percent or more of the carbon in the residue occurs in a cyclopentane structure because 90% of the carbon is removed as cyclopentane by hydrogen at 100°C. Repetition of the standard pretreatment regenerates the initial activity and selectivity.

INTRODUCTION

In view of the current interest in the question of structure sensitivity in heterogeneous catalysis, it appeared of interest to examine a number of catalytic reactions on a set of catalysts with different percentages exposed that were as well characterized as possible and differed as much as possible only in the percentage exposed.

[1] Present address: Institut de Recherches sur la Catalyse, CNRS, Villeurbanne, France.

[2] Present address: Institut für Silicatforschung der Frauenhofergesellschaft, Würzburg, German Federal Republic.

[3] Author to whom inquiries should be made.

This paper reports the results of isotopic exchange between cyclopentane and deuterium on a series of Pt/SiO₂ catalysts with percentages exposed varying from 6 to 81%. The physical characterization of these catalysts is discussed in Parts I and II *(1, 2)* and the effect of percentage exposed upon the hydrogenolyses of cyclopropane and methylcyclopropane and upon the hydrogenation of propylene appears in Part III *(3)*.

Isotopic exchange between cyclopentane and deuterium was chosen as a potentially interesting test reaction. One run provides 10 data which can be expressed as an ex-

401

tensive quantity, loss of unexchanged cyclo-pentane, and 9 intensive properties, the hydrocarbon fractions D_i of any 9 of the 10 exchanged species, d_1 through d_{10}. It was known that supported platinum catalysts lead to the appearance of all species d_1 through d_{10} (4). If two or more processes are involved in forming the various exchanged species and if different sites promote these processes to different degrees, then the exchange reaction should be a useful tool in investigating structure sensitivity. The results of isotopic exchange between cyclopentane and deuterium on Pd/Al_2O_3 have been interpreted to indicate the presence of several different sites on palladium, the relative areal concentrations of which vary from catalyst to catalyst (5). There were preliminary indications that a similar situation exists on Pt/Al_2O_3 (4).

Much of the work described in this paper was done with catalysts which had been stored in air for 1 to 2 years and then given a standard pretreatment before exchange runs: $O_2,300°,0.5$; $H_2,300°,1$; $He,450°,1$ (1). The first and second numbers indicate, respectively, the temperature (in °C) and the time (in hours) of treatment by the gas listed at the beginning of each set. This pretreatment is the one used in the measurement of percentage exposed by hydrogen chemisorption (1). Other pretreatment conditions have also been investigated, in particular, the effects of the temperature of exposure to hydrogen, whether the catalyst is cooled in hydrogen or helium, and whether the catalyst is treated with oxygen at 300°C before exposure to hydrogen or not. The condition of pretreatment turns out to be an important variable.

EXPERIMENTAL METHODS

Deuterium (Matheson, isotopic purity, 99.7%) and hydrogen were passed through a Deoxo unit, a trap of Davison Grade 62 silica gel at $-196°C$, and a trap of $Cr(II)/$ SiO_2 (1) at 25°C. Helium was purified by the two traps.

Cyclopentane (Chemical Samples Company) was distilled from a molten sodium–potassium alloy in a stream of helium and stored under helium. It was chromatographically pure.

A flow of deuterium containing a fixed partial pressure of cyclopentane was prepared by passing the purified deuterium through a Brooks Thermal Mass Flowmeter and then through a U-tube packed with Filtros FS-140 (6). The pores of the macroporous Filtros could be filled with cyclopentane without access of oxygen by inserting a syringe needle down a capillary tube connected above the entrance side of the U-tube while a flow of helium passed out the capillary. The exit was ordinarily closed by the tip of a Teflon needle valve. The plunger was removed for access to the capillary tube. The U-tube was thermostatted at -9.5 or $0°C$ to provide partial pressures of cyclopentane of 64 and 106 Torr, respectively. All runs are at $P_{cp} = 64$ Torr unless otherwise stated.

The deuterium–cyclopentane stream was then passed over a Pt/SiO_2 catalyst (0.05–0.2 g) at flow rates of 20 to 80 cm³ min⁻¹. The amount of catalyst and flow rate were adjusted to keep the fraction of unexchanged cyclopentane greater than 0.94. Samples for mass spectroscopy were collected at intervals by directing the effluent stream for 1 to 2 min through a trap at $-196°C$. The exit pressure was always 1 atm.

The system was devoid of mercury and greased stopcocks. Teflon needle valves and Nupro bellows valves were employed. The system was tested for leaks periodically by inserting a silica gel trap cooled to $-196°C$ beyond the catalyst tube, which was empty in this test. Helium was passed through the apparatus. After about 1 hr, the trap was warmed to room temperature and any pulse of released gas was analyzed chromatographically. Any leak of oxygen

produced less than 0.03 ppm of oxygen in the helium, which during an experiment corresponds to less than 0.001 for O/Pt_s.

Before exchange runs, the Pt/SiO_2 catalysts (1) were given the standard pretreatment unless otherwise stated. A flow of deuterium was established at the chosen temperature of reaction and then the flow of deuterium plus cyclopentane was started.

Rates of isotopic exchange declined during a run but the catalyst was restored to its initial state by repetition of the standard pretreatment, described above. Initial rates were estimated by extrapolation to Time 0. On a given batch of catalyst, the initial rate upon regeneration was reproducible to $\pm 7\%$ and for different batches of the same catalyst the initial rate was $\pm 10\%$.

Exchanged cyclopentane was analyzed on a Consolidated CEC-10-240 mass spectrometer using a nominal ionizing voltage of 10 V. Parent peaks were corrected for ^{13}C and for fragment peaks in the conventional fashion, and the resulting distribution pattern was corrected for isotopic dilution resulting from the exchange reaction (5). Although corrections for isotopic dilution are small at our low conversions, they can be proportionately rather large for D_4 and D_9 when D_5 and D_{10} are large. D_i symbolizes the fraction of species d_i in the total exchanged product d_1 through d_{10}.

RESULTS

Activity and Deactivation

The term activity will be applied to the rate of loss of cyclopentane-d_0, whereas selectivity will refer to the nature of the isotopic distribution pattern, D_1 to D_{10}.

The rate of deactivation increases with increasing temperature and with an increase in P_{cp}/P_{D_2}. Deactivation is unaffected by the insertion of a bed of Pt/SiO_2 at 25°C ahead of the regular reactor. The rate of deactivation is independent of flow rate; for example, with

63-SiO_2-IonX (the beginning number in the catalyst code is the percentage exposed as measured by hydrogen chemisorption, IonX indicates preparation by ion exchange with $Pt(NH_3)_4^{2+}$, and PtCl indicates preparation by impregnation with H_2PtCl_6 aq.) at 81°C, the rates of deactivation were nearly identical for flow rates of 27.7 and 55.6 cc of D_2-C_5H_{10}/min. The initial turnover frequencies, N_t, in molecules of cyclopentane exchanging per second per surface platinum atom were 0.067 and 0.064, respectively. These data indicate that deactivation results from the intrinsic character of the system and not from extrinsic poisons.

For 40-SiO_2-PtCl-S, losses in activity at 81°C after 10, 20, and 40 min were about 12, 20, and 35%, respectively. For 81-SiO_2-IonX, the corresponding losses were 18, 35, and 50%.

The amount and nature of the carbonaceous residue on the catalyst were investigated in several ways, all of which started by abruptly interrupting an exchange run at 81°C by flushing the catalyst with helium for 20 min. One of the procedures, (1) through (4), was then started.

(1) About five times as much oxygen as would be needed fully to oxidize the surface residue was trapped in the reactor and the reactor was heated to 300°C for 80 min. Helium flow was then diverted through the reactor and the exit stream was passed through a silica gel trap at −196°C. The trap was warmed and the released pulse of carbon dioxide was measured catharometrically. No carbon monoxide was detectable. The sensitivity of the analysis was ± 0.01 C/Pt_s (the average number of carbon atoms per surface platinum atom). Figure 1 shows r/r_0 (the final divided by the initial conversion) vs C/Pt_s for 40-SiO_2-PtCl-S. On the less extensively investigated 81-SiO_2-IonX, r/r_0 was about 0.8 at $C/Pt_s = 0.6$.

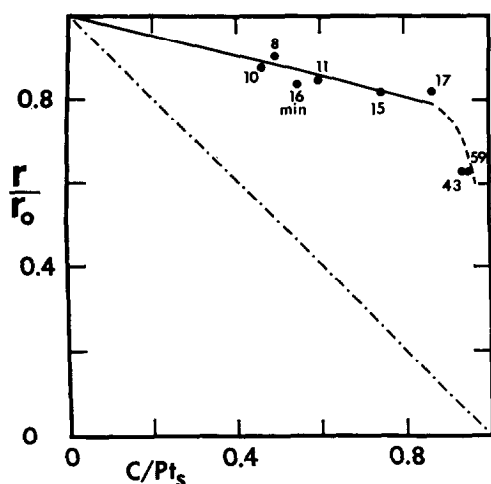In the other techniques, following the helium flush, helium or hydrogen was passed

Fig. 1. Deactivation vs carbon content of catalyst. The y axis, r/r_0, is the extrapolated initial rate, r_0, divided into the rate at a time in minutes shown by the numbers. The x axis represents total moles of carbon as found by oxidation to carbon dioxide divided by moles of surface platinum.

through the reactor and then through a silica gel trap at $-196\,°C$. Any hydrocarbon collected in the trap was released as a pulse for gas chromatographic analysis by rapidly warming the trap.

(2) The flow of helium over a sample of 40–SiO$_2$–PtCl–S for which r/r_0 was 0.81 was continued for 10 min at 81 °C and the reactor was then warmed to 100 °C for 10 min. No hydrocarbon was collected. Hydrogen flow was started. In 10 min at 100 °C, cyclopentane was collected in an amount corresponding to (cyclopentane)/Pt$_s$ = 0.15 (i.e., C/Pt$_s$ = 0.75).

(3) A sample of 40–SiO$_2$–PtCl–S of r/r_0 = 0.84 was heated to 450 °C in flowing helium. An amount of methane was collected which corresponded to CH$_4$/Pt$_s$ = 0.48.

(4) Hydrogen was passed through a sample of 40–SiO$_2$–PtCl–S, r/r_0 = 0.82. The product collected after warming to 100 °C for 10 min was exclusively cyclopentane, (cyclopentane)/Pt$_s$ = 0.10. Similar experiments gave values between 0.10 and 0.15 for this ratio. The reactor was then warmed to 200 °C for 10 min. No hy-

drocarbon was collected. Heating to 300 °C for 10 min led to the collection of methane and a small amount of butane; only methane was collected at 450 °C. The total yield in methane corresponded to CH$_4$/Pt$_s$ = 0.05, and 40% of this was collected between 200 and 300 °C.

Deactivation occurs during isotopic exchange between n-pentane and deuterium. A plot of activity vs the carbon content of the catalyst measured by procedure (1) is of the same form as that shown in Fig. 1, but the rate of deactivation with time was only about one half that of isotopic exchange of cyclopentane. Most of the carbonaceous deposit was released as n-pentan by hydrogen at 100 °C.

Selectivity

Figure 2 shows isotopic distribution patterns for 40–SiO$_2$–PtCl–S in comparison with typical results for Ni/SiO$_2$ and Pd/Al$_2$O$_3$. Figure 3 shows the effect of percentage exposed upon the isotopic distribution patterns at 81 °C with P_{cp} = 64 Torr and P_{D_2} = 680 Torr. To simplify the figure, D_2, D_3, and D_4 are combined as are D_6, D_7, D_8, and D_9. D_i' represents the fraction
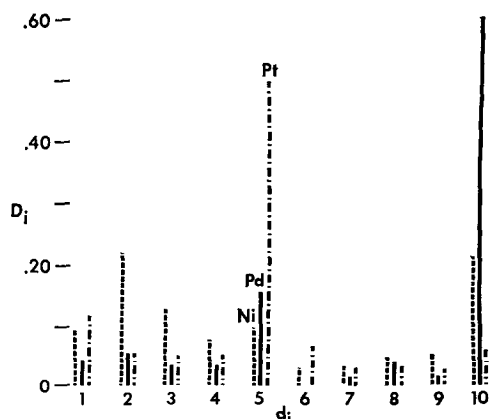

Fig. 2. Initial isotopic distribution patterns in the exchange of cyclopentane on 42% Ni/SiO$_2$ at 70 °C [simple dashed line, at left, Ni-I of Ref. (*4*)] on 5% Pd/γ–Al$_2$O$_3$ at 70 °C [full line, middle, Ref. (*5*)], and Pt/SiO$_2$ (6.3–SiO$_2$–PtCl of this research) at 67.5 °C (doubly dashed line, right).

of cyclopentane-d_i in the exchanged cyclopentane, cyclopentane-d_2 through cyclopentane-d_{10} e.g., $D_6' = D_6/(D_2 + D_3 + \cdots D_{10})$. The proportions of the components of each set changed relatively little with percentage exposed except for D_6. D_1 is excluded, since its value is not very accurate at low conversions because of the large correction applied to the parent plus one peak for content in ^{13}C.

The effect of temperature upon isotopic distribution patterns is shown in Fig. 4 for 81–SiO$_2$–IonX. Other catalysts were generally similar. The activation energies for production of the various isotopically exchanged cyclopentanes were obtained from exchange data at 55, 67.5, and 81°C. Since the temperature range is small, the activation energies are not very accurate and the uncertainty is probably about ±8 kJ/mole. Uncertainty in the relative values, however, is less. Figure 5 shows Arrhenius plots for one catalyst. Plots for the other catalysts were similar. The values of N_t in Fig. 5 are for a partially deactivated catalyst and are smaller than the initial values of N_t mentioned elsewhere in this paper. Activation energies for formation of the various exchanged species are: d_1–d_{10},

FIG. 4. Isotopic distribution patterns of cyclopentane exchanged on 81–SiO$_2$–IonX at 81°C, squares and simple dashed line; at 67.5°C, circles and thick full line; and at 55°C, stars and doubly dashed line.

71; d_2–d_4, 59; d_5, 67; d_6, 82; d_7–d_9, 84; and d_{10}, 98 kJ/mole. There is little change with percentage exposed except that all activation energies rise 8 to 16 kJ/mole at the lowest percentages exposed. The higher values of the range apply to the species more exchanged than d_5.

The selectivity is nearly independent of the degree of deactivation. Table 1 gives the initial isotopic distributions for 81–SiO$_2$–IonX at 81°C and those after 35 and 55% loss of activity. The probable error in these figures is ±0.007. The table also gives data obtained 1 year after the previous data. The only significant difference is a slightly larger value of D_{10} in the later run.
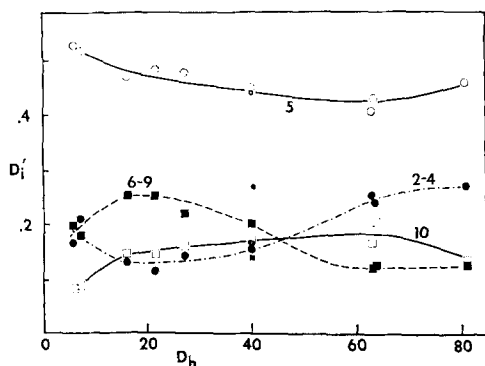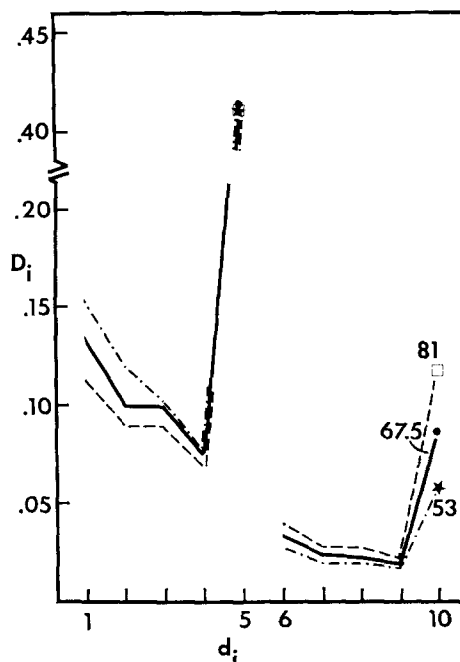

FIG. 3. The variation of the initial isotopic distribution patterns of cyclopentane at 81°C with percentage exposed: D_{2-4}', full circles; D_5', empty circles; D_{6-9}', full squares; and D_{10}', empty squares. D_i' represents the fraction of cyclopentane-d_i in the exchanged cyclopentane, cyclopentane-d_2 through d_{10}. The small symbols are for 40–SiO$_2$–PtCl–L.

Effect of Various Pretreatments

The data presented to this point were determined on catalysts pretreated in the standard fashion used for the measurement of percentage exposed by hydrogen chemi-
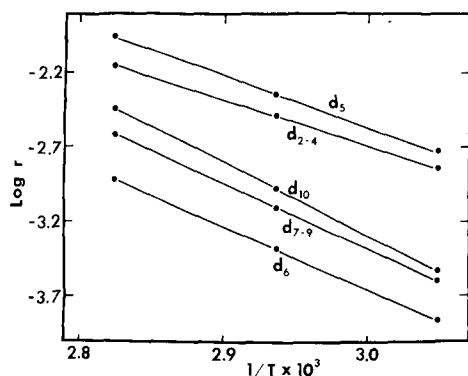
FIG. 5. The rate expressed as turnover frequency for the formation of various isotopically exchanged species of cyclopentane on 81-SiO$_2$-IonX as a function of temperature.

sorption. Data for other pretreatments follow. Results of hydrogen–oxygen titration which are relevant to some of these pretreatments appear in Table 2.

The isotopic distribution patterns and turnover frequencies for 6.3-SiO$_2$-PtCl, 40-SiO$_2$-PtCl-S, and 81-SiO$_2$-IonX subjected to various nonstandard pretreatments appear in Figs. 6 through 11. The exchange reactions were all run at 81°C. In some cases, bars rather than points have been entered to show the range of values obtained on catalysts given the standard pretreatment.

Figure 10 shows that N_t for 81-SiO$_2$-IonX treated O$_2$,300°,0.5; H$_2$,100°,1 was 0.027 sec^{-1}. Protracting the treatment with hydrogen to 15 hr led to the same isotopic distribution patterns and N_t of 0.026 sec^{-1}. Direct reduction of stored catalyst by H$_2$,100°,1 gave $N_t = 0.020$ sec^{-1} and, in a duplicate experiment, 0.022 sec^{-1}. N_t for 81-SiO$_2$-IonX given the standard pretreatment was 0.113 sec^{-1}.

Regeneration

Exposure to O$_2$,300°,0.5; H$_2$,300°,1; He,450° or to H$_2$,300°,1; He,450° of used catalysts which had initially been given the standard pretreatment restored the initial activity and selectivity of the

catalyst. The effect of the treatment H$_2$,450°,1 was investigated on used 6.3-SiO$_2$-PtCl and 40-SiO$_2$-PtCl-S which had initially received the standard pretreatment. Activities and selectivities were indistinguishable from those of catalysts which were originally treated O$_2$,300°,0.5; H$_2$,450°,1.

DISCUSSION

Deactivation

As shown by Fig. 1, deactivation during a run is rather rapid. Conversions were extrapolated to Time 0 on stream to get the initial activity. Selectivity is nearly independent of time on stream, as shown in Table 1. The data of the experimental section established that deactivation is accompanied by and presumably results from the accumulation of carbonaceous deposits on the catalyst. The cyclopentane structure is retained in 90% or more of the carbon in the deposit formed at 81°C, since 90% of the carbon is removed

TABLE 1

Isotopic Distribution Patterns in Cyclopentane Exchanged with Deuterium on 81-SiO$_2$-Ion-X at 81°C[a]

	Time of run (min)			
	0[b]	7.5[c]	14	70
	Loss in activity (%)			
	0	16	35	55
D_1	0.113	0.108	0.125	0.134
D_2	0.089	0.077	0.085	0.085
D_3	0.089	0.082	0.087	0.085
D_4	0.066	0.068	0.069	0.072
D_5	0.412	0.412	0.407	0.392
D_6	0.039	0.041	0.038	0.037
D_7	0.027	0.029	0.026	0.027
D_8	0.027	0.027	0.027	0.029
D_9	0.021	0.024	0.024	0.025
D_{10}	0.177	0.132	0.112	0.116

[a] $P_{D_2} = 680$ Torr, $P_{cp} = 64$ Torr.
[b] Extrapolated to Time 0.
[c] Run 1 year after the other data were collected.

as cyclopentane by hydrogen at 81 to 100°C. The remaining carbon is removed as methane at 200 to 450°C. A deactivated catalyst exposed to the standard pretreatment, $O_2,300°,0.5$; $H_2,300°,1$; $He,450°,1$, is restored to the initial activity.

Since the rate of formation of exchanged cyclopentane decreases with the extent of formation of carbonaceous deposits, it would appear likely that the exchange reaction proceeds upon the surface of the platinum and not upon the carbonaceous residues, although one cannot rigorously exclude the possibility that some active residue is formed in the first few instants of exposure to cyclopentane and that the residue formed later is inhibiting.

Activity and Selectivity Resulting from the Standard Pretreatment

At 81°C on catalysts exposed to the standard pretreatment, N_t is about 0.11 for both extremes of percentage exposed,

TABLE 2

Percentage Exposed Resulting from Various Pretreatments of 40-SiO$_2$-PtCl-S

Treatment	Run[a]	Percentage exposed measured by	
		H_2–O_2 titration	H_2 desorption[b]
O_2, 300°; H_2, 300°; Ar, 450°	A-1	31.5	38.7
	B	32.3	
O_2, 300°; H_2, 300°; Ar, 300°	A-2	32.9	37.0
	C-1	31.3	35.4[c]
	C-2	32.8	37.6
O_2, 300°; H_2, 300°	A-3	31.3	39.0
O_2, 300°; H_2, 450°	A-4	29.5	48.7
	A-5	31.5	46.2

[a] Three samples of catalyst, A, B, and C, were employed. The number denotes the sequence of successive runs on the same sample. After the listed treatments, the catalysts were exposed to O_2 at 25°C for 0.25 hr. Times of treatment with the gases listed in the table were 1 hr for H_2 and Ar and 0.5 hr for O_2. The listed values for H_2–O_2 titration were calculated using one third the amount of hydrogen which reacted.

[b] After the H_2–O_2 titration the catalyst was heated rapidly to 450°C and the evolved hydrogen was collected and measured [see Ref. (1)]. The listed values are hydrogen atoms desorbed per 100 atoms of Pt.

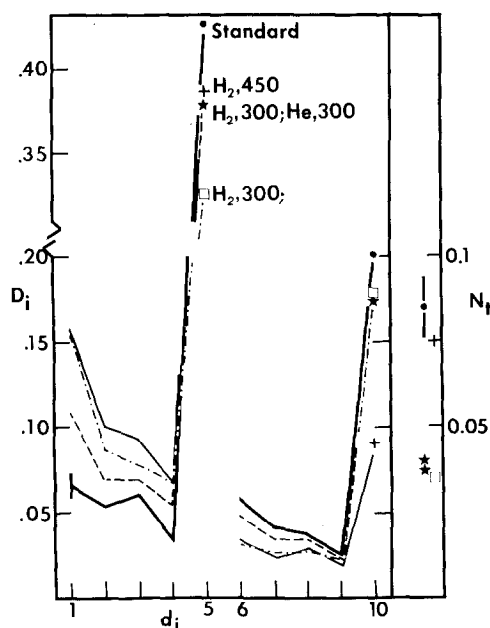[c] The catalyst was heated only to 300°C during the desorption.

FIG. 6. Isotopic distribution patterns of cyclopentane exchanged at 81°C on stored 40-SiO$_2$-PtCl-S of various pretreatments: standard pretreatment, circles and thick full line; $O_2,300°,H_2,450°$, crosses and thin full line; $O_2,300°,H_2,300°,He,300°$, stars and simple dashed line; $O_2,300°,H_2,300°$, squares and doubly dashed line. Exposure times are 0.5 hr for O_2 and 1.0 hr for H_2 and He. Turnover frequencies for total exchange are shown at the right. The bars show the extreme ranges on various samples of the catalyst given the standard pretreatment.

6.3 and 81%. N_t declines as D_h increases and reaches a value of 0.066 at $D_h = 63\%$.

The lower accuracy of extrapolation to Time 0 in the data of the present paper makes conclusions about variation of N_t with D_h less precise than those given in Part III (3).

As shown in Fig. 3, structure sensitivity in selectivity for isotopic exchange of cyclopentane is larger than that in activity for Pt/SiO$_2$ exposed to the standard pretreatment. The structure sensitivity for selectivity, however, appears to be smaller on Pt/SiO$_2$ than on Pd/Al$_2$O$_3$ (5). On Pt/SiO$_2$, D_5 decreases and D_{10} rises as percentage exposed increases, but 81-SiO$_2$-IonX is off the smooth curve. D_{2-4} parallels
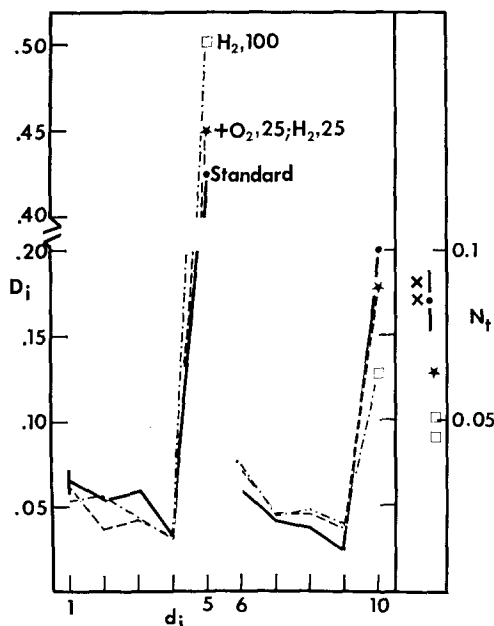
Fig. 7. Isotopic distribution patterns of cyclopentane exchanged at 81°C on stored 40–SiO₂–PtCl-S of various pretreatments: standard, circles and thick full line; standard followed by $O_2,25°$, 0.25; $H_2,25°,0.33$, stars and simple dashed line; $H_2,100°,1$, squares and doubly dashed line; and $O_2,300°,0.5$; $H_2,100°,1$, ×; the isotopic distribution patterns were identical to those of $H_2,100°,1$.
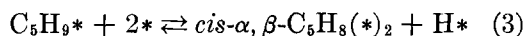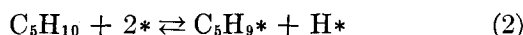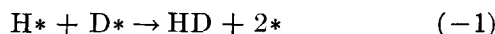
D_5 to $D_h = 20\%$ and then rises substantially as D_h increases further. D_{6-10} rises from 0.28 at $D_h = 7\%$ to 0.40 at 16%. It then falls, becoming 0.39 at $D_h = 24\%$, 0.31 at 63%, and 0.26 at 81%. The distribution within D_6 to D_{10} changes with percentage exposed. The ratio, D_6/D_{10} is particularly significant. The ratio is 0.95 for $D_h = 6.3\%$; 0.81 for 7.1%; 0.57 for 27%; 0.28 for 40%; and 0.21 for 63.5%: The value for $D_h = 81\%$, 0.33, is higher than one would expect if the trend were monotonic.

Agreement between catalysts prepared on the larger and on the smaller mesh silica gel is good except for 40–SiO₂–PtCl–L and 40–SiO₂–PtCl–S. For L, N_t was 0.075 sec⁻¹ vs 0.087 for S, but the selectivity of L resembles catalysts of larger percentage exposed, whereas that of S resembles catalysts of lower D_h. Both, however, exhibited nearly the same value of

D_6/D_{10}. Probably the selectivity changes rapidly in the vicinity of $D_h = 40\%$. In Fig. 3 the smooth curves are drawn through 40–SiO₂–PtCl–S for no very compelling reason.

Mechanistic Considerations

Previous evidence reviewed in Ref. (7) indicates that isotopic exchange of cyclopentane involves the following steps:

$$2* + D_2 \rightarrow 2*D \tag{1}$$

$$H* + D* \rightarrow HD + 2* \tag{-1}$$

$$C_5H_{10} + 2* \rightleftarrows C_5H_9* + H* \tag{2}$$

$$C_5H_9* + 2* \rightleftarrows cis\text{-}\alpha, \beta\text{-}C_5H_8(*)_2 + H* \tag{3}$$

When the forward and reverse of step (3) are fast compared to step (-2), D_5 becomes large compared to D_4 since step (-3) can form C_5H_8D* attached to the surface at a carbon atom differing from that in the initial C_5H_9*. Continued alternation between (3) and (-3) leads finally to $C_5H_5D_4*$. Some additional step is needed to lead to the transfer of the position of adsorption from one side of the cyclo-
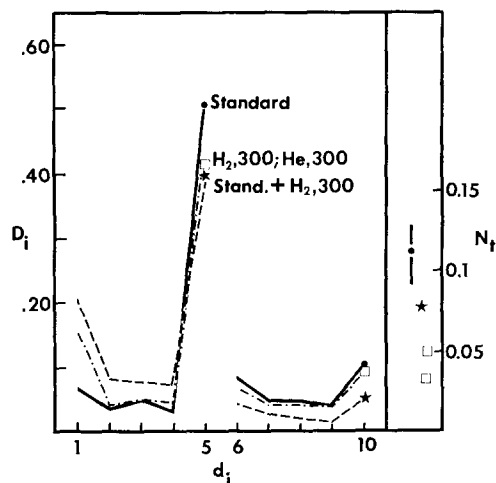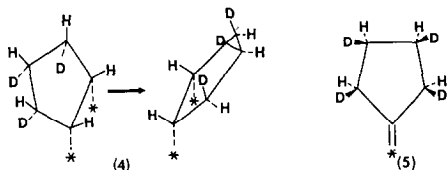

Fig. 8. Isotopic distribution patterns of cyclopentane exchanged at 81°C on stored 6.3–SiO₂–PtCl of various pretreatments: standard, circles and thick full line; $O_2,300°$, $H_2,300°$, $He,300°$, squares and doubly dashed line; standard pretreatment followed by $H_2,300°$, stars and simple dashed line. Exposure times are 0.5 hr for O_2 and 1.0 hr for H_2 and He.

pentane ring to the other and give desorbed cyclopentane more exchanged than d_5. Rollover (4) (7) and formation of α,α-diadsorbed cyclopentane (5) (8)

SCHEME 1

are conceivable steps for effecting such transfer.

Rollover might involve some intermediate transition state or, in the extreme, physically adsorbed cyclopentene. As shown, one rollover process leads to $C_5H_2D_8$, as the maximally exchanged cyclopentane and formation of C_5D_{10} would necessitate two or more rollover process. The species (5), once formed, could revert either to a species
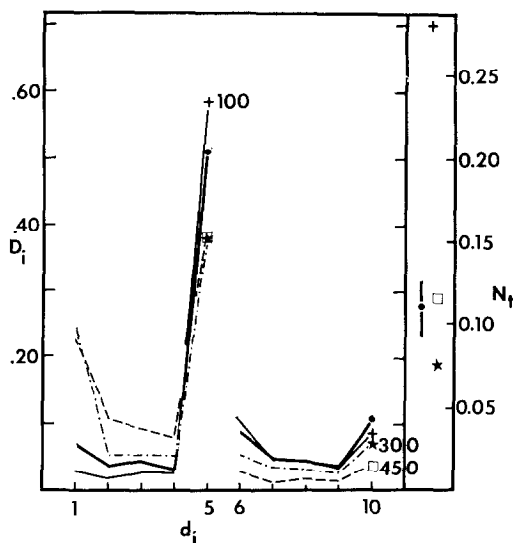

FIG. 9. Isotopic distribution patterns of cyclopentane exchanged at 81°C on stored 6.3–SiO₂–PtCl of various pretreatments: standard, circles and thick full line; O₂,300°,0.5; H₂,300°,1, stars and doubly dashed line; O₂,300°,0.5; H₂,450°,1, squares and simple dashed line; H₂,100°,1, crosses and thin line (in a duplicate experiment, the selectivity was the same and N_t was 0.285 sec⁻¹ rather than 0.277). O₂,300°; H₂,100° led to the same selectivities as H₂,100° and to $N_t = 0.34$, 0.31, and 0.32 sec⁻¹.
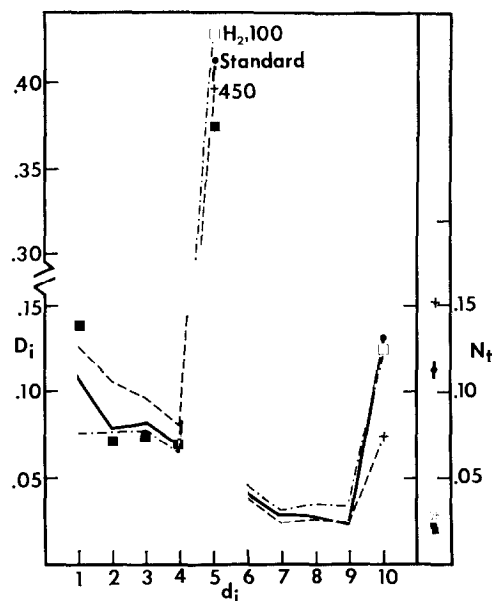

FIG. 10. Isotopic distribution patterns of cyclopentane exchanged at 81°C on stored 81–SiO₂–IonX of various pretreatments: standard, circles and thick full line; O₂,300°,0.5; H₂,450°,1, crosses and simple dashed line; O₂,300°,0.5; H₂,100°,1, empty squares and doubly dashed line; H₂,100°,1, full squares (not entered for D_6–D_{10} but these values were about 4% lower than those for O₂,300°; H₂,100°).

adsorbed on the original side of cyclopentane and leading to the maximally exchanged cyclopentane, $C_5H_4D_6$, or it could react to form a species adsorbed on the other side and proceed thence to form C_5D_{10}. Thus, under conditions in which both D_5 and D_{10} are substantial, rollover should give little D_6 and it might give a maximum at D_8. On the contrary, species (5) should lead to substantial amounts of D_6 (9) and should not give a maximum at D_8. On palladium, as shown in Fig. 2, D_6 is zero and there is a maximum at D_8. Accordingly, extensive exchange of cyclopentane on palladium would appear to proceed via relatively rapid but not extremely rapid rollover. The present data on Pt/SiO₂ are consistent with the occurrence of exchange beyond d_5 via the simultaneous progress of both processes. On the catalysts of large D_h where D_6/D_{10}
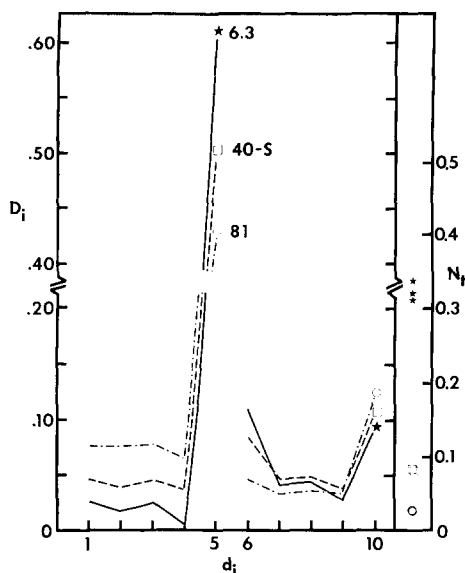
FIG. 11. Isotopic distribution patterns of cyclopentane exchanged at 81°C on stored catalysts treated with $O_2,300°,0.5$; $H_2,100°,1$. 81–SiO_2–IonX, circles and doubly dashed line; 40–SiO_2–PtCl–S, squares and simple dashed line; 6.3–SiO_2–PtCl, stars and thin full line.

is small, rollover would predominate, whereas on the catalysts of small D_h where D_3/D_{10} is large, extensive exchange via α,α-diadsorbed cyclopentane would predominate. If the ratio of edge atoms to face atoms increases with increasing D_h, then rollover is favored on platinum at edge atoms and α,α-diadsorbed cyclopentane is favored at face atoms.

Unlike cyclopentane, all hydrogen atoms of n-pentane can be exchanged by the sequence: step (2), alternation between steps (3) and (−3), and finally step (−2). The isotopic distribution pattern of n-pentane should then depend only upon r_3/r_{-2}. On 40–SiO_2–PtCl–S at 81°C the exchanged pentane is D_1, 0.25; D_2, 0.11; D_3, 0.10; D_4–D_8, 0.07 declining to 0.06; D_9–D_{11}, 0.05 declining to 0.04; and D_{12}, 0.105. As Anderson and Kemball first noted (10), no single ratio of r_3/r_{-2} can account for such a distribution; i.e., in the present case, no single ratio can give large values of D_1–D_3 and a large value of D_{12}. Instead, differing sets

of sites must exhibit *at least* two different ratios, one large (for D_{12}) and one small (for D_1, D_2, and D_3). Similar considerations apply to the values of D_1–D_5 for cyclopentane. Since here $D_5 + D_{10}$ is about 0.6, one of the values of r_3/r_{-2} must be large and the sites with this large value are a major contributor to the overall reaction. The data of Fig. 3, however, indicate that the contribution from sites with small values of r_3/r_{-2} is relatively more important on catalysts of larger D_h.

In the interpretation given above, activity results from the absolute areal rate of step (2), which appears to be only modestly structure sensitive. Selectivity results from the relative rates of steps (2), (3), (4), and (5) and there is substantial sensitivity in these.

The rate of exchange, r_2 or r_{-2}, which are equal at the steady state, is much larger than that of formation of the residues of cyclopentane structure which accompany deactivation. Thus, N_t for exchange is about 0.1 sec^{-1}, whereas from Fig. 1,

$$(\text{cyclopentane residues})/Pt_s$$

becomes about 0.1 in 10 min. Thus, exchange is 600 times faster than deposition of surface cyclopentane residues. The rate of removal of these residues at 81 to 100°C by hydrogen alone is much slower than step (−2) but still substantial. If the mechanism of Eqs. (1) to (5) is correct, the residues of cyclopentane structure could be neither mono- nor diadsorbed cyclopentanes, the surface species involved in exchange. Presumably they are species which are more deficient in hydrogen (11).

Results with Nonstandard Pretreatments

The data so far considered were obtained on catalysts given the standard pretreatment, $O_2,300°$; $H_2,300°$; He,$450°$ with cooling in helium. On 6.3–SiO_2–PtCl, 40–SiO_2–PtCl, and 81–SiO_2–IonX, other pretreatments produced selectivities which

often diverged substantially from those resulting from the standard pretreatment (Figs. 6–11). Furthermore, N_t/N_t^0 was often substantially different from unity. Here, N_t^0 represents the turnover frequency resulting from the standard pretreatment.

The pretreatments can be classified into two groups according to the nature of the deviation of the resulting selectivity from that of the standard pretreatment. Reduction by hydrogen at 300 or 450°C followed by cooling in hydrogen gave larger D_1–D_4, smaller D_5, and smaller D_6–D_{10} (see Figs. 6, 9, and 10). This type of distribution pattern will be called the $H_2,450°$ pattern. Relative to the standard pretreatment, reduction with hydrogen at 100°C gave smaller D_1–D_3, larger D_5, and smaller D_{10} (see Figs. 7, 9, and 10). In general, this type of pattern (the $H_2,100°$ pattern) diverged less from the standard pattern than did that resulting from the pretreatment $O_2,300°$; $H_2,450°$, particularly for 81–SiO$_2$–IonX.

Although the pretreatment $O_2,300°$; $H_2,450°$ gives the extreme form of the $H_2,450°$ isotopic distribution pattern, N_t/N_t^0 was not far from unity as shown in Table 3. On catalysts 6.3–SiO$_2$–PtCl and 40–SiO$_2$–PtCl–S, $O_2,300°$; $H_2,300°$; He,300° gave less extreme versions of the $H_2,450°$ selectivity as did the standard pretreatment followed by H$_2$, 300°. With these pretreatments, N_t/N_t^0 was in the general vicinity of 0.5. The pretreatment $H_2,100°$ gives nearly the same selectivity as for $O_2,300°$; $H_2,100°$ but the resulting activities differ, as shown in Table 3.

Activity measured on catalyst of the standard pretreatment is only slightly structure sensitive. Use of $O_2,300°$; $H_2,450°$ increases the extent of the dip in N_t vs D_h. For catalyst exposed to O_2, 300°; $H_2,100°$, however, N_t declines substantially with increasing D_h. These results would suggest that conclusions about structure sensitivity derived from just one pretreatment condition might be incomplete.

TABLE 3

Values of N_t/N_t^0 at Several Pretreatment Conditions

	Catalyst, D_h		
	6.3	40-S	81
N_t^0	0.111	0.087	0.113
N_t/N_t^0 after H$_2$,100°	2.5	0.56	0.18
N_t/N_t^0 after O$_2$,300°; H$_2$,100°	2.9	1.0	0.23
N_t/N_t^0 after O$_2$,300°; H$_2$,450°	1.0	0.86	1.35

The effect of pretreatment upon activity and selectivity poses rather difficult problems For example, changing the conditions of pretreatment from the standard to O_2, 300°; $H_2,100°$ makes only relatively modest changes in the selectivities exhibited by 6.3–SiO$_2$–PtCl and 81–SiO$_2$–IonX. The rate with the former catalyst, however, increases by a factor of 3 and that with the latter decreases by a factor of 4. Are the rates of all processes (2) through (5) nearly equally augmented or depressed?

We do not think that the percentage exposed varies with the various conditions of pretreatment by large factors. It has been established (1) that none of these treatments leads to transfer of platinum among the platinum crystallites of the catalysts. It would appear unlikely that changing $H_2,100°$ to $H_2,450°$ (Table 3) for 81–SiO$_2$–IonX could lead to an increase in D_h by a factor of 7. Unfortunately, one cannot measure D_h on catalysts cooled in hydrogen. One can, however, expose the catalysts cooled in hydrogen to oxygen at 25°C, which apparently converts surface "hydride" to surface "oxide" (1). One can now pass pulses of hydrogen [the hydrogen–oxygen titration of Benson and Boudart (12)] and measure a percentage exposed D_t, which on our catalysts is somewhat smaller than D_h but approximately proportional to it (1). As shown in Table 2, on 40–SiO$_2$–PtCl D_t is the same after standard pretreatment and after the treatment, $O_2,300°$; $H_2,450°$. Furthermore, as shown in Table 2 of Ref. (1), reduction of stored

6.3–SiO$_2$–PtCl and 40–SiO$_2$–PtCl–S by hydrogen for 1 hr at 100°C leads to the same values of D_t as the standard. Reduction by hydrogen at 25°C for 1 hr of stored 6.3–SiO$_2$–PtCl first treated for 0.5 hr with oxygen at 300°C gives, however, a D_t about 1.4 times that resulting from the standard pretreatment (Table 3 of Ref. 3). Thus, in most cases the temperature of the hydrogen pretreatment appears to have little effect upon the percentage exposed. Reduction of the catalyst of lowest percentage exposed at low temperatures after exposure to oxygen at 300°C leads, however, to a material of augmented percentage exposed. This may well contribute to the augmented value of 6.3–SiO$_2$–PtCl (Table 3) but it can hardly explain an increase in activity by a factor of 3.

If 40–SiO$_2$–PtCl–S is pretreated O$_2$,300°; H$_2$,450°, exposed to the hydrogen–oxygen titration, and then heated to 450°C, the liberated hydrogen exceeds that observed with the pretreatment O$_2$,300°; H$_2$,300; Ar,450° by about 9 atoms of hydrogen per 100 total atoms of platinum (Table 2). This excess hydrogen does not react with oxygen at 25°C, but it is liberated upon reheating to 450°C. The excess considerably exceeds the equilibrium solubility of hydrogen in bulk platinum (13), but the solubility of hydrogen in mesoclusters of platinum may exceed that in bulk. Alternatively, the excess hydrogen might be located at the interface between platinum and silica or on the silica (spillover). Dissolved hydrogen might cause changes in rate and selectivity, but spillover would be unlikely to result in such changes. Excess hydrogen resulting from the pretreatment O$_2$,300°; H$_2$,300° is small or zero.

It is conceivable that pretreatment conditions affect the degree to which impurities in the silica, for example, iron, might migrate to the surface of the platinum clusters. The iron content of Davison grade 62 as reported by the manufacturer amounts, however, to only 2.5 μmole g^{-1},

an amount which is much smaller than the 51 μmole g^{-1} of platinum in a 1% Pt/SiO$_2$ catalyst. The content in titanium is, however, 11 μmole g^{-1}.

It is also conceivable that the degree of reduction of the platinum surface increases as the temperature of pretreatment by hydrogen increases. There are recent reports of the formation of difficulty reducible oxide formed on platinum by exposure to oxygen at high temperatures (14–16). Although our catalysts after initial reduction were never exposed to oxygen at temperatures exceeding 300°C, we have no formal proof that pretreatment by hydrogen even at 450°C results in complete removal of surface oxide. Protraction of exposure to hydrogen at 100°C from 1 to 15 hr led, however, to no change in activity or selectivity. Furthermore, previous work indicates that reduction of surface oxide is as complete at 100°C as at 300°C (1).

Most likely, then, the surface morphology of platinum crystallites varies with the various conditions of pretreatment. Reduction of surface oxide by hydrogen at low temperatures might well lead to a surface morphology differing from that resulting from the standard pretreatment. We have, however, no independent evidence for this except for 6.3–SiO$_2$–PtCl.

We feel that pretreatment conditions need to be considered carefully in studies of structure sensitivity.

ACKNOWLEDGMENTS

REFERENCES

1. Uchijima, T., Herrmann, J. M., Inoue, Y., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **50**, 464 (1977).

2. Sashital, S., Cohen, J. B., Burwell, R. L., Jr. and Butt, J. B., *J. Catal.* **50**, 479 (1977).

3. Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **50**, 494 (1977).

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

5. Schrage, K., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **88**, 4549 (1966).

6. Patterson, W. R., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **93**, 833 (1971). Patterson, W. R., Roth, J. A., and Burwell, R. L., Jr., *ibid.*, **93**, 839 (1971).

7. Burwell, R. L., Jr., *Acc. Chem. Res.* **2**, 289 (1969).

8. Anderson, J. R., and Kemball, C., *Proc. Roy. Soc. (London)* **A226**, 472 (1954).

9. Schrage, K., and Burwell, R. L., Jr., *J. Amer. Chem. Soc.* **88**, 4555 (1966).

10. Anderson, J. R., and Kemball, C., *Proc. Roy. Soc. (London)* **A223**, 361 (1954). See also Rowlinson, H. C., Burwell, R. L., Jr., and

Tuxworth, R. H., *J. Phys. Chem.* **59**, 225 (1955).

11. V. Eskinazi in these laboratories finds similar deactivation to accompany isotopic exchange between deuterium and 2,2-dimethylbutane. Probably, then, an adsorbed allylic species is not required for deactivation.

12. Benson, J. E., and Boudart, M., *J. Catal.* **4**, 704 (1965).

13. Ebisuzaki, Y., Kass, W. J., and O'Keefe, M., *J. Chem. Phys.* **49**, 3329 (1968).

14. McCabe, R. W., and Schmidt, L. D., *Surface Sci.* **60**, 85 (1976).

15. Merrill, R. P., American Chemical Society, Chemical Congress of North American Continent, Mexico City, December 1–5, 1975.

16. Matsushima, T., and White, J. M., National Meeting of the American Chemical Society, March 21–27, 1977.

17. Reference (*1*) Table 3, Footnote *h*. There is, however, some possibility that further reduction of any surface oxide by adsorbed hydrogen may have occurred during heating from 100 to 450°C.