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Pt/Al_2O_3

II. Activity and Selectivity Patterns for Methylcyclopropane Hydrogenolysis and Cyclopentane Exchange with Deuterium: Comparison with Pt/SiO_2

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The activity and selectivity of a series of Pt/Al_2O_3 catalysts for the hydrogenolysis of methylcyclopropane and exchange between deuterium and cyclopentane have been determined. The series investigated included the range from 4.1 to 106 percentage exposed of platinum (D_h). Turnover frequencies, N_t, for methylcyclopropane hydrogenolysis at 0°C determined after high-temperature pretreatment ($H_2, T_p > 350°, 1$) were independent of D_h as were the activation energies for i-butane and *n*-butane formation, 36.4 ± 2 and 42.3 ± 4 kJ mol^{-1}, respectively. For cyclopentane–deuterium exchange at 81°C the isotopic distribution patterns were clearly dependent upon D_h, particularly noted as a decrease in $d_{10}/(d_2–d_{10})$ with increasing D_h. Activation energy for overall exchange was about 75 kJ mol^{-1} with some dependence on D_h for the individual distributions. Catalyst pretreatment conditions affect activity for both reactions. For methylcyclopropane a minimum is observed for T_p about 200°C, with an inversion in ordering of N_t vs D_h at higher temperatures, as previously observed for Pt/SiO_2. For cyclopentane, N_t decreases with increasing D_h at T_p = 450°C. The method of catalyst preparation also showed some effect on N_t for methylcyclopropane, but not for cyclopentane. A summary discussion of the factors responsible for various pretreatment effects on Pt/SiO_2 and Pt/Al_2O_3 is given for both reactions.

INTRODUCTION

In previous studies of this series (*1*, *2*) we reported the detailed characterization of a series of Pt/SiO_2 catalysts ranging in percentage metal exposed from 6.3 to 81. Detailed information on activity and selectivity patterns (structure sensitivity) for the hydrogenolysis of methylcyclopropane and cyclopropane, the hydrogenation of propylene, and isotopic exchange between cyclopentane and deuterium are given in Ref. (*3*–*5*) and for oxidation of carbon monoxide in Ref. (*6*). The present study deals with a corresponding activity/selectivity investigation for the hydrogenolysis of methylcyclopropane and deuterium exchange with cyclopentane on a series of Pt/Al_2O_3 catalysts whose preparation and characterization are given in Ref. (*7*).

EXPERIMENTAL

The catalysts investigated in this study were those described in Table 1 of Ref. (*7*), with the addition of one, 32–Al_2O_3–PtCl, 0.234 wt% Pt, prepared by impregnation to incipient wetness with H_2PtCl_6;air,500°,1; H_2,500°,2.5 and additional PtNN preparations of D_h = 9, 22, 53, and 95.5%. In reporting activity and selectivity patterns here, only the percentage exposed evalu-

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ated by hydrogen chemisorption, D_h, will be employed.

The experimental methods employed for turnover frequency measurements for methylcyclopropane (MCP) hydrogenolysis have been described in (*3*) and (*5*). Experimental conditions for these measurements were 0°C with a feed mixture of approximately 16:1 H_2:MCP; low conversion levels (<15%) were maintained in all experiments.

The normal pretreatment sequence consisted of either heating the catalyst in O_2, 300°,0.5;He,300°,0.25;H_2,370°,1 or O_2,300°, 0.5;He,300°,0.25;H_2,480°,1. In the sequence of experiments involving variable reduction temperatures the sequence was O_2,300°,0.5;He,300°,0.25 and then H_2,25 to 480°,1 in 50° increments. After pretreatment at each temperature level the catalyst was cooled in hydrogen to 0°C and the reaction measurement carried out (*5*). The temperature range from 0 to 35°C was employed in determination of activation energies for methylcyclopropane hydrogenolysis.

Isotopic exchange of cyclopentane was carried out also by the same methods detailed earlier (*4*), primarily at 81 but also at 67.5 and 55.0°C. The total pressure was 1 atm and the ratio cyclopentane:D_2 was 0.0093. In most experiments for exchange the catalysts were given slightly different pretreatments than in the MCP series; here the standard was O_2,300°,0.5;He,300°,0.2; H_2,300°,1;He,450°,1 with cooling in He to reaction temperature. The other pretreatments were O_2,300°,0.5;He,100°,0.2;H_2, 100°,1 and O_2,300°,0.2;He,300°,0.2;H_2, 100°1 and O_2,300°,0.2;He,300°,0.2;H_2, cases. Rates for both methylcyclopropane and cyclopentane reactions are given in terms of the turnover frequency, N_t, molecules reacted (or exchanged) per second per surface atom of platinum. N_t for catalysts of experimental D_h > 100 were calculated on the basis of 100% exposed.

RESULTS

Effects of Percentage Exposed on Turnover Frequency and Selectivity in the Hydrogenolysis of Methylcyclopropane on Pt/Al_2O_3

Turnover frequencies for the formation of the major product, i-butane, at 0°C are shown in Fig. 1 for pretreatment H_2,370°,1

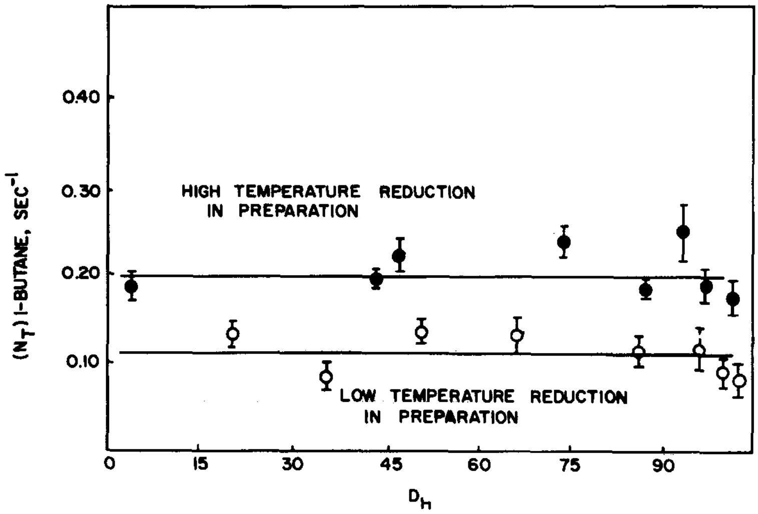

FIG. 1. N_t i-butane vs percentage exposed for methylcyclopropane hydrogenolysis at 0°C on the Pt/Al_2O_3 series, pretreatment H_2,370°,1. Solid circles for catalysts reduced at 400–500°C in preparation, open circles for catlaysts reduced at 300°C in preparation.

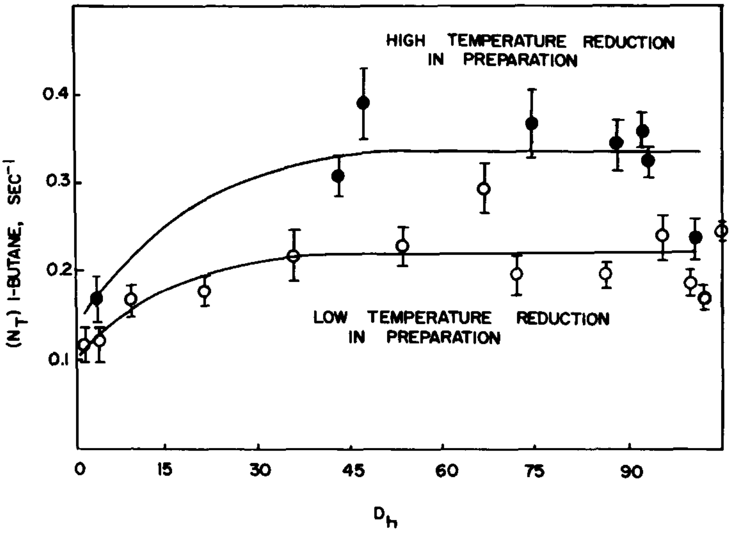

FIG. 2. N_t i-butane vs percentage exposed for methylcyclopropane hydrogenolysis at 0°C; pretreatment H_2,480°,1. Symbols as for Fig. 1.

and Fig. 2 for H_2,480°,1.[6] Corresponding selectivity data (i-butane rate/*n*-butane rate) for both sets of pretreatment conditions are shown in Fig. 3. These data on N_t indicate two different levels of activities for the series of catalysts which are caused by the method of preparation rather than pretreatment conditions. All the catalysts, after impregnation with $[Pt(NH_3)_3(NO_2)_2](NO_2)$ solution in preparation, were calcined and then reduced at two basic temperature levels, as shown in Table 1 of the previous paper (*7*). For those catalysts that were reduced at a higher temperature (400 ~ 500°C) in preparation, the activities are higher than those catalysts reduced at a lower temperature (300°C). However, the selectivity ratio is independent of the method of preparation and constant with an average value of about 15 for the series, as shown in Fig. 3.

The chloride-containing catalyst, 32.0–Al_2O_3–PtCl, gave after H_2,480°,1 an initial large value of N_t with enhanced formation of *n*-butane (selectivity was 3); however the *n*-butane activity declined over a period of 1 hr while i-butane activity remained constant. The final steady values for N_t were 0.17 and 0.026 sec^{-1} for i-butane and *n*-butane, respectively, and were similar to those for PtNN catalysts of comparable D_h. This enhanced activity for *n*-butane formation has been shown to be directly related to the chloride content of the catalyst; the rate of formation of i-butane showed no decline with time and was independent of chloride content.

There is an apparent compensation between the extremes of preparation conditions and pretreatment conditions. Those catalysts reduced at low temperature in preparation and high temperature in pretreatment have the same activity as those reduced at high temperature in preparation and low temperature in pretreatment. This is shown for the major reaction product, i-butane, in Fig. 4.

Effect of Pretreatment Conditions on Catalytic Activity for the Hydrogenolysis of Methylcyclopropane.

We have previously shown (*4, 5*) that the structure-sensitive behavior of Pt/SiO_2 was dependent upon the temperature of pre-

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[6] The sequence of O_2,300°,0.5;He,300°,0.25 was always conducted prior to reduction in hydrogen for both reactions, so it is not repeated here or subsequently.

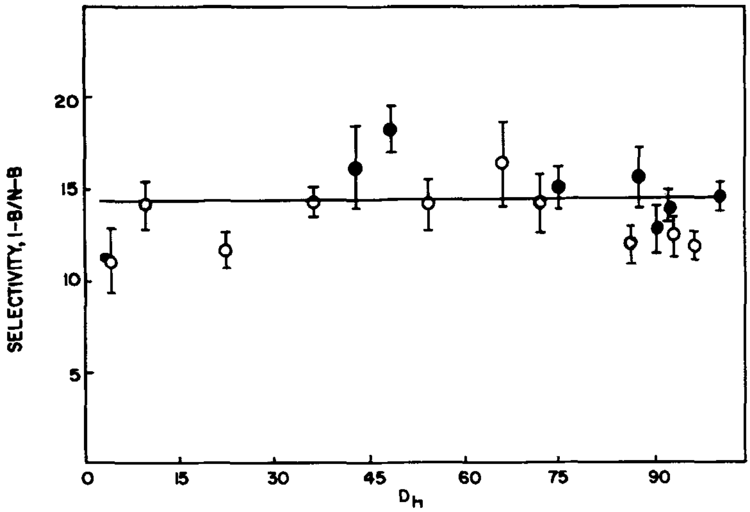


FIG. 3. Selectivity for methylcyclopropane hydrogenolysis at 0°C. Open circles low-temperature reduction in preparation, pretreatment H_2,480°,1. Closed circles, high-temperature reduction in preparation, pretreatment H_2,370°,1.

treatment in hydrogen before carrying out the reaction, both for methylcyclopropane and cyclopentane. As mentioned before, one of the major objectives of the present study was to determine whether the same effect would be observed for the Pt/Al_2O_3 series.

Catalysts originally calcined and reduced in preparation and then stored in air were subjected to O_2,300°,1;He,300°,0.25 and then successively pretreated, H_2,1, at temperatures ranging from 25 to 480°C, after which N_t was evaluated. The results are illustrated in Fig. 5 for i-butane product; trends for n-butane were similar.

Several catalysts were examined for a pretreatment condition consisting of H_2; 300°,1;He,480°,1, essentially corresponding to that employed in the exchange experiments. The N_t results are given in Table 1 in

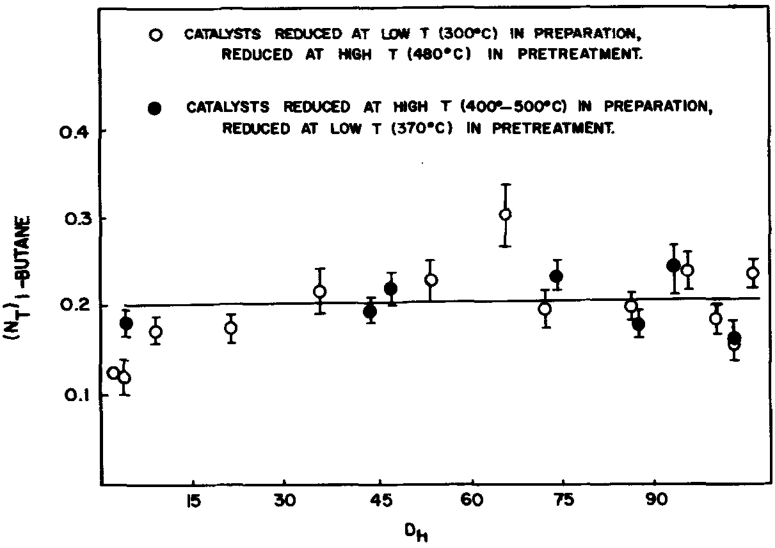


FIG. 4. Preparation and pretreatment combination effects for N_t i-butane.

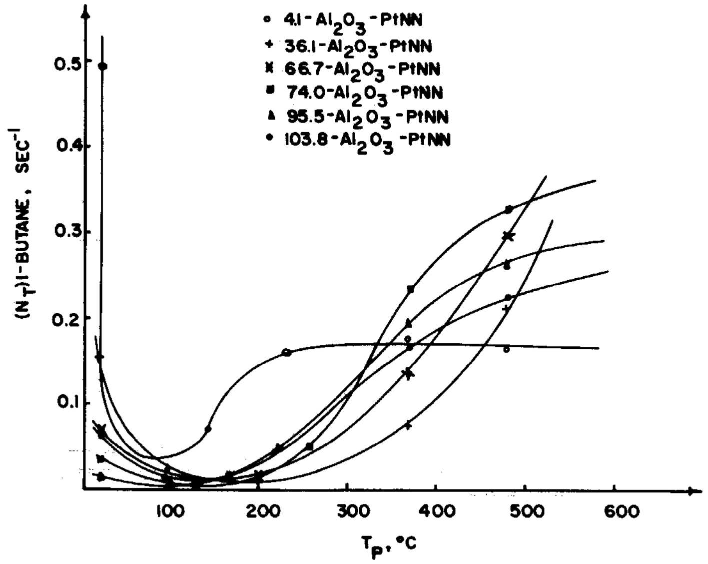


FIG. 5. The effect of pretreatment temperature upon N_t i-butane at 0°C for Pt/Al_2O_3.

comparison with H_2,480°,1. The values are very similar; hence temperature appears to be the controlling variable in pretreatment.

The i- and *n*-butane turnover frequencies were evaluated at four different temperatures in the range 0 to 35°C, after H_2,480°,1 on samples of 4.1, 36.1, 43.6, 88.4, 95.5, and 100.9 D_h. The activation energies are, as in the case of Pt/SiO_2, independent of D_h with average values of 36.4 ± 2.3 kJ mol^{-1} for i-butane and 42.3 ± 4.2 kJ mol^{-1} for *n*-butane. The resultant selectivities, of course, are also structure insensitive at all temperatures within this range and decrease from 15 at 0°C to about 9 at 35°C.

TABLE 1

Influence of Final Pretreatment Temperature on N_t for Hydrogenolysis of Methylcyclopropane.

Catalyst	Pretreatment conditions			
	O_2,300°,0.5 H_2,480°,1		O_2,300°,0.5 H_2,300°,1 He,480°,1	
	N_t i-b[a]	N_t *n*-b	N_t i-b	N_t *n*-b
4.1-Al_2O_3-PtNN	0.168	0.015	0.211	0.014
36.1-Al_2O_3-PtNN	0.215	0.015	0.277	0.013
66.7-Al_2O_3-PtNN	0.298	0.018	0.329	0.021
74.0-Al_2O_3-PtNN	0.310	0.020	0.260	0.019

[a] i-b, isobutane; *n*-b, *n*-butane.

These selectivity and activation energy results are in good agreement with other literature data for hydrogenolysis of methylcyclopropane on platinum (*8*).

The N_t values for Pt/SiO_2 are also in good accord with those reported elsewhere, as we have shown previously (*5*). However, Naccache *et al.* (*9*) claim a promotion of activity for methylcyclopropane hydrogenolysis when Pt is supported on NaY zeolite. At 22°C,1 atm, and hydrogen : methylcyclopropane of about 30 : 1 they report $N_t \simeq 1.0$ sec^{-1} for Pt/NaY, $D_h = 85$, versus $N_t = 0.01$ sec^{-1} for Pt/SiO_2, $D_h = 77$. At the same temperature with a molar ratio of 16, we have measured $N_t = 0.4$ sec^{-1} for Pt/SiO_2, $D_h = 40$. It would appear that their N_t, for Pt/SiO_2 at least, is anomalously low; the value reported for Pt/NaY is essentially the same as that obtained in this laboratory for Pt/SiO_2.

Isotopic Exchange between Cyclopentane and Deuterium on Pt/Al_2O_3

Operating parameters were adjusted to obtain conversions of no more than 5%. Slow deactivation was observed in most runs and N_t's were extrapolated to zero time on stream. The isotopic distribution patterns were independent of time. In later runs, there was usually no deactivation. We suspect that traces of oxygen may have been responsible for the observed deactivation. Similar deactivation by traces of oxygen was observed during hydrogenolysis of cyclopropane and hydrogenation of ethylene on 40–SiO_2–PtCl (*10*).

The values of N_t at 81°C (for 22 catalysts with D_h between 4.1 and 106%) were between 4.3 and 6.1 × 10^{-2} sec^{-1} except for 39.4–Al_2O_3–PtNN for which N_t was 3.3 × 10^{-2}; 66.7–Al_2O_3–PtNN, 3.7 × 10^{-2}; and 106–Al_2O_3–PtNN which was 3.1 × 10^{-2} sec^{-1}. In addition, 4.2–Al_2O_3–PtNN had $N_t = 9.9 \times 10^{-2}$ but accuracy in the measurement of such low values of D_h is not as good as for larger values and 4.1–Al_2O_3–PtNN gave $N_t = 6.1 \times 10^{-2}$ sec^{-1}. The average deviation in N_t between replicated pairs of runs was 0.005 sec^{-1}. Unlike the situation in the hydrogenolysis of methylcyclopropane, there was no significant difference in N_t between catalysts originally reduced at 300°C and those reduced at 400–500°C.

The effect of temperature on the isotopic distribution patterns obtained on 47.6–Al_2O_3–PtNN is shown in Fig. 6. Twelve other catalysts were examined with generally similar results. $E_a(1-10)$ (for formation of d_1–d_{10}) was 75 kJ mol^{-1} except that at $D_h \geq 96.7$ it was 67 kJ mol^{-1}. Of course the temperature range investigated was not large enough to provide E_a's of high accuracy. $E_a(10)$ (for formation of d_{10}) was 108 kJ mol^{-1} for $26.1\% \leq D_h \leq 94.2\%$ but $E_a(10)$ was smaller for low and high D_h. $E_a(5)$ was 78 kJ mol^{-1} with no trend with D_h. E_a (2–4) was 71 kJ mol^{-1} but probably a little lower at higher and low D_h. E_a (1) was 63 kJ mol^{-1} with no clear trend with D_h. Runs were duplicated on two catalysts. The spread between values was less than 4 kJ mol^{-1}. With a few exceptions, to be considered later, the activation energies given above were within ± 4 kJ mol^{-1} of the average values listed.

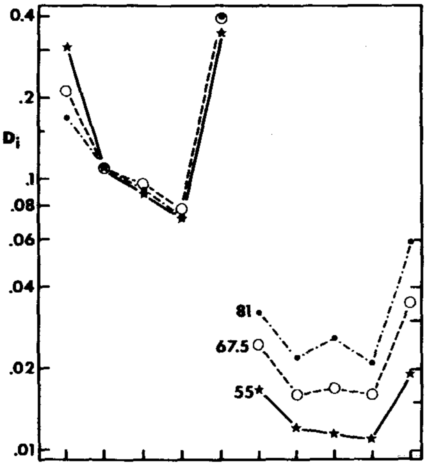


FIG. 6. The effect of temperature upon the isotopic distribution patterns in the exchange between cyclopentane and deuterium on 47.6–Al_2O_3–PtNN: $D_i = d_i/(d_f-d_{10})$ on y-axis vs number of deuterium atoms introduced. The patterns are shown for 81, 67.5, and 55°C.

Figure 7 exhibits the effect of D_h upon the amounts of various d_i expressed as fractions of the sum d_2 to d_{10}, $\sum_{2}^{10} d_i$. Cyclopentane-d_1 is excluded from consideration because its amount is of lower accuracy than that of the other exchanged species owing to the large correction for $^{13}C^{12}C_4H_{10}$. In 17 catalysts, with two exceptions, $\sum_{1}^{10} d_i$ was between 0.12 and 0.20 without a clear trend with D_h. The ratio d_6/d_9 is particularly structure sensitive and increases nearly monotonically from ~0.2 at $D_h = 26.1\%$ to ~0.85 at 100%. The values of the ratio for $D_h = 4.1$ and 4.2% are off this trend, being ~0.55.

Isotopic distribution patterns were obtained at 81°C for six Al_2O_3–PtNN catalysts, 4.2, 39.4, 46.1, 66.7, 94.2, and 106%, after three pretreatments, standard, H_2, 100°,1, and H_2,450°,1. In the latter two pretreatments, the catalysts were cooled to 81°C in hydrogen. Fresh samples of catalyst were employed for each run. Relative values of N_t are given in Table 2. The values of d_5 and d_{10} were about 20% larger after the H_2,450° treatment than after the

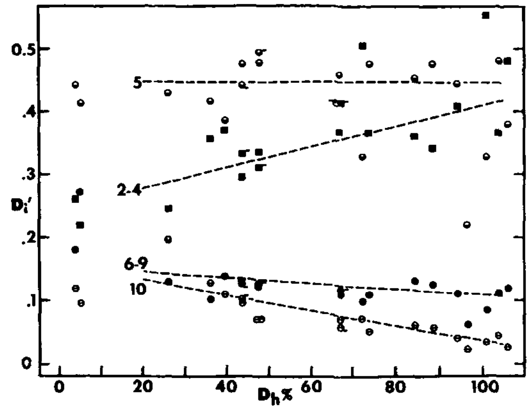


FIG. 7. Isotopic distribution patterns for cyclopentane exchanged on Al_2O_3–PtNN catalysts at 81°C. D_i' on the y-axis: $(d_2\text{–}d_4)/(d_2\text{–}d_{10})$, squares; $d_5/(d_2\text{–}d_{10})$, half-filled circles; $(d_6\text{–}d_9)/(d_2\text{–}d_{10})$, filled circles: $d_{10}/(d_2\text{–}d_{10})$, barred circles. On the x-axis: percentage exposed of platinum, D_h. In duplicate runs which are shown for 43.6–, 47.6–, and 66.7–Al_2O_3–PtNN, a bar is adjoined to the symbols for one of the runs.

standard pretreatment for the two catalysts of largest D_h. In general, however, the differences among the pretreatments at any given D_h were not large. After the isotopic distribution run on 36.1–Al_2O_3–PtNN, pretreated O_2,300°,0.5;H_2,100°,1, the catalyst was treated O_2,300°,0.5;H_2,450°,1 and then O_2,300°,0.5;H_2,100°,1. The isotopic distribution patterns were essentially identical for the first and second runs after H_2,100°, but N_t was larger in the second run by a factor of 3.3 and it was nearly as large as N_t for the standard pretreatment. After a run on 94.2–Al_2O_3–PtNN given the same pretreatment, the catalyst was pretreated O_2,300°,0.5;H_2,450°,1 and an isotopic distribution pattern was determined. The pattern and N_t were almost identical to those obtained on a fresh catalyst after the H_2,450° treatment.

Analysis of Carbonaceous Residues on the Catalysts during Deuterium Exchange with Cyclopentane

The nature and amount of hydrocarbons released by passage of hydrogen over the catalysts at successively higher temperatures were investigated by a method like that of number (4) previously used with Pt/SiO_2 catalysts (*4*). An isotopic exchange run was interrupted after 20 min on stream by evacuation to 10^{-2} Torr for 20 min. Helium was then passed through the catalyst bed for 10 min as the temperature was raised to 100°C and the released hydrocarbon was trapped in a small bed of silica gel (Davison Grade 62) at −196°C. The catalyst was isolated for 15 min while the collected sample of hydrocarbon was analyzed gas chromatographically. A flow of hydrogen through the catalyst bed was then established and effluent hydrocarbon was trapped for 30 min, the catalyst was isolated, and the hydrocarbon was analyzed. The hydrogen flow was reestablished, the catalyst was heated to 200°C for 20 min, and effluent hydrocarbon was trapped and analyzed. The process was then repeated at 300 and 450°C.

A similar run was made on the alumina support and also another on alumina in which helium flow was used throughout the run. Nearly the same results were obtained in the two runs. Unlike silica, alumina retained cyclopentane. About 6 μmol g^{-1}

TABLE 2

N_t for Isotopic Exchange between Deuterium and Cyclopentane at 81°C on Al_2O_3–PtNN Catalysts

D_h (%)	N_t^{0}[a] ($\times 10^2$)	$N_t(100°)$[b]$/N_t^0$	$N_t(450°)$[c]$/N_t^0$
4.2	9.9	1.0	0.6
6.3[d]	*11.1*	*2.9*	*1.0*
36.1	4.4	0.3	2.3
39.4	3.3	0.64	1.4
40-S	*8.7*	*1.0*	*0.9*
66.7	3.7	0.22	1.1
81	*11.4*	*0.23*	*1.4*
94.2	4.6	0.41	2.7
106	3.1	0.23	2.7

[a] Turnover frequency after the standard pretreatment.

[b] $N_t(100°)$ designates N_t after the pretreatment H_2,100°,1.

[c] $N_t(450°)$ designates N_t after H_2,450°,1.

[c] Italic values are for Pt/SiO_2 catalysts, taken from Ref. (*4*).

was released in helium at 100°C and about the same amount in hydrogen, mostly at 100°C.

In flowing hydrogen, larger amounts of hydrocarbon were released from Pt/Al_2O_3 and a little over one-half was released at 200°C. Only very small amounts were released at 300 and 450°C. The product was almost entirely cyclopentane. The retention of cyclopentane residues by catlaysts was calculated as that released during the treatment by hydrogen at 100°C and up, less that released by pure alumina during these steps. Uncertainty in just how to correct for adsorption on alumina introduces an error of $\pm 10\%$ into the resulting numbers.

Catalysts of $D_h = 39.4$ and 66.7% given the standard pretreatment of H_2,450°,1 led to values of molecules of cyclopentane retained per Pt_s of between 0.32 and 0.41, whereas for $D_h = 106$, the value was 0.20. The pretreatment H_2,100°,1 led to considerably smaller values. An attempted run with the catalyst of $D_h = 4.2\%$ led to values of the ratio of very low precision but the pretreatment H_2,100° clearly led to less release of cyclopentane.

DISCUSSION

Hydrogenolysis of Methylcyclopropane on Pt/Al_2O_3

From Figs. 1 and 2 it is seen that except for catalysts of extreme D_h (less than 15% or greater than 90%) the N_t's for i-butane do not depend upon D_h and this reaction is essentially structure insensitive. The selectivity is seen also to be independent of D_h and the same for both pretreatment conditions. Error bars shown on the figures represent the range of values obtained in repeat experiments; normally 6 to 10 replications were carried out for each catalyst. In Fig. 5 it is shown that only catalysts 4.1–Al_2O_3–PtNN and 36.1–Al_2O_3–PtNN have high activities after H_2,25°,1 and that, in general, N_t's for the remainder are quite low for pretreatment <200°C. This behavior is analogous to that of the Pt/SiO_2 series although the minimum in N_t with T_p occurs some 50–75°C lower for Pt/Al_2O_3. Figure 8 indicates more directly the variation of structure sensitivity with T_p; for low temperature pretreatment (<100°C) the dependence of N_t upon conditions of original preparation disappears. The selectivity ratios are independent of catalyst preparation procedures under all conditions (c.f., Fig. 3) and are structure insensitive, although they decrease from a value of about 15 for $T_p = 370°$ to 10 for $T_p = 25°C$.

The low activity at low pretreatment temperatures for catalysts of higher D_h may be the result of very strong chemisorption of oxygen and only partial reduction; it is probable that the two low D_h catalysts are completely reduced, H_2,25°1, after O_2,300°,0.5, but those of higher D_h are not. However, there are a number of factors aside from extent of reduction which are important; these are discussed in more detail subsequently.

For pretreatment temperatures greater than 200°C, the general pattern seen in Fig. 5 is increasing activity with increasing T_p. Such behavior has been noted in other studies and a number of explanations set forth. Aboul-Gheit and Cosyns (*11*) attributed increases in the activity of some 0.35% Pt/Al_2O_3 catalysts for hydrogenation of aromatics, with $200 < T_R < 500°C$, to increasing reduction of platinum oxide bound to the support. Khassan *et al.* (*12*) have reported some results, quite similar to those reported here, for the effect of heat treatment on the activity of Pt/Al_2O_3 for hydrogen peroxide decomposition. Their data, obtained for D_h of 29.3, 50.8, and 58.7, indicated a minimum in activity in the region of 200°C pretreatment temperature, and qualitatively similar variation to the N_t–D_h results of Fig. 5. Their interpretation of the increase in activity with pretreatment temperature was based on an increase in mobility of metal atoms on the support, surface rearrangement, and consequent increase in the number of active centers. However, we have measured D_h both be-

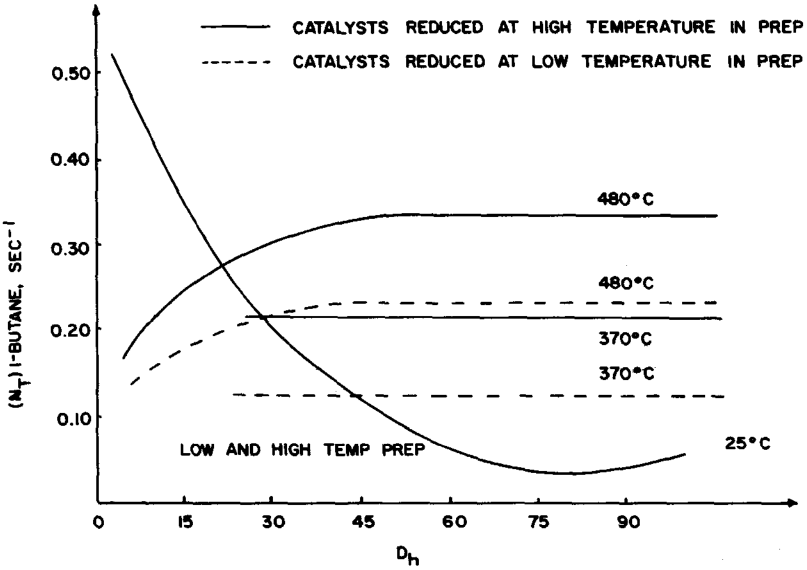


FIG. 8. Summary of structure sensitivity, N_t i-butane at 0°C for T_p = 25, 370, and 480°C.

fore and *after* various thermal treatments and reaction experiments on both the Pt/SiO_2 and Pt/Al_2O_3 series and find only changes within experimental error. In fact, the catalysts of both series are quite hardy under the conditions of thermal treatment we have employed below 500°C.

Most recently, however, Menon and Froment (*13*) have reported a decrease in hydrogenolysis activity for *n*-pentane and *n*-hexane at 400°C on a commercial Pt/Al_2O_3, 0.6 wt% Pt, as the pretreatment temperature in hydrogen is increased from 400 to 600°C. Relative isomerization activity, on the other hand, increased slightly with increasing pretreatment temperature. The suppression of hydrogenolysis activity at these high temperatures of reduction may be associated with chloride, which was present on the initial catalyst in amount about equal to platinum (0.67 wt%). We did not include 32-Al_2O_3-PtCl in our sequential reduction experiments, however, so there is no direct comparison with their results. The behavior of chloride-containing catalysts in the Pt/SiO_2 series was similar to those prepared by ion exchange (*5*) containing no chloride, although one would expect considerable differences between Cl^- on SiO_2 and Cl^- on Al_2O_3.

Some evidence exists that the presence of water may have substantial influence on activity for low-temperature pretreatment ($T_p < 100$°C) and the extent of dehydroxylation may be important for high-temperature pretreatment ($T_p > 200$°C). At low temperatures, water can be formed which migrates to and is strongly adsorbed at the metal–support interface, depressing the activity (*10*). A number of experiments were conducted to investigate this (*4*). Several of the high D_h catalysts that were reduced at high temperature in preparation were stored in a water-saturated atmosphere for 2 days at room temperature and N_t then determined after pretreatment, H_2,370°,1. The results are shown in Table 3; reductions in N_t from 20 to 30% occurred after prolonged exposure to water vapor. It was also found that large excesses of water (~20 monolayer equivalent) completely deactivated 47.6-Al_2O_3-PtNN after H_2,480°,1; however, even treatment in He,300°,1 restored about 65% of the original activity for hydrogenolysis at 0°C. Also in Table 3 is shown the sensitivity of the effects of water to final

TABLE 3

Effect of H_2O on the Activity of the Al_2O_3 Series

Catalyst	Pretreatment conditions			
	O_2,300°,0.5 H_2,370°,1		Rehydration[a] O_2,300°,0.5 H_2,370°,1	
	N_t i-b[b]	N_t n-b	N_t i-b	N_t n-b
74.0–Al_2O_3–PtNN	0.238	0.017	0.162	0.008
88.4–Al_2O_3–PtNN	0.184	0.015	0.152	0.014
94.2–Al_2O_3–PtNN	0.249	0.020	0.196	0.016
	O_2,300°,0.5 H_2,480°,1		Rehydration[a] O_2,300°,0.5 H_2,480°,1	
	N_t i-b	N_t n-b	N_t i-b	N_t n-b
74.0–Al_2O_3–PtNN	0.332	0.022	0.365	0.024

[a] After the pretreatment at the left, the catalyst was exposed in air at 25°C and 100% relative humidity for 2 days, then subjected to the pretreatment listed below.

[b] i-b, isobutane; n-b, n-butane.

treatment temperature; reduction of rehydrated 74.0–Al_2O_3–PtNN at 480°C completely restored the activity of the catalyst. Similar, but less severe, effects were noted for Pt/SiO_2. A reduction in N_t of 85% was measured for 40–SiO_2–PtCl after H_2,480°,1 and exposure to ca. 20 monolayers (*14*).

In the case of high-temperature pretreatment the situation is somewhat different. It is well known that the extent of surface hydroxylation of γ-Al_2O_3 depends upon thermal history (*15, 16*); surface coverage with OH decreases from about 80 to 20% as temperature increases from 200 to 600°C. Thus with increasing pretreatment temperature we may have both changes in the surface morphology of platinum and an increasing concentration of coordinatively unsaturated (electrophilic) aluminum in the support surface capable of electron transfer from platinum; that is, an increasing strength of metal–support interaction as dehydroxylation occurs.

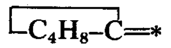
Deuterium Exchange with Cyclopentane on Pt/Al_2O_3

The detailed isotopic distribution patterns obtained with the Pt/Al_2O_3 series are shown in Fig. 7. These result from one period of residence on the surface and they provide a large information content. In addition to initial chemisorption of cyclopentane, presumably to form monoadsorbed cyclopentane, C_5H_9*, and $H*$, at least three other simultaneous elementary processes are involved:

(1) A process leading to multiple exchange via alternation between the initial monoadsorbed cyclopentane and a *cis*-diadsorbed cyclopentane in which the ratio of the rate of reaction of C_5H_9* to form $C_5H_8(*)_2$ to that of desorption of C_5H_9* is rather small. In this process $d_1 > d_2 > d_3$.

(2) A process like (1) but in which the ratio is large and $d_5 > d_4 > d_3$. It is assumed that the positions of adsorption cannot transfer from one side of the cyclopentane ring to the other.

(3) Some process like "rollover" or formation of



$$C_4H_8-C{=}*$$

(and probably both on platinum (*4*)) which transfers the position of adsorption from one side of the ring to the other, and which, therefore, permits access to cyclopentane-d_6–d_{10}.

All isotopic distributions patterns on Pt/Al_2O_3 were of the same basic type, that is, all values of d_i were finite and there were pronounced maxima at d_5 and d_{10}. However, there was a clear element of dependence upon D_h as shown in Fig. 7. The fraction of d_5 in d_2–d_{10} is nearly independent of D_h but d_{10}/d_2–d_{10} falls substantially as D_h increases. As D_h increases, it appears probable that d_6–d_9/d_2–d_{10} falls a little and d_2–d_4/d_2–d_{10} rises. Thus, the relative rate of process (3) seems to decline as D_h increases. The ratio d_6/d_{10} increases nearly monotonically from 0.2 at D_h = 25% to 0.85 at D_h = 100%. The catalysts of $D_h \simeq 4\%$ are somewhat out of line as they also are in some other items of selectivity and $d_6/d_{10} \simeq$ 0.55.

However, the data of Fig. 7 exhibit considerable scatter. In particular, the isotopic distribution patterns of D_h = 100.9, 96.7, and 72.4% are anomalous and all in the same way: d_5 is low and d_2–d_4 is large primarily because d_2 is large, 21–36% in these runs vs 12–13% in other runs in this range of D_h. Further, d_1 is substantially smaller than d_2. Similar anomalies appeared in runs at the lower temperatures. The most extreme isotopic distribution pattern, that for 96.7–Al_2O_3–PtNN, is shown in Fig. 9, along with that of the normal 94.2–Al_2O_3–PtNN.

Clearly, there is some factor influencing the catalytic behavior of the catalysts which has an effect as large as that of variation in D_h and we do not know what it is. The anomalous catalysts were all reduced at 300 or 200°C (D_h = 72.4%) but 66.7–Al_2O_3–PtNN and 106–Al_2O_3–PtNN, which were reduced at 300°C, gave isotopic distribution patterns of the normal type. These three anomalous catalysts were also out of line with respect to methylcyclopropane hydrogenolysis; for D_h = 100.9 and 96.7 N_t for i-butane was 50% smaller than other catalysts of comparable D_h; N_t for n-butane, while slightly depressed, was not so much changed. As a result, the (i-butane/n-butane) selectivities were ~9.5 vs 15 for other catalysts. for D_h = 72.4, N_t's for both i- and n-butane were depressed by about 30%; overall selectivity remained at about 15.

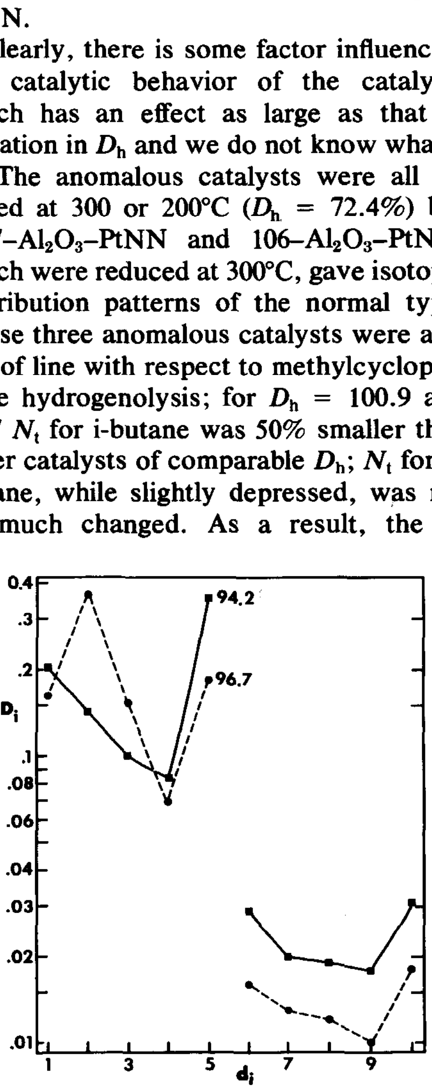


FIG. 9. The isotopic distribution patterns, D_i = $d_i/(d_1$–$d_{10})$, on a log scale vs number of hydrogen atoms exchanged for 94.2–Al_2O_3–PtNN, solid squares; and 96.7–Al_2O_3–PtNN, solid circles. The temperature of the run was 81°C.

Dessing and Ponec (*17*) have examined isotopic exchanges between cyclopentane and deuterium on evaporated films of platinum. The partial pressures employed in that work were so much lower than those in the present work that comparison of isotopic distribution patterns is difficult. However, on films formed at 300°C, d_i declined continuously from d_1 to d_5. On a film formed at 0°C, d_5 was a large maximum and the pattern was rather like that on Pt/Al_2O_3 of small D_h. Thus, the films exhibited an effect of structure sensitivity at least as large as that in the present work.

There was no clear element of structure sensitivity in N_t for formation of exchanged cyclopentane at 81°C. The activation energy for exchange, E_a(1–10), was about 75 kJ mol^{-1}. In accord with Fig. 6, E_a(10) and, to a lesser degree, E_a(6–9) were larger and E_a(2–4) and, to a greater degree, E_a(1) were smaller. However, E_a's for the catalysts with the anomalous isotopic distribution patterns were lower than those of the other catalysts and especially E_a(2–4), E_a(6–9), and E_a(1–10). However, at 81°C, N_t (i.e., N_t(1–10)) was normal for the anomalous catalysts.

As shown in Table 2, the nature of the pretreatment had an substantial effect upon N_t. $N_t(H_2,100°)/N_t^0$ is unity for catalysts of the smallest D_h. As D_h increases, the ratio falls substantially. $N_t(H_2,450°)/N_t^0$ is less than unity at small D_h and the ratio rises to 2.7 at the largest D_h. The effect of pretreatment upon isotopic distribution patterns is finite but not large. There is no clear effect of D_h upon differences among differing pretreatments except that H_2,450°,1 appears to result in substantially augmented values of d_5 and d_{10} for catalysts of large D_h.

As with Pt/SiO_2 (*4*), the exchange reaction is accompanied by formation of hydrocarbon residues on the catalyst. However, unlike silica, the alumina support alone retains hydrocarbon. If alumina was exposed to cyclopentane in hydrogen at 81°C, most of the retained cyclopentane was released at 100°C either in flowing hydrogen or flowing helium and exclusively as cyclopentane. Hydrogen passed over Pt/Al_2O_3 after an exchange run liberated much more hydrocarbon. Roughly equal amounts of hydrocarbon were released at 100 and 200°C and only traces at 300–450°C. Released hydrocarbon was nearly exclusively cyclopentane. The amount of retained cyclopentane amounted to 0.2–0.4 molecules per Pt_s. A similar number was observed on Pt/SiO_2. The rate of exchange usually declined during a run, but it is difficult to see how the slow rate of decline is compatible with such a large coverage of platinum by inactive residues. Perhaps some species, C_5H_x, migrate from the platinum onto the surface of the alumina. This matter is discussed in more detail elsewhere (*10, 18*).

COMPARISON OF Pt/Al_2O_3 AND Pt/SiO_2

Methylcyclopropane Hydrogenolysis

Prior results for Pt/SiO_2 (*5*) were obtained for catalysts reduced at low temperature (~300°C) in preparation, so comparison is made here for the low-temperature Pt/Al_2O_3 series. In general the comparisons for both i- and *n*-butane products are similar, so only results for i-butane and selectivity are illustrated (Figs. 10–12). For these conditions of pretreatment the activities of the two series of catalysts are similar for $D_h < 40$; however, the Pt/SiO_2 is twice as active as Pt/Al_2O_3 for $D_h = 80$. Selectivity trends follow the same pattern, as shown in Fig. 12.

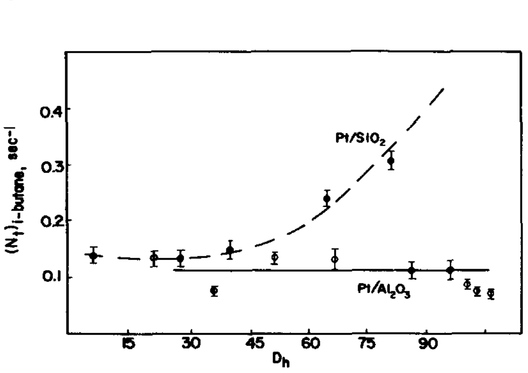


FIG. 10. Comparison of N_t i-butane vs D_h at 0°C for Pt/SiO_2 and Pt/Al_2O_3, pretreatment H_2,370°,1.

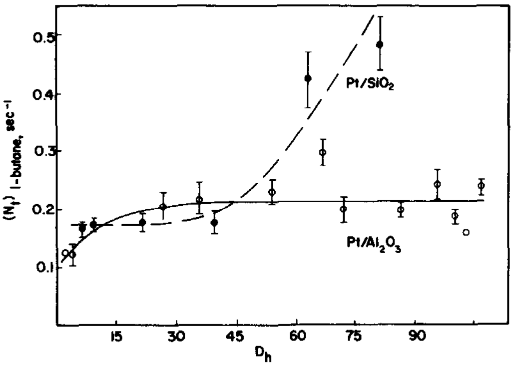


FIG. 11. Comparison of N_t i-butane vs D_h at 0°C for Pt/SiO_2 and Pt/Al_2O_3, pretreatment H_2,480°,1.

Lest one conclude prematurely from these illustrations that there are really only differences in detail between the behavior of the Pt/SiO_2 series and the Pt/Al_2O_3 series, we present another comparison of N_t for i-butane vs D_h for T_p = 25°C in Fig. 13. For catalysts in the midrange of $D_h > 35$, the difference in N_t ranges between a factor of 5 and 10. Hence not only is the pretreatment condition important in determining structure sensitivity within a given series, the nature of support interactions also appears greatly influenced by this variable. We have modeled the Pt/SiO_2 series in terms of isodimensional crystallites and demonstrated some correlation of activity with the fraction of low-coordination-number atoms on the surface of the metal crystallites (*5*). However, the generally structure-insensitive behavior on Pt/Al_2O_3 for high T_p suggests that apparently there are no comparable preferred sites for the methylcyclopropane reaction on this series.

Cyclopentane–Deuterium Exchange

After the standard pretreatment, N_t was relatively structure insensitive on the

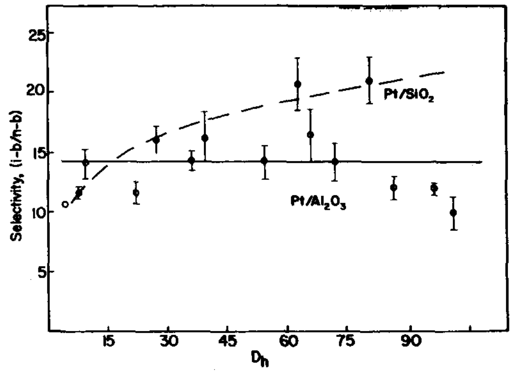


FIG. 12. Comparison of selectivities vs D_h at 0°C for Pt/SiO_2 and Pt/Al_2O_3.

TABLE 4

Properties of Silica Gels[a]

	Grade		
	62	81	950
Area ($m^2\ g^{-1}$)	285	600	700
Pore volume ($cm^3\ g^{-1}$)	1.2	0.7	0.4
Average pore diam (nm)	14	5	2.6
Fe (wt%)	0.02	0.02	0.005
Ti (wt%)	0.09	0.09	0.06
Zr (wt%)	0.03	0.03	0.03

[a] Manufacturer's specifications, except the textural properties for grade 62 were measured in this laboratory (*1*).

Pt/SiO_2 catalysts previously examined (*4*). The silica gel employed for these catlaysts was Davison grade 62, a wide-pore gel (see Table 4). The value of N_t was about twice that found in the present work with Pt/Al_2O_3. Although the isotopic distributions were of the same general type on both sets of catalysts and $d_5/d_2–d_{10}$ was about 0.45 on both sets, there were divergences among the proportions of the other exchanged species which increased progressively as D_h increased. In particular, $d_{10}/d_2–d_{10}$ was nearly constant at about 0.15 on Pt/SiO_2 at D_h = 16–81%. On Pt/Al_2O_3, the ratio was only about one-half as large as D_h = 16–81% (Fig. 7). At D_h = 4–7%, $d_2–d_4/d_2–d_{10}$ and $d_6–d_9/d_2–d_{10}$ were approximately in agreement on the two catalysts, but the second ratio was much larger on Pt/SiO_2 at larger D_h and particularly at D_h = 25–60%. Typical distribution patterns on Pt/SiO_2 and Pt/Al_2O_3 of comparable D_h are shown in Fig. 14. E_a's appeared to be larger on Pt/Al_2O_3 except at the lowest values of D_h.

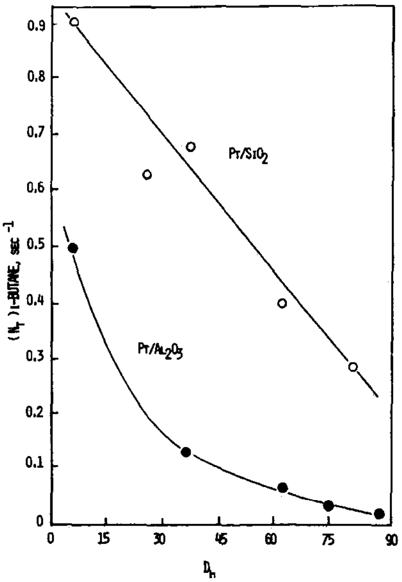


FIG. 13. Comparison of N_t i-butane vs D_h for Pt/SiO_2 and Pt/Al_2O_3, pretreatment H_2,25°,1.

Influence of the Support; Pt/SiO_2

The intercomparisons above are derived from one alumina and one silica gel. We have also examined a set of catalysts on the narrow-pore Davison grade 950 silica gel (see Table 4) prepared in the same fashion as the catalysts on grade 62. These were prepared either by impregnation with H_2PtCl_6 aq (designated PtCl) and reduced directly or after calcining or prepared by ion exchange with $Pt(NH_3)_4^{2+}$ (IonX) and reduced directly or after calcining. The values of D_h were respectivley 98, 63.6, 69.5, and 48.2% and those of N_t for exchange at 55°C were respectively 0.132, 0.123 ± 0.005, 0.065 ± 0.002, and 0.048 sec^{-1}. The percentage platinum was 2.1 for PtCl and 2.01 for IonX. The high activity of

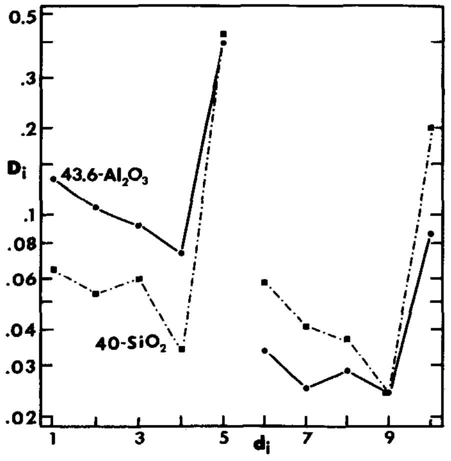


FIG. 14. The isotopic distribution patterns, D_i = $d_i(d_1–d_{10})$, fraction of each exchanged species in total exchanged cyclopentane, vs number of hydrogen atoms exchanged for 43.6–Al_2O_3–PtNN, solid circles; and 40–SiO_2–PtCl–S from Ref. (*4*), solid squares. D_i is on a log scale. The temperature of the run was 81°C.

the catalysts required running the isotopic exchanges at the lower temperature in order to obtain initial isotopic distributions. Two PtCl catlaysts with 1.87 wt% Pt were also prepared on Davison grade 81 silica gel. As reduced directly or after calcining, D_h was 44.7 and 18.2%, respectivley, and N_t was 0.034 sec^{-1} for both catalysts. At 55°C, the average N_t for catalysts on grade 62 was 0.015 sec^{-1}.

The isotopic distribution for D_h = 98% on grade 950 was very close to that of D_h = 81% on grade 62 and that for D_h = 69.5 on grade 950 was close to the catalyst of D_h = 63.6% prepared on grade 62 in the same fashion. Catalysts on grades 950 and 81 whose preparation involved calcining gave somewhat greater deviation in isotopic distributions than those on grade 62 with neighboring values of D_h.

Activity patterns for hydrogenolysis at 0°C were generally consistent with those for exchange, with N_t increasing in the sequence grade 62, 81, 950. Results for D_h = 63.6% (grade 62), 44.7% (grade 81), and 69.5% (grade 950) were N_t (i-butane) 0.235, 0.247, and 0.315 sec^{-1}, respectively. Corresponding selectivities were 19.5, 16.8, and 15.7. For the low D_h catalysts, N_t (i-butane) was 0.146 sec^{-1} for 7.1% (grade 62) and 0.222 sec^{-1} for 18.2% (grade 81), with selectivities of 12 and 12.5, respectively.

Clearly then, the catalytic activity is influenced by the nature of the support and even by the nature of the silica gel when the support is silica gel. Ideally, one would expect that such an effect would be least pronounced when D_h is small, and, indeed, the differences among alumina and the various silica gels were the least at small D_h. If the effect of support arises from inorganic impurities migrating to the surface of the platinum crystallites, the matter is more complicated. The extent of release of impurities from the support might differ between silica and alumina. Among the silica gels, the effect would depend upon content in impurity; it would decrease with percentage platinum and decrease with D_h. The nearly constant value of N_t for exchange at nearly constant percentage platinum varying D_h does not readily accord with this expectation.

The presence of iron or sulfate has been reported to influence rather strongly the catalytic character of palladium and platinum on silica and alumina (*18*, *19*). The pretreatments of alumina (*7*) and silica (*4*) should have substantially reduced any sulfate which was present. As analyzed in the Triga Mark I nuclear reactor at Reed College, Portland, Oregon, the contents in Fe for grades 62 and 950 silica gel and the Aerocat alumina after the pretreatments were 48 ± 15, 25 ± 8, and 30 ± 10 ppm. Dr. V. Eskinazi in these laboratories determined a Fe content of 40 ppm in grade 62 gel by atomic adsorption spectroscopy after dissolving the gel in hydrofluoric acid. It seems rather unlikely that such amounts of iron would significantly affect the catalytic behavior of catalysts containing 3000 to 20,000 ppm of platinum. However, we cannot completely exclude this possibility. The much larger amounts of titanium in silica gel also pose a problem which needs examination.

CONCLUSIONS

Effect of Pretreatment Conditions on the Activity of Pt/SiO$_2$ on Pt/Al$_2$O$_3$

From the foregoing, it appears that a number of factors are involved in the effect of the conditions of pretreatment upon catalytic activity and selectivity. Since Pt/SiO$_2$ and Pt/Al$_2$O$_3$ are materials and not chemicals, this is not surprising.

(1) Traces of oxygen in the hydrogen led to a continuous decline in the activity of 40–SiO$_2$–PtCl for the hydrogenolysis of cyclopropane at 0°C, which saturated at a reduction in activity of about 20% for larger amounts of oxygen (*10*). It was suggested that this was the result of water formation and blocking of sites at the metal–support interface as mentioned previously. One would expect such a process to lead to a larger degree of blockage on small than on large crytallites of platinum of the same shape. However, this process could hardly be involved in the depression of the rate of dehydrogenation of cyclohexane on Pt/Al$_2$O$_3$ at high temperatures which was reported to reuslt from the presence of oxygen during reduction, H$_2$,480° (*20*).

(2) Our pretreatment starts with a stored and oxygen-covered catalyst which is exposed to O$_2$,300°,0.5. The platinum crystallites become rather heavily oxidized and to a degree which depends upon D_h (*1, 7*). The extent of oxidation is larger than that resulting from O$_2$,300°,0.5 on clean platinum starting with a freshly prepared catlayst. The final oxide is much more difficultly reduced when one starts with a stored catalyst and the difficulty increases with increasing D_h. Stored Pt/SiO$_2$ and Pt/Al$_2$O$_3$ pretreated O$_2$,300°,0.5;H$_2$,25°,1 appear to be incompletely reduced except possibly catalysts of D_h = 4–7%. We have no evidence as to the location of the residual oxygen. Pt/SiO$_2$ samples pretreated O$_2$, 300°,0.5;H$_2$,100°,1 are essentially free of residual oxygen (*1*), but after the same pretreatment some Pt/Al$_2$O$_3$ samples may contain residual oxygen. When an isotopic exchange was run on fresh 36.1–Al$_2$O$_3$–PtNN pretreated O$_2$,300°,0.5;H$_2$,100°,1, then pretreated O$_2$,300°,0.5;H$_2$,450°,1, and then exposed again to the first pretreatment, the low N_t in the first run (Table 2) increased nearly to that observed after the standard. As a comparison of Table 2 and Fig. 5 indicates, incomplete reduction affects hydrogenolysis more than isotopic exchange.

(3) If, as we think, removal of oxygen is complete after H$_2$,150°,1, reaction of stored catalyst exposed to O$_2$,300°,0.5 must lead to a platinum surface whose detailed surface morphology depends upon the temperature of exposure to hydrogen. Otherwise, it is difficult to see how N_t's for hydrogenolysis could fall as the temperature of exposure to hydrogen increases, pass through a low minimum at about 150°C, and then increase by factors which are very large except for the catalysts of the smallest D_h (Fig. 5). The progressive annealing of vacancies produced by O$_2$,300°,0.5 on platinum (*21*) as T_p is increased has been suggested to explain this low-temperature pretreatment behaivor (*5*). Thus the effect of H$_2$,100°,1 on 36.1–Al$_2$O$_3$–PtNN in (2) above may not be primarily one of the extent of reduction. Further, in some cases, the surface morphology of the platinum crystallites may depend, at least in part, upon the degree of dehydroxylation of the support which will in turn depend upon the conditions of the original preparation of the catalyst and its pretreatment.

(4) As judged by hydrogen–oxygen titration, pretratment of stored 6.3–SiO$_2$–PtCl by O$_2$,300°,0.5;H$_2$,25°,1 led to percentages exposed which were about 40% larger than those after the standard pretreatment. Exposure to Ar,450°,1 returned D_t to its normal value (*1*). 40–SiO$_2$–PtCl did not exhibit an exalted D_t under these condtions. Thus, after pretreatment by hydrogen at 25–100°C, the true D_h of catalysts with small D_h may have been larger than we assumed in calculating N_t. An anomalous surface morphology may well have been present on

these catalysts after H_2,25°. Maire *et al.* (*22*) have reported that exposure to hydrogen-induced step coalescence and terrace broadening on a stepped surface of platinum, (*S*)-[6(111) × (100)], and that the initial surface was restored upon exposure to vacuum at 700°C. Such stepped surfaces are unlikely to be present on platinum particles of large D_h.

(5) Cooling Pt/SiO_2 from 450°C in hydrogen was reported to result in an amount of sorbed hydrogen substantially in excess of that resulting from H_2,25° on clean catalyst (*1*). The excess hydrogen is liberated in flowing helium at 450°C, but it does not react with oxygen at 25°C. It is probably inside the crystallites of platinum but at a concentration well in excess of the solubility of hydrogen in *bulk* platinum. A somewhat similar phenomenon has been reported for Pt/Al_2O_3 and Pt/SiO_2 by Charcosset *et al.* (*23*). Such excess hydrogen appears to have relatively little effect upon N_t in the hydrogenolysis of methylcylopropane on Pt/Al_2O_3 (Table 1), but it may contribute to the augmentation of N_t for isotopic exchange on catalysts of higher D_h (Table 2 and Ref. (*1*)).

Another effect of hydrogen was noted for the hydrogenolysis of cyclopropane at 0°C and for the hydrogenation of ethylene at −31°C. Initial activity was nearly twice as high on 40–SiO_2–PtCl after the standard pretreatment as after H_2,450°,1 (cool in H_2). However, activity after the standard pretreatment declined rather rapidly and exposure of such a catalyst to hydrogen at 25°C reduced the values of N_t to those resulting from H_2,450°,1 (*10*). This transient effect seems to result from the slow formation of some inhibitive form of adsorbed hydrogen. In the present studies of methylcyclopropane hydrogenolysis a similar effect was observed for Pt/SiO_2 but not for Pt/Al_2O_3. Results on 40–SiO_2–PtCl were very close to those given above for cyclopropane. However, enhancement of activity by the standard pretreatment was somewhat less on 7.1–, 63.5–, and 81–SiO_2. Besenyei *et al.* (*24*) have reported a similar effect in the hydrogenation of several olefins.

ACKNOWLEDGMENT

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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., Butt, J. B., and Burwell, R. L., Jr., *J. Catal.* **50,** 479 (1977).
3. Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **50,** 494 (1977).
4. Inoue, Y., Herrmann, J. M., Schmidt, H., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **53,** 401 (1978).
5. Otero-Schipper, P. H., Wachter, W. A., Butt, J. B., Burwell, R. L., Jr., and Cohen, J. B., *J. Catal.* **53,** 414 (1978).
6. Cant, N. W., *J. Catal.* **62,** 173 (1980).
7. Kobayashi, M., Inoue, Y., Takahashi, N., Burwell, R. L., Jr., Butt, J. B., and Cohen, J. B., *J. Catal.* **64,** 74 (1980).
8. Bond, G. C., and Newham, J., *Trans. Faraday Sco.* **56,** 1501 (1960); Anderson, J. R., and Avery, N. R., *J. Catal.* **8,** 48 (1967).
9. Naccache, C., Kaufherr, N., Dufaux, M., Bandiera, J., and Imelik, B., *ACS Symp. Ser.* **40,** 538 (1977).
10. Hattori, T., and Burwell, R. L., Jr., *J. Phys. Chem.* **83,** 241 (1979).
11. Aboul-Gheit, A. K., and Cosyns, J., *J. Appl. Chem. Biotechnol.* **16,** 15 (1976).
12. Khassan, S. H., Emel'yanova, G. I., Lebeder, V. P., and Kobozev, N. I., *Russ. J. Phys. Chem.* **44,** 6 (1970).
13. Menon, P. G., and Froment, G. F., *J. Catal.* **59,** 135, (1979).
14. Otero-Schipper, P. H., Ph.D. dissertation, Northwestern University, Evanston, Illinois, 1977.
15. Peri, J. B., and Hannon, R. B., *J. Phys. Chem.* **64,** 1526 (1960).
16. Peri, J. B., *J. Phys. Chem.* **69,** 211 (1965).
17. Dessing, R. P., and Ponec, V., *J. Catal.* **44,** 494 (1976).
18. Maurel, R., Leclercq, G., and Barbier, J., *J. Catal.* **37,** 324 (1975).
19. Fuentes, S., And Figueras, F., *JCS Faraday Trans. I* **74,** 174 (1978).
20. Mills, G. A., Weller, S. W., and Cornelius, E. B., *Proc. 2nd Int. Congr. Catal.* Editions Technip, Paris, p. 2221 (1960).

21. Ratnasamy, P., *J. Catal.* **31,** 466 (1973).
22. Maire, G., Bernhardt, P., Lazare, P., and Lindauer, G., *Proc. Int. Vac. Congr. 7th* **1,** 861 (1977).
23. Charcosset, H., Barbier, J., Blanchard, G., Frety, R., Neff, B., Perrichon, V., Turdy, B., and Varloud, J., *Thermochim. Acta* **28,** 85 (1979). However, in contrast to our observations, these authors report that the hydrogen adsorbed at high temperatures reduces the amount of hydrogen adsorbed at room temperature. They locate the hydrogen sorbed at high temperatures in the Pt/support interface. We have reinvestigated 40–SiO_2–PtCl by a different method. The catlayst was cooled in hydrogen to 25°C from various temperatures, flushed with argon, and the amount of hydrogen released at 450°C was meausred. For adsorption of hydrogen after 25, 300, 450, and 500°C, desorbed hydrogen expressed as H/Pt was 0.39, 0.43, 0.47, and 0.496, though it is possible that this effect is also structure sensitive.
24. Besenyei, G., Moger, D., and Nagy, F., *Mag. Kem. Foly.* **81,** 313 (1975); *Chem. Abstr.* **83,** 205514f (1976).