

Pt/SiO₂

V. The Effect of Pretreatment on Apparent Structure Sensitivity for Methylcyclopropane Hydrogenation Activity and Selectivity

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The hydrogenation activity and selectivity of a set of Pt/SiO₂ catalysts, ranging in percentage of metal exposed from 6.3 to 81%, has been investigated for methylcyclopropane as a function of the pretreatment conditions. All catalysts had been originally reduced in hydrogen and stored in air. These catalysts were then subjected to an initial oxygen pretreatment at 300°C for 0.5 hr, followed by a purge of helium at 25°C for 0.25 hr. Samples were then successively reduced in hydrogen for 1 hr at temperatures ranging from 25 to 480°C. The turnover frequencies on each catalyst vary considerably as hydrogen pretreatment conditions are changed. This variation consists of high activity for room temperature pretreatment, passing through a minimum in the region of 200°C, and again increasing for temperatures greater than 250°C. The results show that any of three types of apparent structure sensitivity (i.e., none, increasing activity with percentage exposed-Type 1, decreasing activity with percentage exposed-Type 2) can be obtained with these catalysts depending on pretreatment conditions.

INTRODUCTION

This paper reports the influence of pretreatment procedures, particularly reduction in hydrogen, on the activity and selectivity of a series of Pt/SiO₂ catalysts, previously described (1, 2, 3), for methylcyclopropane hydrogenation. This is a particularly convenient reaction to use as a probe because of its prior use for similar purposes, experimental convenience, and because a catalytic selectivity function between iso- and *n*-butane products is involved.

Our initial work was with cyclopropane and it was noted at that time that catalysts pretreated in hydrogen at temperatures about 200°C were very low in activity and that reduction temperatures in flowing H₂ (2 hr) of 300°C or higher were required for stable and reproducible activity behavior (4). These experiments were carried out primarily with a single catalyst of the series, 40-SiO₂-PtCl-L,⁴ and the temperature range investigated was 180 to 450°C. All subsequent experiments with

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⁴ Catalyst notation: 40 = percentage exposed (*D_h*); SiO₂ = Davison Grade 62 silica support; PtCl = prepared by impregnation, H₂PtCl₆(aq); IonX = prepared by ion exchange with Pt(NH₃)₄²⁺; L = 70-80 mesh, S = 120-140 mesh (1).

the cyclopropanes were conducted after reduction at 350°C in flowing hydrogen for 2 hr (3). In view of this early result and the pronounced effect of pretreatment conditions on the behavior of these catalysts for isotopic exchange between cyclopentane and deuterium (5), a systematic investigation of catalyst pretreatment effects on the hydrogenation of methylcyclopropane was undertaken.

EXPERIMENTAL

The details of reagents, purification procedures, apparatus, and analytical methods have been given previously (3). In the present experiments from 0.1 to 0.4 g of each catalyst sample, typically stored in air from 6 to 18 months, was placed in the flow reactor system and subjected to an initial oxygen pretreatment at 300°C for 0.5 hr, followed by a purge of helium at 25°C for 0.25 hr. Hydrogen was then passed over the catalyst at 25°C for 1 hr, normally at about 30 cm³/min.⁵ The catalyst activity was then evaluated by passing a 14:1 mixture of hydrogen:methylcyclopropane over the sample at 0°C and 1 atm. Such conditions gave conversions on the order of 5 to 10% so that rates and turnover frequencies were evaluated directly. In addition, the compositions of *n*- and isobutane in the effluent were determined, so catalyst selectivity as well as activity was measured in this test. After this first activity determination following the 25°C hydrogen pretreatment, the catalyst was reoxidized at 300°C for 0.5 hr following a brief helium purge at 25°C. Hydrogen reduction was then repeated at a higher temperature, and the hydrogenation activity was redetermined under the standard reaction conditions of 0°C and 14:1 hydrogen:hydrocarbon. The full procedure for these pretreatment experiments on a given sample is given in Table 1.

⁵ Oxygen content of the hydrogen was less than 0.1 ppm in all cases.

TABLE 1
A Typical Pretreatment Experiment

Run	Conditions
a	O ₂ , 300°, 0.5; He, 300°C, 0.25; H ₂ , 25°, 1; React at 0°C
b	O ₂ , 300°, 0.5; He, 300°C, 0.25; H ₂ , 135°, 1; React at 0°C
c	O ₂ , 300°, 0.5; He, 300°C, 0.25; H ₂ , 260°, 1; React at 0°C
d	O ₂ , 300°, 0.5; He, 300°C, 0.25; H ₂ , 370°, 1; React at 0°C
e	O ₂ , 300°, 0.5; He, 300°C, 0.25; H ₂ , 480°, 1; React at 0°C
f	O ₂ , 300°, 0.5; He, 300°C, 0.25; H ₂ , 25°, 1; React at 0°C

The reproducibility of turnover frequency measurements was good and in accord with those reported previously (3); activity maintenance was excellent, and no deactivation was noted in any of the experiments reported here (6).

RESULTS

Hydrogen Pretreatment

The results of these pretreatment experiments for five of the 10 samples of the original Pt/SiO₂ series are shown in Figs. 1 and 2. These samples encompass the entire range of percentage of metal exposed of the full series. Shown on the figures are

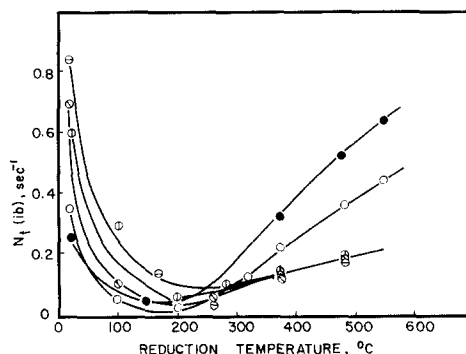


FIG. 1. Isobutane turnover frequency at 0°C as a function of hydrogen pretreatment temperature: ⊖, 7.1-SiO₂-PtCl-S; ⊕, 27-SiO₂-IonX-S; ⊙, 40-SiO₂-PtCl-S; ⊗, 63-SiO₂-IonX-S; ●, 81-SiO₂-IonX-S.

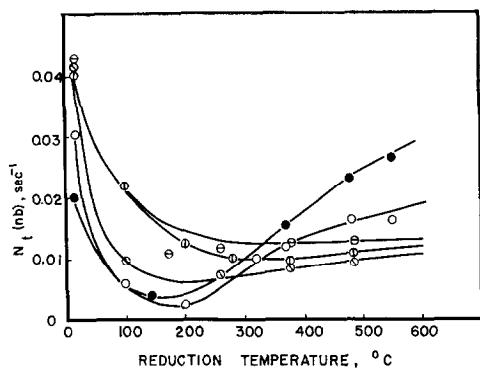


FIG. 2. *n*-butane turnover frequency at 0°C as a function of hydrogen pretreatment temperature.

the turnover frequencies for isobutane (Fig. 1) and *n*-butane (Fig. 2) formation plotted vs the temperature of reduction.

It is evident that the hydrogen pretreatment conditions have a significant influence on the activity of these catalysts. Turnover frequencies for both iso- and *n*-butane are high at low pretreatment temperatures, pass through a minimum in the region of 150 to 200°C, and increase as the pretreatment temperature increases. The increase is proportionately greater for catalysts of $D_h > 50$ in the region above 300°C and continues up to 550°C pretreatment.⁶ Note also that both the iso- and *n*-butane reactions are essentially structure insensitive on catalysts of $D_h < 50$ following pretreatment above 300°C.

The activities of the series of catalysts as a function of D_h for a given pretreatment temperature are presented in Figs. 3 and 4 for isobutane and *n*-butane reactions, respectively. To avoid clutter only the limiting low and high temperature results are given, but it is seen in each case that the apparent structure sensitivity of activity depends on pretreatment conditions, changing from Type 2 to Type 1 as the reduction temperature is increased. It is also evident

⁶ There is a slight decline in turnover frequency for both reactions for pretreatment temperatures greater than 550°C due to sintering of the metal surfaces.

from Figs. 1 and 2 that there is a range of reduction temperatures in the vicinity of 250 to 300°C where both reactions are nearly structure insensitive over the entire range of D_h . Hence we may induce *any* type of apparent structure sensitivity for the hydrogenation of methylcyclopropane on these catalysts by appropriate choice of the temperature of reduction in hydrogen. Similar results obtain for the selectivity, (isobutane/*n*-butane), as shown in Fig. 5. The most pronounced difference here is between low and high temperature pretreatments; the trends and magnitude of selectivity for reductions at 370 and 480°C are quite similar.

The activation energies for isobutane and *n*-butane formation reactions were evaluated for catalyst 40-SiO₂-PtCl-S for low-temperature pretreatment conditions and compared with our previously reported values (3) obtained after high-temperature reduction. The results are given in Table 2;

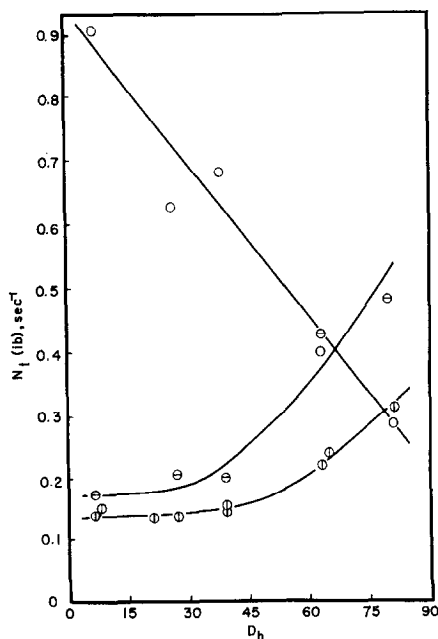


FIG. 3. Structure sensitivity at 0°C, isobutane formation, for low and high pretreatment temperatures: O, H₂ reduction at 25°C; ⊙, H₂ reduction at 370°C; ⊗, H₂ reduction at 480°C.

within experimental error there is no difference in the two sets of values. This suggests that the variation in turnover frequency resulting from different pretreatments resides mainly in the preexponential factor, but the relatively large uncertainties in the activation energy results preclude an unequivocal conclusion to this effect.

Structure-sensitive behavior depends on the environment of surface metal atoms, and it is clear that hydrogen pretreatment temperature has a significant effect on this environment. The differences between high- and low-temperature environments may be due either to structural or chemical factors, and a series of experiments was conducted to investigate the latter possibility.

Other Pretreatment Experiments

The high activity levels measured at low pretreatment temperatures could be suggestive of the influence of an impurity promoter which was removed at high temperatures. To investigate this, catalyst ac-

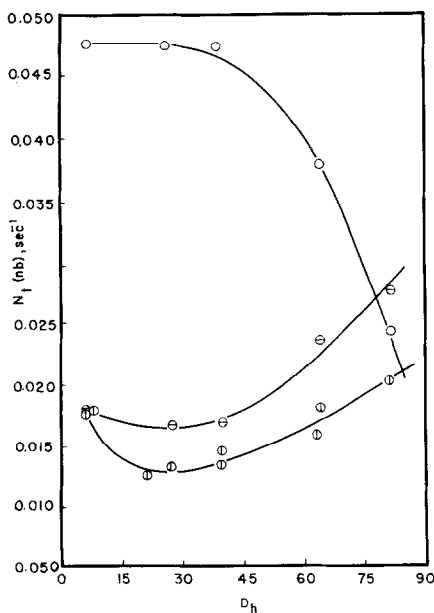


FIG. 4. Structure sensitivity at 0°C, *n*-butane formation, for low and high pretreatment temperatures.

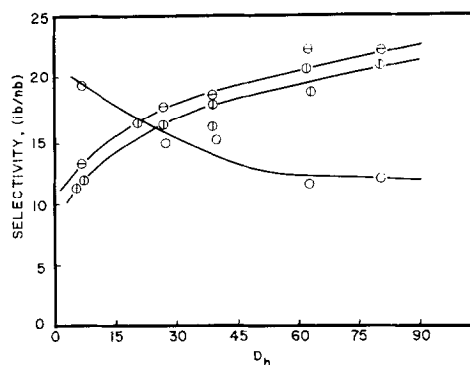


FIG. 5. Structure sensitivity of selectivity, (isobutane/*n*-butane), at 0°C for low and high pretreatment temperatures.

tivity was compared for low-temperature pretreatment before and after high-temperature reduction (a and f in Table 1). The turnover frequencies for both conditions are given in Table 3a, where it is apparent that turnover frequencies remained unchanged after the high-temperature treatment with the exception of 7.1-SiO₂-PtCl-S. For this catalyst the overall activity decreased by about 40% after high-temperature reduction.

A plausible hypothesis for the behavior of 7.1-SiO₂-PtCl-S is that low-temperature reduction is not sufficient to remove chloride from very low percentage-exposed catalysts, and the reduced activity is due to removal of chloride at high temperatures. Accordingly, after run f this sample was treated in flowing Cl₂, 25°, 0.5; O₂, 300, 0.5; He, 25°, 0.25; H₂, 25, 1. The activity of the catalyst was not affected by this treatment, as shown in Table 3b.

Several catalysts were examined for a pretreatment consisting of O₂, 300°, 0.5; He, 25°, 1; H₂, 25°, 1; He, 480°, 1 in comparison with those with a final reduction at 480°C in H₂. Table 4 indicates that the activities for 480°, He are in excellent agreement with those for 480°, H₂, so high-temperature treatment in an inert gas atmosphere after reduction in hydrogen at room temperature is equivalent to hydro-

TABLE 2

Activation Energies for Low- and High-Temperature Reduction Procedures, 40-SiO₂-PtCl-S

Pretreatment	<i>E</i> (kJ/mol)	
	iso-C ₄	<i>n</i> - C ₄
O ₂ , 300°, 0.5; H ₂ , 370°, 1 ^a	39.6 ± 2.3	43.4 ± 2.1
O ₂ , 300°, 0.5; H ₂ , 25°, 1	34.9 ± 4.2	43.5 ± 6.0

^a As reported in Ref. (3).

gen treatment at the same temperature. Thus it would appear that temperature is a controlling variable in these pretreatment experiments. A separate series of experiments on catalysts 81-SiO₂-IonX-S and 40-SiO₂-PtCl-S at reduction temperatures of 25 and 135°C revealed that the duration of hydrogen pretreatment beyond 1 hr had no effect on turnover frequency or selectivity for methylcyclopropane hydrogenation at the test reaction conditions (6).

After exposure to hydrogen at high temperature a number of samples were exposed to O₂, 25°, 0.25; He, 25°, 0.25; H₂, 25°, 1. This pretreatment is equivalent to an hydrogen-oxygen titration experiment. Benson and Boudart (7) proposed that all of the adsorbed oxygen will be removed by hydrogen titration at room temperature, forming water which is adsorbed by the support. An example of the effect of this pretreatment is given in Table 5 for 40-SiO₂-PtCl-S. The brief exposure to oxygen at room temperature does not change activity or selectivity from the values determined after high-temperature hydrogen pretreatment. Since high-temperature pretreatment in hydrogen ensures a surface devoid of water or oxygen, the agreement in activity after the titration experiment verifies that oxygen adsorbed at room temperature is completely removed by hydrogen at room temperature, and the water that is formed has no effect on the

activity of this catalyst.⁷ Similarly, exposure of a catalyst to the hydrogen-oxygen titration has little effect upon activity or selectivity for isotopic exchange between cyclopentane and deuterium [Ref. (5), Fig. 7]. Comparison of the activity of catalyst 40-SiO₂-PtCl-S evaluated after a titration experiment with the activity evaluated after the catalyst has been exposed to oxygen at 300°C (run a in Table 1) indicates that the oxidation of the catalyst at 300°C alters the surface environment of the catalyst, while a brief oxidation at 25°C on a clean catalyst surface has no effect on the surface structure of the catalyst. A final possible factor which might influence activity and selectivity is the retention on platinum of strongly bonded water (8). For example, water might be retained during pretreatment by hydrogen at 25°C but not at the higher temperatures.

DISCUSSION

The results presented above show that the apparent structure sensitivity of methylcyclopropane hydrogenation cannot be determined in detail using a single set of pretreatment conditions. Since the activation energies of both reactions are approximately independent of both *D_h* and pretreatment conditions, an interpretation in terms of structural effects seems warranted. To determine whether the observed behavior is due to surface topography alone, however, other factors must first be eliminated. These are discussed in turn below.

Effect of Chlorine

From the results it would appear that the presence of chlorine on Pt/SiO₂ catalysts does not promote isomerization of methylpropane. Chloride compounds, however, have been shown by Dorling *et al.* (9) to affect ethylene hydrogenation over plati-

⁷ Large amounts of water, considerably in excess of monolayer coverage, will deactivate these catalysts (6).

TABLE 3a
Turnover Frequencies Evaluated at Pretreatment Runs a and f

Catalyst	Pretreatment conditions			
	Run a		Run f	
	$(N_t)_{\text{iso-butane}}$	$(N_t)_{\text{n-butane}}$	$(N_t)_{\text{iso-butane}}$	$(N_t)_{\text{n-butane}}$
7.1-SiO ₂ -PtCl-S	0.860	0.045	0.548	0.033
27-SiO ₂ -IonX-S	0.614	0.043	0.456	0.042
40-SiO ₂ -PtCl-S	0.695	0.046	0.687	0.051
63-SiO ₂ -IonX-S	0.357	0.032	0.404	0.043
81-SiO ₂ -IonX-S	0.290	0.024	0.320	0.030

num on silica catalysts that were pretreated at low temperatures (below 250°C) in hydrogen, and we have observed a similar effect for propene hydrogenation. High activity for ethylene hydrogenation was reported on catalysts prepared with chloroplatinic acid, but for a hydrogen pretreatment temperature of 450°C chloride compounds were desorbed in the form of HCl, and the activity of the H₂PtCl₆ catalysts was comparable to catalysts prepared by ion exchange with Pt(NH₃)₄²⁺ (9).

A comparison of pretreatment experiments on impregnated and ion-exchanged catalysts here indicates little effect of chloride compounds. Activity was high on catalysts 40-SiO₂-PtCl-S and 7.1-SiO₂-PtCl-S after the low-temperature hydrogen pretreatment as well as for catalyst 27-SiO₂-IonX-S, which was prepared without any chloride compounds. The activities of all three catalysts decreased when the hydrogen pretreatment temperature was increased. The chloride content of catalyst 7.1-SiO₂-PtCl-S was examined before and after a pretreatment in hydrogen at 500°C, which was sufficient to reduce chloride from 0.11 to 0.05% (10). The low temperature pretreatment in hydrogen was again examined after the catalysts had been exposed to hydrogen at 480°C. Catalyst 40-SiO₂-PtCl-S exhibited the same activity as after the initial low-temperature

pretreatment, so the desorption of chloride compounds at 480°C had no effect on the activity. When catalyst 7.1-SiO₂-PtCl-S was exposed to the same pretreatment procedure as catalyst 40-SiO₂-PtCl-S, however, the activity after the second low-temperature pretreatment condition was considerably lower than it was after the initial low-temperature pretreatment. This catalyst was then exposed to Cl₂, 25°, 0.25; no effect on the rates was noted (Table 3b). Thus, the presence of chloride compounds on the Pt/SiO₂ catalysts apparently does not affect activity for methylcyclopropane hydrogenation at any hydrogen pretreatment temperature, and the high activities observed on initial low-temperature pretreatment are not due to the interaction of chlorine.

TABLE 3b
Effect of Cl₂ Addition on Catalyst 7.1-SiO₂-PtCl-S

Pretreatment conditions	$(N_t)_{\text{iso-butane}}$ [reactions/ (sec-site)]	$(N_t)_{\text{n-butane}}$ [reactions/ (sec-site)]
Run f in Table 1	0.548	0.033
Run f followed by: Cl ₂ , 25°, 0.5; O ₂ , 300°, 0.5; H ₂ , 25°, 1	0.606	0.034

TABLE 4
Turnover Frequencies Evaluated after Exposure to a High-Temperature Helium Treatment

Catalyst	Pretreatment conditions			
	O ₂ , 300°, 0.5; H ₂ , 480°, 1		O ₂ , 300°, 0.5; H ₂ , 25°, 1; He, 480°, 1	
	(<i>N_t</i>) _{iso-butane}	(<i>N_t</i>) _{n-butane}	(<i>N_t</i>) _{iso-butane}	(<i>N_t</i>) _{n-butane}
7.1-SiO ₂ -PtCl-S	0.165	0.0126	0.148	0.0110
40-SiO ₂ -PtCl-S	0.177	0.0117	0.198	0.0109
63-SiO ₂ -IonX-S	0.420	0.0186	0.468	—

Effect of Oxygen

The interaction of oxygen and hydrogen has been studied extensively on platinum catalysts, mostly with respect to the characteristics of hydrogen-oxygen titration. For this series of catalysts we have previously reported on the reactivity of surface oxygen with hydrogen and its dependence on D_h (1). One conclusion was that exposure of a clean platinum surface to oxygen for a short time results in only partial adsorption, leaving gaps of pure metal on the surface. Hydrogen is readily able to dissociate on the metal and react with the surface oxygen. As oxygen is adsorbed further, however, either by long-term storage in air or by oxidation at 300°C, the gaps in the surface layer are filled, and penetration into the lattice occurs. This

latter effect is structure-sensitive and most pronounced on higher percentage-exposed catalysts. Comparison of the first two entries of Table 5 supports the hypothesis that all the adsorbed oxygen resulting from short exposure of a clean surface is removed by hydrogen at room temperature.

The very high activity reported for the third entry in Table 5 is that of a catalyst stored in air for 1 year and further treated in O₂, 300°, 0.5 before room temperature reduction. One might reasonably suspect this to be the result of strongly adsorbed oxygen, not removed at the mild reduction conditions. The present data are not definitive in this regard, but there are some differences with our previous results concerning the reactivity of surface oxygen (1). With the exception of 7.1-SiO₂-PtCl-S, discussed below, each catalyst has essentially the same activity after low-temperature pretreatment of the stored, oxidized sample (Run a, Table 1) after low-temperature reduction following H₂, 480°, 1; O₂, 300°, 0.5 (Run f, Table 1). The turnover frequencies on catalysts 81-SiO₂-IonX-S and 63-SiO₂-IonX-S are much lower than on 40-SiO₂-PtCl-S and 27-SiO₂-IonX-S at the low-temperature pretreatment conditions. This could be due to the fact that not all the oxygen has been removed by H₂, 25°, 1, since a trapped pulse of hydrogen on these high-percentage-exposed catalysts required over 500 min to reduce the catalyst completely (1). The

TABLE 5

Turnover Frequencies Evaluated after Short-Time Exposure to Oxygen at Room Temperature, 40-SiO₂-PtCl-S

Pretreatment	(<i>N_t</i>) _{iso-butane}	(<i>N_t</i>) _{n-butane}
O ₂ , 300°, 0.5; H ₂ , 480°, 1; O ₂ , 25°, 0.25; H ₂ , 25°, 1	0.210	0.016
O ₂ , 300°, 0.5; H ₂ , 480°, 1	0.177	0.012
O ₂ , 300°, 0.5; ^a H ₂ , 25°, 1 ^a	0.687	0.051

^a Run f of Table 1.

turnover frequencies on catalyst 81-SiO₂-IonX-S, however, are independent of the duration of low-temperature pretreatment in flowing hydrogen for any period beyond 1 to 10 hr, and those on 40-SiO₂-PtCl-S are independent of pretreatment time for 1 to 4 hr. These results suggest that either all the oxygen is removed by hydrogen, that a steady-state condition is attained, or that the hydrocarbon possibly aids in the reduction. We know that higher-percentage-exposed catalysts are more difficult to reduce because of incorporation of oxygen into the lattice (1), so it is possible that the exact mechanism of oxygen removal is dependent upon D_h .

For catalyst 7.1-SiO₂-PtCl-S, the activity was much higher for the stored, oxidized sample, Run a, Table 1, than for Run f. This is due, at least in part, to the value of percentage exposed used in calculating the turnover frequency. The figure of 7.1% was determined for catalysts which had been exposed to temperatures up to 450°C. It has been shown (1) for a similar catalyst in the series, 6.3 SiO₂-PtCl-L, that the percentage exposed of the stored, oxidized sample was about 30% greater after low-temperature reduction only than after high-temperature treatment. If we apply the same correction to 7.1-SiO₂-PtCl-S, the percentage exposed of the stored, oxidized catalyst is 9.2%, and the overall turnover frequency for Run a in Table 3a is reduced to 0.69 from 0.91 sec⁻¹. This is in relatively good agreement with the value of 0.58 sec⁻¹ (based on 7.1%) reported for Run f.

Nature of the Active Surface: Low Temperature and High Temperature

Although the catalysts appear to be completely reduced at low temperatures in hydrogen, the activities are very different from those observed after high-temperature reduction. We have previously shown (3) that the fraction of low-coordination atoms,

such as edges and corners of a perfect crystallite, is related to the activity of these catalysts for cyclopropane and methylocyclopropane hydrogenation.

Ratnasamy *et al.* (11) have concluded from radial electron distribution data that the adsorption of oxygen on supported platinum at room temperature, following H₂, 400°, 8, creates a surface with many vacancies in the outer layer. When hydrogen at 100°C is introduced to such surfaces, the ratio of metal atom to metal vacancy is reported to be unity (12), hence the surface contains many more low-coordination sites than would be expected on the basis of perfect crystallite models. For our catalysts, then, exposure to oxygen at 300°C followed by hydrogen reduction at 25°C would produce a high concentration of vacancies according to this model. As the temperature of the pretreatment in hydrogen or an inert gas is increased, the platinum surface anneals to a more ordered structure, decreasing the concentration of vacancies. Now for the initial low-temperature pretreatment, the isobutane and *n*-butane turnover frequencies are high but decrease when the temperature of pretreatment is increased to 250°C as shown in Figs. 1 and 2. The rapid decline in the rates with increasing pretreatment temperature in hydrogen to 250°C does correlate with this view of the concentration of vacancies on the surface. At any given pretreatment temperature, after sufficient time the surface will contain an equilibrium concentration of vacancies, and pretreatment beyond this point would be unimportant. Present results are also in accord with this hypothesis, because the turnover frequencies are independent of pretreatment time beyond 1 hr. After each oxidation at 300°C the platinum surface will tend to random order, increasing the concentration of vacancies on the surface, again in accord with the reversibility of the pretreatment experiments observed experimentally. Corresponding results for these catalysts have been obtained

for isotopic exchange between cyclopentane and deuterium (5).

Similar behavior has also recently been reported by Hanson (13) for cyclohexene hydrogenation on Pt/SiO₂. His results indicate that the turnover frequency increased from 1.79 (400°C, H₂ reduction) to 2.30 sec⁻¹ after the catalyst had either been stored in air or oxidized at 300°C for 0.5 min followed by a low-temperature hydrogen pretreatment. Activity increase is attributed to the reconstruction of the platinum surface when the catalyst is exposed to oxygen followed by low-temperature hydrogen pretreatment. Exposure of the oxidized catalyst to a 400°C pretreatment in hydrogen decreased activity to 1.80 sec⁻¹, again suggestive of annealing of the surface on exposure to high-temperature hydrogen treatments.

In summary, a surface model based on concentration of vacancies seems to correlate well with the activity of Pt/SiO₂ for these hydrogenation and exchange reactions on catalysts reduced below 250°C. This view, however, is not compatible with the increasing activity of catalysts reduced above 300°C here, nor is it in accord with our results on propene hydrogenation (3). The latter reaction is Type 1 structure sensitive, as is methylcyclopropane hydrogenation, but the largest increase in turnover frequency occurs for the lowest-percentage-exposed catalysts and thus does not appear to be correlated with the frac-

tion of low-coordination atoms on the surface.

ACKNOWLEDGMENTS

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