Structure Sensitivity in the Hydrogenation of Hindered Hydrocarbons

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Abstract: Hydrogenation of the following compounds has been investigated in a batch reactor at 20 °C on a series of Pt/Al_2O_3 and Pt/SiO_2 catalysts with dispersions ranging from 0.3 to 100%: cyclopentene, di-*tert*-butylacetylene (the absorption of which should involve serious adsorbate-surface interactions), 3-hexyne, and *cis*-di-*tert*-butylethylene. Product compositions during hydrogenation were determined for the last three. The unusually large value of the ratio, isomerization/hydrogenation of the cis-ene, 2.5 to 9, is presumably related to the large heat of isomerization of the cis to the trans isomer. The turnover number of cyclopentene varied by less than a factor of 2 on the catalysts and exhibited no trend with dispersion. The ratio of the turnover number of the acetylene to that of cyclopentene varied from 0.3 to 0.9 and increased with increasing dispersion. Much larger effects of structure sensitivity appeared in the competitive ratio of the acetylene to the cis olefin. The value of the ratio appeared to result from the relative sticking coefficients at free sites on platinum, it varied from 1 to >50, increased with increasing dispersion, and was larger for Pt/Al_2O_3 than for Pt/SiO_2. Apparently, the acetylene adsorbs more readily at edge atoms than at atoms in faces. The activity of highly dispersed Pt/Al_2O_3 increases during hydrogenation of 3-hexyne which promotes rearrangement of platinum particles to ones of higher activity. Since the acetylene when alone hydrogenates readily on catalysts of low dispersion, we suggest that semiextractive adsorption is involved, i.e., that the atoms of platinum involved in binding are elevated somewhat above the surface crystal planes.

The idea that the catalytic characteristics of a particular type of heterogeneous catalyst would depend upon the detailed geometric environment of the catalytic site is old. Taylor, for example, concluded that adsorption data indicated that the surfaces of certain catalysts were nonuniform.[1] The view that such nonuniformity would be linked to what we now call the nature of the coordinative unsaturation of the site is also old. Thus, with metallic catalysts, one might expect that the catalytic characteristics would depend upon the ratio of edge to surface atoms, upon the proportions of various crystal planes which are exposed, upon the amount and nature of surface defects, and, perhaps, upon the identity of the support.

One of the difficulties in testing these views is the difficulty in varying and in characterizing the surfaces of materials with any close relation to conventional catalysts. In recent years there has been considerable interest in testing these views by examining a series of catalysts which ideally would differ only in the dispersion (the percent of the total metal atoms which are at the surface) of the particles of metal. It is assumed that increasing dispersion would be correlated with decreasing size of the metal particles. On this basis one would expect the particles of higher dispersion to have a larger ratio of edge to nonedge atoms. But even though one might not be able fully to characterize the nature of the surfaces, one would expect that the particles of different dispersion would certainly differ in the exact details of their surfaces. Papers 44–48 presented at the Fifth International Congress on Catalysis in 1972 exemplify studies of the type just described.[2-6]

Boudart, who has made major contributions to this area, has contributed new data and correlated old with the conclusion that one can classify presently known types of chemical reactions proceeding on heterogeneous catalysts into two types: those whose areal (i.e., divided by area) rates are nearly independent of support and of the method of catalyst preparation and those whose areal rates vary with preparation and, in particular, with dispersion.[7] The first would be called structure insensitive (or facile) and the second, structure sensitive (or demanding). The hydrogenation of ethylene on platinum catalysts appears to be nearly structure insensitive,[8] whereas that of the hydrogenolysis of neopentane is structure sensitive.[7]

However, a classification based merely upon rate could be misleading. Effects which appeared beyond a rate-limiting step might not appear in a rate. Further, compensation (for example, in k and K, surface rate constants and binding constants) might lead rather differing catalysts to give nearly the same rate. The addition of selectivity features to rate data could greatly augment the basis for recognizing structure sensitivity. Further, selectivity data permit conclusions which are independent of exact measurement of dispersion.

One of the earliest clear demonstrations of structure sensitivity came from selectivity data provided by the substantial variations in the isotopic distribution patterns of hydrocarbons exchanged with deuterium. Such variation was correlated with the nickel particle size (measured magnetically) of various nickel catalysts (reduced nickel oxide, evaporated nickel films, reduced nickel/silica) in isotopic exchange between deuterium and heptane and cyclohexane[9] and with the identity of the support in platinum catalysts used in exchange between deuterium and *p*-xylene.[10] Different palladium catalysts gave different isotopic distribution patterns in isotopic exchange between deuterium and cyclopentane and it was argued that these variations indicated the presence of varying proportions of five different types of sites on the surface of palladium.[11] These exchange reactions would appear to be structure sensitive whether or not there was variation in areal rates. Oliver and Wells[2] have presented the advantages of considering selectivity data.

The present paper, which has been the subject of a preliminary communication,[12] deals with the extension of these ideas to hydrogenation reactions which, at least in the case of ethylene, have been classified as structure insensitive using the rate criterion alone. A variety of Pt/SiO_2 and Pt/Al_2O_3 catalysts have been prepared and the dispersions of the platinum measured by hydrogen chemisorption. The principal diagnostic reaction has been the hydrogenation of di-*tert*-butylacetylene. This compound was chosen because the two bulky *tert*-butyl groups which surround the acetylene function should induce severe adsorbate–surface hindrance in the adsorption complex of the acetylene on more densely packed planes like (111) and (100) of platinum. Models indicate that the adsorption complex, either a π complex at one atom or a diadsorbed *cis*-di-*tert*-butylethylene at two platinum atoms, would be so hindered that its hydrogenation at any detectable rate would be somewhat surprising. One might expect such hindrance to be considerably less at atoms at edges or at steps. Also determined were the rates of hydrogenation of cyclopentene on all of these catalysts. Cyclopentene was chosen because it should provide as little adsorbate–surface hindrance as any olefin which could be used in liquid-phase hydrogenation and because it cannot undergo detectable isomerization, either cis–trans or by double bond migration. 3-Hexyne has also been studied as an example of an acetylene which should give minimal adsorbate–surface hindrance.

Experimental Section

Techniques. Rates of hydrogenation were measured in a constant volume, batch system by following the fall in pressure as hydrogen was consumed. Since however, the fall in pressure was limited to 1% of the total pressure of hydrogen, the system provided the advantages of both constant volume and constant pressure systems. The reactor was of the Hussey type[13] modified by Kosco.[14] The reaction chamber in this modification was completely closed except for an opening about 2 mm in diameter in a Teflon rod. This design reduced the loss of catalyst by splattering into inaccessible regions and it reduced back diffusion of vapors from the reactor. The reactor was agitated by circular rotation about a circle 3 mm in radius at 1850 rpm. The contents of the reaction vessel become essentially an aerosol. The system contained a set of thermostated bulbs, various ones of which could be connected into the system as required. For example, if a consumption of hydrogen of 20 cm^3 was expected, a 2-l. volume was connected. The pressure fall was recorded by means of an electronic capacitance manometer, the Barocel of CGS Datametrics, usually with full scale being 10 mm. The reference pressure was a bulb open to the system until the very start of the hydrogenation. The valves were Teflon needle valves, and the system was free of mercury. Grease (Apiezon Grease N) was used only on the bottom half of a standard taper joint which joined the reactor to the system. Hydrogen was produced electrolytically and purified by diffusion through the Pd,Ag cathode (Elhygen, Milton Roy and Co.).

In typical runs, the catalyst was added to the reaction vessel along with enough inert diluent to bring the mass of catalyst plus diluent to 60–80 mg. This procedure followed Kosco[14] who found it was necessary in order to obtain rates proportional to the amount of catalyst. The inert diluent was usually Baker Analyzed Reagent aluminum oxide suitable for chromatographic use, most of which was 200–270 mesh. It was calcined at 450 °C before use, and it gave zero activity for hydrogenation. Davison Grade 59 silica gel, 140–200 mesh, gave the same results. After the addition of catalyst and diluent, the system was evacuated, 1 atm of hydrogen was added, and the system was reevacuated. Hydrogen was reintroduced, and 1 cm^3 of cyclohexane solvent was added. During this period the water flow through the jacket of the reactor was adjusted to 20 °C. The reactor was agitated for 10 min, the unsaturated hydrocarbon added, and the fall in pressure recorded. Usually 10–70 mg of catalyst and one of the following were employed: 0.06 cm^3 of cyclopentene, 0.07 cm^3 of di-*tert*-butylacetylene (generally to be called the *acetylene*), 0.04 cm^3 of 3-hexyne, 0.12 cm^3 of *cis*-di-*tert*-butylethylene (the *cis-ene*), and 0.15 cm^3 of *trans*-di-*tert*-butylethylene (the *trans-ene*).

Deviations from the ideal conditions of a constant volume reactor were as follows. The hydrogen pressure was not constant but declined 0.5 to 1% during a run. During the preliminary agitation of the reactor, some vapor of cyclohexane diffused into a chamber of about 30 cm^3 capacity which adjoined the reaction chamber. However, this produced a partial pressure of only 12 Torr out of a total of 760.

Hydrocarbons. Careful purification followed by thorough asceptic precautions were required in order to obtain rates of hydrogenation free of effects of poisoning.[13] Poisons at 1 ppm could significantly affect the data. All C_{10} hydrocarbons (Chemical Samples Co.) were refluxed with potassium, distilled, purified by preparative gas chromatography, and stored under nitrogen over potassium. Samples for injection into the reaction vessel were distilled from the storage vessel just before use. Cyclopentene and 3-hexyne were treated similarly but gas chromatographic purification was unnecessary. All unsaturated hydrocarbons were distilled from the storage vessel just before use, whereas cyclohexane was removed directly. The cis-ene was prepared by hydrogenation of the acetylene on 109-Al_2O_3-PtCl followed by preparative chromatography (see footnote *a* of Table I).

Catalysts. The support for Pt/SiO_2 was 270–400 mesh Davison Grade 59 silica gel (measured by BET, nitrogen: specific area 314 m^2 g^{-1}; pore volume 1.1 cm^3 g^{-1}; average pore diameter 12 nm) which had been crushed, sieved, washed with 0.1 M hydrochloric acid, rinsed, and dried. The preparation by ion exchange with Pt(IV) ammine followed Dorling, Lynch, and Moss.[15,16] Before reduction, some samples were calcined at a higher temperature to produce catalysts of lower dispersions. Reduction was in hydrogen for 2 h at 25 °C followed by a rise in temperature over a period of 2 h to 300 °C and a hold at that temperature for 2 h. The contact time of silica gel with $Pt(NH_3)_5(NH_2)^{3+}$ plus $Pt(NH_3)_4(NH_2)Cl^{2+}$ [17,18] in 1 M NH_4OH was held to 3 min because of fears that solution and reprecipitation of silica might cover up platinum. However, a preparation on 400+ mesh silica gel with but one-fifth the usual loading and with a much longer contact time with the basic solution gave a dispersion not far from 100%. Thus, the fears appear to have been groundless, and the higher dispersion may, at least in part, have resulted from more uniform distribution of Pt(IV) ammine throughout the granules of silica gel.

Other Pt/SiO_2 catalysts were prepared by impregnation with aqueous chloroplatinic acid, drying at 97–120 °C, calcination for 4–5 h, and reduction. Pt/SiO_2 catalysts were not rehydrated before use.

A catalyst with large particles of platinum was prepared by impregnating the macroporous, siliceous Filtros FS-140 with chloroplatinic acid. It was not rehydrated.

Catapal SB alumina (Continental Oil Co.) of 400+ mesh was calcined at 650 °C and rehydrated at 25 °C in an atmosphere of 100% relative humidity. Pt/Al_2O_3 catalysts were prepared in two ways, by impregnation with aqueous solutions of chloroplatinic acid or with diaminodinitroplatinum. They were dried in air at 120 °C, calcined in flowing oxygen for 4–5 h, reduced in hydrogen for 3 h, cooled, and rehydrated. Both Pt/Al_2O_3 and Pt/SiO_2 were cooled in hydrogen following reduction.

Doubly distilled water was used in the preparation of the catalysts. The metal portion of the compounds employed was 99.99% Pt. Oxygen and hydrogen were purified by passage through traps of silica gel cooled at −78 and −196 °C, respectively.

Table I records the calcination and reduction temperatures and the dispersions of the various catalysts. Dispersions were measured by a pulse method similar to that of Freel[19] using ultrapure helium as the carrier and converting hydrogen to water before the catharometer by passage over hot cupric oxide. In later experiments, the helium was replaced by neon just before pulse injection and the hydrogen was determined as such. Three catalysts were run with both methods: 109-Al_2O_3-PtCl gave 131 in He, 109 in Ne; 24-Al_2O_3-PtCl, 30 and 24; 54-SiO_2-IonX gave 54 and 54. 20-SiO_2-PtCl gave 20 with neon and 22 in the pulse adsorption of carbon monoxide run by Dr. Aidan O Cinneide. We have used the values obtained with the later and more developed technique using neon as the carrier gas for the two Pt/Al_2O_3 catalysts. Our dispersions for SiO_2-IonX agree well with those reported by Dorling, Lynch, and Moss[15] after whom we patterned our catalyst preparations: 54-SiO_2-IonX vs. 53%, 14-SiO_2-IonX vs. 17%, 7-SiO_2-IonX vs. 6%, and 20-SiO_2-PtCl vs. 22%.

The dispersions of the SiO_2-IonX designated by the footnote *j* (Table I) were examined for dispersion by Drs. T. Uchigima and J. M. Herrmann in these laboratories in much greater detail than were those of our other catalysts. These catalysts were of larger sieve size and were crushed and sieved after measurement of dispersion as were those identified by the footnote *k*. Since the values of N_{cp} accord well with those of the other catalysts, no significant blockage of pores accompanied the crushing.

Rates of Hydrogenation. The hydrogenation of cyclopentene was taken as the reference standard for rates of hydrogenation. In all runs with other substances, cyclopentene was injected first, after its hydrogenation was complete the other substance was injected, and finally cyclopentene was injected. Unless both runs with cyclopentene were strictly zero order in cyclopentene and unless both runs agreed to within 5%, the runs were rejected.[13] The second cyclopentene run was usually slightly faster than the first. Figure 1 illustrates the procedure with runs with cyclopentene sandwiching one of the acetylene.

In all systems investigated, the rate of hydrogen consumption was linearly proportional to the amount of catalyst used. The average deviation of the rates from the best straight line in the plot of rate vs. weight of catalyst was ±5%. This linearity establishes that the concentration of hydrogen in the liquid phase was always that corresponding to equilibrium with gas-phase hydrogen. The values of turnover numbers at 20 °C listed in Table I derive from the slope of the plots of rate of hydrogen consumption vs. weight of catalyst using at least four separate samples of the catalyst. In converting these slopes to turnover numbers, we take the partial pressure of hydrogen in the

Table I. Catalysts and Turnover Numbers at 20 °C, Total Pressure = 1 atm

Catalyst[a]	Loading[b] %	T_{cal}, °C[c]	T_{red}, °C[d]	N_{cp}[e]	N_{ac}/N_{cp}[f]	N_{hyne}/N_{cp}[g]	N_{3ene}[h]
109-Al_2O_3-PtCl	0.27	500	500	7.3	0.49	0.31	
24-Al_2O_3-PtCl	1.15	500	780	8.6	0.89	0.59	5.4
100-Al_2O_3-$PtNO_2$[i]	1.0	500	350	2.7	0.36		
84-Al_2O_3-$PtNO_2$	0.30	500	350	4.2	0.50		
23-Al_2O_3-$PtNO_2$	0.96	500	800	10.4	0.56		
0.28-Filtros	4.1	490	490	11	0.54[n]	0.43	7.6
54-SiO_2-IonX	0.5	None	300	15.7[l]	0.65	0.48	9.3
14-SiO_2-IonX	1.9	450	300	12	0.71		
7-SiO_2-IonX	2.1	600	300	8.8	0.89	0.68	6.9
20-SiO_2-PtCl	1.1	None	210	14	0.58		
87-SiO_2-IonX[m]	0.10	None	300	11.0	0.34		
63-SiO_2-IonX[j]	0.48	None	305	14.9			
27-SiO_2-IonX[j]	1.48	435	305	8.3			
40-SiO_2-PtCl[j]	1.17	None	205	11.3			
7-SiO_2-PtCl[j]	1.91	279	205	14			
59-SiO_2-IonX[k]	0.53	None	400	8.6			
57.5-SiO_2-IonX[k]	2.3	None	400	(4.3)			

[a] The number at the left of the code is the dispersion. The next term gives the support, and the last term identifies the method of preparation: PtCl means impregnation with aqueous chloroplatinic acid, $PtNO_2$ means impregnation with diaminodinitroplatinum, IonX means ion exchange with Pt(IV) ammine unless $Pt(II)(NH_3)_4^{2+}$ is shown. [b] Percent Pt based on the support dried several days over Drierite. [c] Temperature of calcination in air for catalysts on SiO_2, in oxygen for those on Al_2O_3 and Filtros. [d] Temperature of reduction in hydrogen. [e] Turnover number of cyclopentene in molecules of cyclopentene reacting per surface Pt atom per s at 20 °C. [f] Turnover number in the hydrogenation of di-*tert*-butylacetylene at 20 °C. [g] Turnover number in the hydrogenation of the 3-hexyne at beginning of run. [h] Turnover number in the hydrogenation of the 3-hexene produced in the hydrogenation of 3-hexyne. [i] Prepared by Dr. Donald Barry, on η-Al_2O_3, see ref 12. [j] Prepared by Dr. Toshio Uchijima. In SiO_2-IonX, $Pt(NH_3)_4^{2+}$ was used. [k] Supplied by Professor M. Boudart, prepared from $pt(NH_3)_4^{2+}$, preparation and measurement of dispersion by Dr. H. A. Benesi. The samples were crushed and sieved. The listed N_{cp} are for 270-400 mesh. 400+ mesh catalyst gave the same value of N_{cp} with 59-SiO_2-IonX but N_{cp} of 57.5-SiO_2-IonX was increased to 5.5. Measurement of the dispersions at Stanford gave 56 and 62%, respectively, for 59- and 57.5-SiO_2-IonX. [l] A duplicate preparation used for testing the degree of diffusional influence gave N_{cp} = 11.0, dispersion 56%. [m] Prepared by ion exchange with $Pt(NH_3)_4^{2+}$, dispersion measured by the techniques used in footnote *j*. A catalyst with the same loading on 400+ mesh silica gel was prepared by exposure to ammonaical Pt(IV) ammine for much longer than usual since the material was isolated from this solution by centrifugation. This catalyst gave results similar to 87-SiO_2-IonX including product distributions from the acetylene. The contact time in the ion exchange of 87-SiO_2-IonX was 100 min. [n] A 2.57% Pt/Filtros of the same method of preparation and pretreatment gave 0.48.

reactor as equal to the total pressure less the partial pressure of cyclohexane at the reaction temperature. The total pressure was generally near 1 atm. Rates were corrected to 1 atm by the assumption that the rates were first order in hydrogen.[13,20] Assuming further that the ratio of hydrogen atoms chemisorbed to surface atoms of platinum was unity, a turnover number with the units of molecules of *hydrocarbon* reacting per surface platinum atom per second was computed and entered in Table I. For the alkynes and the cis-ene, this computation involved the conversion of rate of hydrogen consumption to rate of hydrocarbon consumption by stoichiometric data described later. Turnover numbers in ref 12 were in terms of *hydrogen* rather than *hydrocarbon* consumption.

Serious concentration gradients of hydrogen in the pores of the catalysts appear to be absent. 54-SiO_2-IonX was duplicated as carefully as possible on 400+, 200-270, and 120-140 mesh silica gel. Rates of hydrogen uptake in the hydrogenation of cyclopentene were 0.21, 0.21, and 0.108 $cm^3\ min^{-1}\ mg^{-1}$ and of norbornene, 0.44, 0.44, and 0.145. There are clearly serious concentration gradients of hydrogen in the pores of the catalyst granules of the largest mesh but there appear to be none in the two smaller mesh catalysts. The values of the rates with norbornene which hydrogenates twice as fast as cyclopentene strongly support this conclusion. Similar results were obtained with 0.5% Al_2O_3-$PtNO_2$, calcined at 630 °C for ½ h and reduced in hydrogen at 350 °C. With both 400+ and 200-270 mesh catalyst, the rate of hydrogen consumption was 0.051 $cm^3\ min^{-1}\ mg^{-1}$ for cyclopentene and 0.106 with norbornene. The dispersion of the 200-270 mesh Pt/SiO_2 was 56.2% whence N_{cp} = 12.5. The dispersion of the 200-270 mesh Pt/Al_2O_3 was 45% whence N_{cp} = 3.8.

We believe that contamination of the platinum surface of our catalysts by carbonaceous residues was negligible. The activities of 7-SiO_2-IonX, 109-Al_2O_3-PtCl, and 84-Al_2O_3-$PtNO_2$ were unchanged after exposing these catalysis to flowing oxygen and then hydrogen at 300 °C for 1 h each, a process shown by Schlatter and Boudart[8] to eliminate such residues.

As shown in Figure 1, the kinetic order in cyclopentene is zero. In

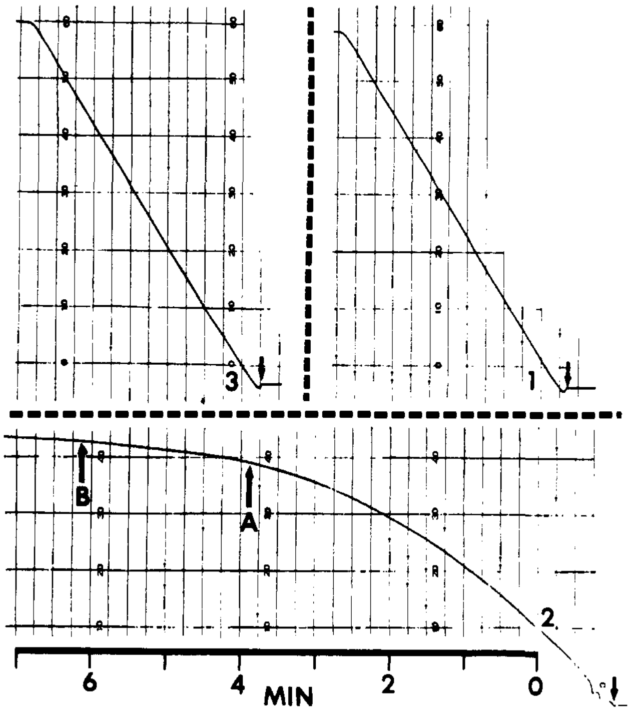


Figure 1. Successive injections of 0.06 cm^3 of cyclopentene (no. 1), 0.07 cm^3 of di-*tert*-butylacetylene (no. 2), and 0.06 cm^3 of cyclopentene (no. 3), 25.4 mg of 54-SiO_2-IonX. $-\Delta P$ is plotted vertically, and time is plotted horizontally increasing from right to left. The times of injections are marked by small arrows.

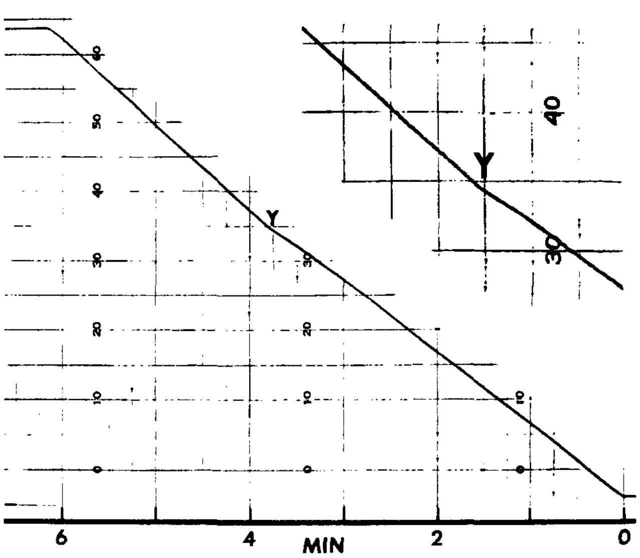


Figure 2. Hydrogenation of 0.04 cm^3 of 3-hexyne on 20.2 mg of 54-SiO_2-IonX. The coordinates are as in Figure 1. Insert at upper right is magnified ×2.

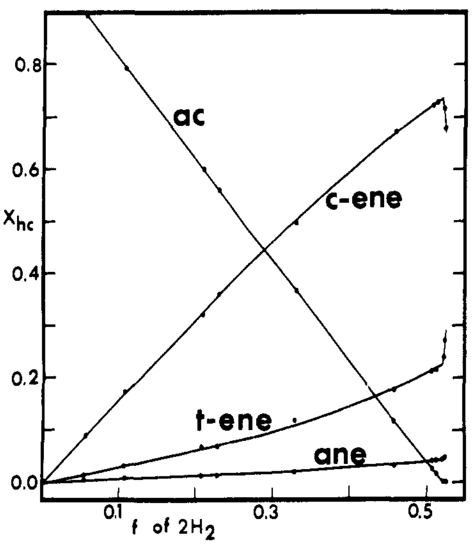


Figure 3. Course of hydrogenation of di-*tert*-butylacetylene on catalyst 109-Al_2O_3-PtCl. X_{hc} on the y axis is the hydrocarbon fraction of various products and reactants; f of $2H_2$ on the x axis is the fraction of total consumption of hydrogen in hydrogenating the acetylene to alkane. Curve ac shows the fraction of the acetylene; c-ene shows the fraction of *cis*-di-*tert*-butylethylene; *t*-ene, that of *trans*-di-*tert*-butylethylene; and ane, that of 2,2,5,5-tetramethylhexane.

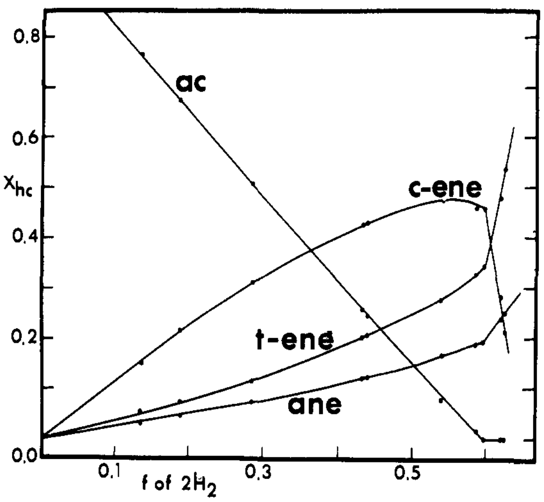


Figure 4. Course of hydrogenation of di-*tert*-butylacetylene on catalyst 54-SiO_2-IonX. Symbols are as in Figure 3.

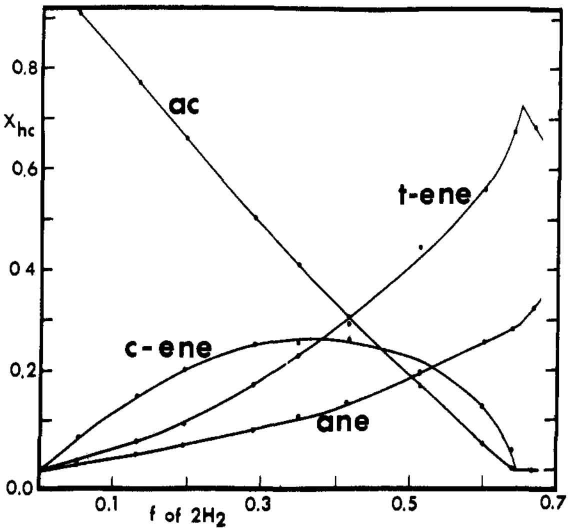


Figure 5. Course of hydrogenation of di-*tert*-butylacetylene on catalyst 7-SiO_2-IonX. Symbols are as in Figure 3.

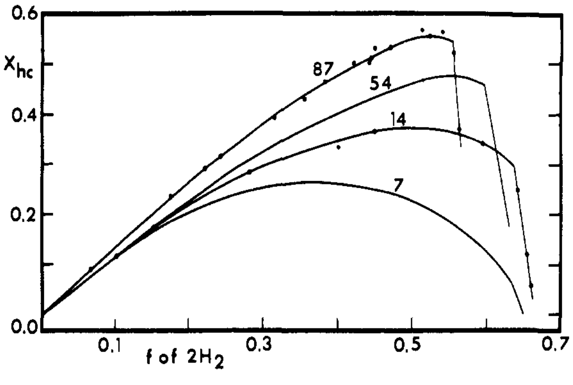


Figure 6. Hydrocarbon fraction of *cis*-di-*tert*-butylethylene vs. fraction of total consumption of hydrogen in hydrogenating the acetylene to alkane. 87 is for catalyst 87-SiO_2-IonX, 54 is for 54-SiO_2-IonX, 14 is for 14-SiO_2-IonX, and 7 is for 7-SiO_2-IonX.

Figure 2 the graph of pressure vs. time during the hydrogenation of 3-hexyne exhibits two linear portions which correspond to zero order hydrogenations of 3-hexyne and 3-hexene. That these hydrogenations were zero order in hydrocarbon was confirmed by measurement of initial rates with different initial concentrations of substrate. This method also showed that hydrogenation was zero order in the acetylene, a result not immediately apparent from Figure 1.

Reaction Products and Selectivities. The measurement of rates of hydrogen consumption was extended to measurement of the composition of the hydrocarbon in the reaction flask. Samples were removed from the reaction chamber through the septum at periodic intervals and analyzed gas chromatographically. A 5-m column of Silicone DC550 on Chromosorb P at 100–120 °C was employed for the C_{10} hydrocarbons and a 12.2-m column of 20% dimethylsulfolane on Chromosorb P at 0 or 30 °C for the C_6 hydrocarbons.

Figures 3, 4, 5, and 6 exhibit the course of the hydrogenation of the acetylene and Figure 7 of 3-hexyne. Three separate runs from each of which several samples were removed were needed to construct these graphs. The data of these figures show that point A of Figure 1 corresponds to the disappearance of the acetylene and point B to the disappearance of the cis olefin. Beyond B the reaction is entirely the hydrogenation of the trans-ene which is a much slower reaction than the others. Similarly, point Y in Figure 2 corresponds to the disappearance of 3-hexyne. The data in these figures and those on other catalysts permit one to calculate the initial products of reaction in the hydrogenations of the alkynes (see Table II).

Table II. Initial Product Distributions in the Hydrogenations of Di-*tert*-butylacetylene, 3-Hexyne, and *cis*-Di-*tert*-butylethylene

	Products from *t*-Bu-C≡C-*t*-Bu,[a] %			Products from 3-Hexyne,[b] %			Products from *cis*-*t*-Bu-ene,[c] %		
	c-ene	t-ene	ane	c-ene	t-ene	ane	t-ene	ane	S(ac/cis)[d]
54-SiO_2-IonX	66	21	13	81	6	13	81	19	~11
14-SiO_2-IonX	66	21	13				69	31	3.0
7-SiO_2-IonX	66[e,f]	21[e,f]	13[e,f]	77	7	16	70[e]	30[e]	1.0
87-SiO_2-IonX	70	23	7				90[h]	10[h]	~15
20-SiO_2-PtCl	66	18	16						2.5
0.28-Filtros[i]	76[e]	13[e]	11[e]	78[g]	8[g]	14[g]	79	21	3.3
109-Al_2O_3-PtCl	81	16	3	83	6	11	90	10	>50
24-Al_2O_3-PtCl	73	14	13	82	7	11	84	16	~17
84-Al_2O_3-$PtNO_2$	81	15	4				91	9	>50
23-Al_2O_3-$PtNO_2$	77	12	11				87	13	~20
100-Al_2O_3-$PtNO_2$[j]	81	15	4						

[a] Di-*tert*-butylacetylene and below it the products of hydrogenation, *cis*- and *trans*-di-*tert*-butylethylene and di-*tert*-butylethane. [b] The major products of hydrogenation of 3-hexyne were *cis*- and *trans*-3-hexene and hexane. Small amounts, never exceeding 0.5% of *cis*-2-hexene, were present as initial products. [c] Products in the hydrogenation of *cis*-di-*tert*-butylethylene were its trans isomer and the alkane. [d] The ratio of the gross rate constants for reaction of di-*tert*-butylacetylene to that of *cis*-di-*tert*-butylethylene in mixtures of the two. See the text. [e] These values were unchanged upon rehydrating the catalyst before use. [f] The initial curvature of the product vs. % reduction curves (see Figure 5) make accurate measurement of product proportions difficult. However, they are not much if any changed from the other SiO_2-IonX catalysts. [g] Derived from data on just one experiment. [h] On the high dispersion SiO_2-IonX prepared from Pt(IV) ammine, see footnote *m* of Table I. [i] 2.57% Pt/Filtros (footnote *n* of Table I) gave 72, 17, and 11% for the products of hydrogenation of the acetylene and the same values of S(ac/cis) as 0.28-Filtros. [j] On η-Al_2O_3, see Table I.

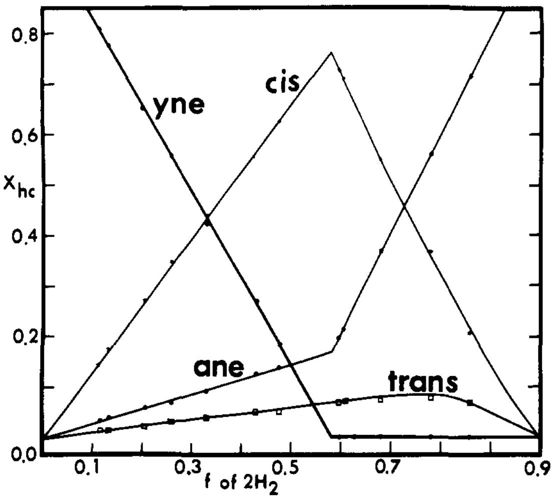


Figure 7. Hydrocarbon fractions vs. fraction of total consumption of hydrogen in hydrogenating 3-hexyne to hexane. Curve yne shows the fraction of hexyne; cis, of *cis*-3-hexene; trans, of *trans*-3-hexene; and ane, of hexane. The fraction of *cis*-2-hexene amounted to about 0.007 at 0.6 hydrogenation and 0.010 at 0.8 hydrogenation.

The product ratios are clearly independent of conversion on Pt/Al_2O_3 of higher dispersion as may be seen in Figure 3. This is presumably also true with other catalysts but curvatures make this difficult to establish. The data for the initial products from the cis-ene were obtained by direct hydrogenation of the olefin. Rate data were of lower accuracy because so much of the product resulted from isomerization (Table II). The trans-ene produced did not react further until at least 95% of the cis-ene had disappeared.

S(ac/cis) represents the competitive reactivities of the acetylene and the cis-ene defined as follows. If the adsorptions of the two substrates are at quasiequilibrium and follow Langmuir adsorption isotherms, the ratio of the coverages by the acetylene θ_a and by the cis-ene θ_c in competition is

$$\theta_a/\theta_c = (K_a[a])/(K_c[c]) \qquad (1)$$

Here, K_a and K_c are the Langmuir equilibrium constants and the denominator common to both θ_a and θ_c, $(1 + K_c[c] + K_a[a])$, has canceled. However, eq 1 also follows from the model in which adsorption is assumed to be irreversible, although K_a/K_c would now be the ratio of the sticking coefficients of the acetylene and cis-ene. Where the fraction of the cis-ene passes through a maximum in Figures 3-5, the rate of formation of the cis-ene is zero, thus

$$d[c]/dt = f_c k_a \theta_a f(P_{H_2}) - k_c \theta_c F(P_{H_2}) = 0 \qquad (2)$$

where $f(P_{H_2})$ and $F(P_{H_2})$ are kinetic functionalities in P_{H_2} and f_c is the fraction of the acetylene which goes to cis olefin (taken from Table II). f_c is assumed to be independent of conversion. If the functions of P_{H_2} in both terms are the same (and, in fact, both reactions appear to be essentially first order in hydrogen), then

$$\theta_a'/\theta_c' = k_c/(f_c k_a) \qquad (3)$$

where θ_i' designates the value at the maximum. Combining eq 1 and 3 we get

$$S(\text{ac/cis}) = (k_a K_a)/(k_c K_c) = [c']/(f_c[a']) \qquad (4)$$

where [c′] and [a′] are the concentrations at the maximum of the cis-ene and of the acetylene, respectively. Although eq 4 may not be exact, it should give a reliable indication of trend. Because of the division by [a′] in the term at the right of eq 4, accuracy in S(ac/cis) falls drastically as [a′] becomes small, i.e., when S(ac/cis) becomes larger than about 6.

Effect of Sintering. Samples of 14-SiO_2-IonX and 0.28-Filtros were additionally treated at temperatures higher than those used in their preparation. Product proportions in the hydrogenation of the acetylene were unchanged by these treatments. 14-SiO_2-IonX was exposed to flowing oxygen for 15 min at 300 °C and then sintered in helium at 500 °C (19 h), 650 °C (4 h), or 750 °C (4 h). The catalyst was cooled to 500 °C, treated with flowing hydrogen for 20 min, cooled in hydrogen, and rehydrated. The hydrogen (cm^3) adsorbed per minute per gram of catalyst fell from the initial value of 200 to 150, 100, and 76. The dispersion after the 750 °C treatment was 6.6% whence N_{cp} was 9.7. The ratio N_{ac}/N_{cp} was initially 0.71 and then 0.73, 0.94, and 0.93. S(ac/cis) was initially 3.0 and then 2.6, 2.6, and 1.7. 0.28-Filtros was first heated in oxygen to 500 °C, purged with nitrogen, heated in hydrogen at 850 °C for 4 h, cooled in hydrogen, and then rehydrated. The rate of hydrogen absorption during the hydrogenation of cyclopentene fell from 7.7 to 3.7, N_{ac}/N_{cp} from 0.54 to 0.29, and S(ac/cis) was unchanged. A portion of the unrehydrated catalyst was sintered in helium at 850 °C for 4 h, treated with H_2 at 500 °C, cooled in hydrogen, and rehydrated. The rate of hydrogen absorption fell to 2.1 and N_{ac}/N_{cp} fell to 0.22.

Effect of Cooling in Helium. All catalysts had been cooled in hydrogen following reduction. Catalysts 109-Al_2O_3-PtCl, 24-Al_2O_3-PtCl, and 0.28-Filtros were heated in hydrogen to 450 °C, kept at 450 °C for ½ h, kept in helium for ½ h, and cooled in helium. The first two

Table III. Effect of Silylation upon Catalytic Properties

%C[a]	N_{cp}	N_{ac}/N_{cp}	S(cp/ac)	Cis[b] %	Trans[b] %	Ane[b] %
54-SiO_2-IonX						
0.00	15.7	0.65	90	66	21	13
3.27	13	0.50	110	65[c]	15[c]	20[c]
3.20	13	0.50	110	65	15	20
3.07[d]	12	0.32	200	65	15	20
3.52[d]	9.6	0.29	200	65	15	20
24-Al_2O_3-PtCl						
0.00	8.6	0.89	140	73[e]	14[e]	13[e]
1.08	5.9	0.40	420	68	14	18
0.73	5.9	0.40	420	68	14	18
0.28-Filtros						
0.00	10.8	0.54		76	13	11
0.031	8.5	0.37		76	13	11

[a] Percent carbon by weight after silylation, by microanalysis. [b] Product distribution in hydrogenation of the acetylene. [c] S(ac/cis) was little affected by the silylation. [d] The preliminary protective treatment at 150 °C was in hydrogen rather than in oxygen. [e] S(ac/cis) was decreased upon silylation. In hydrogenating 3-hexyne, N_{hyne}/N_{cp} decreased from 0.59 to 0.41, and the initial products were 77% cis-ene, 8% trans-ene, and 15% hexane, see Table II.

catalysts were rehydrated. The helium-cooled Pt/Al_2O_3 catalysts gave the same values for N_{cp} as originally, and 109-Al_2O_3-PtCl exhibited the original behavior in hydrogenating 3-hexyne. However, N_{cp} was increased 40% over the original value for 0.28-Filtros.

Effect of Silylation. Three catalysis were silylated with hexamethyldisilazane at 100 °C after first treating them with oxygen at 150 °C to form a protective coating on the platinum of oxygen atoms. After silylation the catalysis were treated with hydrogen at 150 °C.[18] These treatments omitting the silylation had no effect upon the catalytic properties. Results are shown in Table III.

Discussion

Because of experiments described in the Experimental Section, we believe that the rates, product distributions, and competitive ratios reported in this paper are free from the effects of gradients of the fugacity of hydrogen within the catalyst pores and between gas phase and solution, from effects of any initial contamination by hydrocarbon of the catalysts, and from effects of extrinsic poisons in hydrogen and hydrocarbons. This last conclusion follows from the sandwiching technique, illustrated in Figure 1, which was regularly employed.

The data are mainly of four types: (a) absolute rates, (b) rate ratios, (c) initial product distributions during hydrogenation, (d) competitive factors derived from the detailed analysis of composition vs. time during hydrogenation. Absolute rates are meaningful for present purposes only when they are converted into some type of areal rates. We have used turnover numbers and their accuracy involves the accuracy of the measurement of dispersion. The conversion of the amount of hydrogen chemisorbed into dispersion involves an assumption (one atom of hydrogen corresponds to one surface atom of platinum), potential errors in which are difficult to evaluate. The measured values of items b, c, and d are independent of the measurement of the dispersion and, since dispersion is used here only to order the catalysts into a sequence, results are less dependent upon high accuracy in the measurement of dispersion. Additional possible variables are the distribution of particle sizes of platinum (the dispersion of the dispersion) and the uniformity of the distribution of the platinum particles throughout the granules of the support. We know little about these matters but the last factor should not be significant because of the absence of serious concentration gradients in the pores of the catalysts.

Since, in general, the hydrogenation reactions are zero order in hydrocarbon, the surface of platinum is fully covered during hydrogenation and rates and initial product distributions (items a, b, and c) do not depend upon rates of adsorption or desorption of the hydrocarbon substrates but rather upon rates of reaction of surface intermediates. On the contrary, if the rates of desorption of the reactants are negligible, the competitive factors will depend upon the relative sticking coefficients of the two compounds competing for surface sites. That the reaction be zero order is a necessary but not a sufficient condition for the rate of desorption being negligible. The low rates of double bond migration and cis-trans isomerization during the hydrogenation of olefins on platinum has generally been taken to indicate that desorption of olefin from platinum is slow.[13] Rates of desorption of acetylenes should be even slower. However, since the kinetic order in the cis-ene appears to be very slightly positive, the rate of desorption of the cis-ene during its hydrogenation may be a little larger than in the case of cyclopentene and the alkynes.

Relative Rates of Hydrogenation. N_{cp} is about one-half $N_{norbenene}$ and twice N_{hyne}. The rates of reaction (not the rate of consumption of hydrogen) of the acetylenes, the cis-ene, and 3-hexene lie between those of cyclopentene and 3-hexyne. In the hydrogenation of the cis-ene, the value of (rate of isomerization to the trans-ene)/(rate of hydrogenation to alkane) approaches 10 (see Table II), a value without precedent in hydrogenations on platinum, the ratio usually being 0.05–0.1.[13,20,21] This large value of the ratio is presumably related to the high degree of steric strain in the cis-ene and weak adsorption of trans-ene. The enthalpy of isomerization to the trans-ene is −9 kcal per mol.[22]

The rate of hydrogenation of trans-ene is much the smallest of all the compounds studied, about one-fourth of the rate of *hydrogenation* of the cis-ene. However, this value is valid only at the concentration of the trans-ene employed, 0.7 M. The trans-ene is exceptional, its kinetic order is about +0.4 and the rate of its desorption under reaction conditions is clearly substantial.[23]

Structure Sensitivity in N_{cp}. The values of N_{cp} for a large number of Pt/SiO_2 catalysts (Table I) fall within a factor of less than 2; there is no apparent difference among SiO_2-IonX from Pt(IV) ammine, SiO_2-IonX from Pt(II) ammine, and SiO_2-PtCl; and there is no clear trend of N_{cp} with dispersion. Even the Pt/Filtros of very low dispersion fits into this set. A sample of 14-SiO_2-IonX was sintered at 750 °C. Since 750 °C is above the Tammann temperature equilibrium crystallites should have resulted. N_{cp} was still in the band for Pt/SiO_2.

However, the Pt/Al_2O_3 catalysts of very high dispersion, especially Al_2O_3–$PtNO_2$, gave low values of N_{cp}. Further, the turnover number for the hydrogenation of the trans-ene on 109-Al_2O_3–PtCl was only 0.12 as compared with 0.81 on 24-Al_2O_3–PtCl and 1.43 on 14-SiO_2–IonX.[23]

Structure Sensitivity in Ratios of $N_{\rm I}$'s and in the Initial Distributions of Products. The extreme factor by which these quantities vary is given below. Pt/Filtros is often anomalous, and its consideration will be postponed.

Initial Distribution of Products. 3-Hexyne. The distribution is structure insensitive and accords with previous work.[20]

Acetylene. The distribution is structure sensitive; the proportion of alkane decreased with increasing dispersion. The effect is noticeable with Pt/SiO_2 only at the highest dispersion. The ratio of the highest proportion of alkane to the lowest is about 4.

Rate Ratios. Isomerization/Hydrogenation for the Cis-ene. On Pt/SiO_2, the ratio increased with increasing dispersion by a factor of about 3.

N_{hyne}/N_{cp}. The ratio decreased with increasing dispersion by a factor of about 2.

N_{ac}/N_{cp}. The ratio decreased with increasing dispersion by a factor of about 3.

Because of the sandwiching technique used in rate determinations, we believe that these variations are real and that the rate ratios in Table I are accurate to better than ±10%.

Although the effect of the support and of the method of preparing a catalyst were usually minor, Pt/Al_2O_3 gave less di-*tert*-butylethane in the hydrogenation of the acetylene than did Pt/SiO_2 of the same dispersion, N_{ac}/N_{cp} was lower on SiO_2–PtCl than on SiO_2–IonX, and lower on 23-Al_2O_3–$PtNO_2$ than on 24-Al_2O_3–PtCl.

Structure Sensitivity in S(A/B)'s. The quantities of the preceding section depend primarily upon rates of reaction of surface intermediates. Much larger effects of structure sensitivity appear in certain selectivities related to competition between two compounds for the surface where the values of S(A/B) depend primarily upon the relative sticking coefficients of A and B for free sites as they are formed on the surface of the platinum crystallites. This is seen in an extreme form in comparing Figures 3 and 5. It would hardly appear that the two figures relate to the same kind of catalyst. Part of the difference in appearance results from the higher yield of cis-ene and the lower yield of alkane for the highly dispersed 109-Al_2O_3–PtCl vs. the 7-SiO_2–IonX of low dispersion. The main origin of the difference, however, is variation in the competitive ratio of the acetylene and the cis-ene for the surface of the catalyst. Little of the cis-ene formed by hydrogenation on 109-Al_2O_3–PtCl reacts until the acetylene has disappeared, as one can see from the fact that the curves for the three products vs. conversion are nearly linear, from the sharp breaks in the lines at the conversion at which the acetylene disappears, and from the large value of the hydrocarbon fraction of the cis-ene at its maximum value. The competitive ratio S(ac/cis) (acetylene to cis-ene) is too large to measure with any accuracy. On 7-SiO_2–IonX, the relative yield of the cis-ene falls steadily and those of the trans-ene and alkane rise with conversion. The total yield of cis-ene maximizes at a rather low value and long before the acetylene has disappeared. On this catalyst, S(ac/cis) is about unity. Figure 6 shows that S(ac/cis) is primarily dependent upon the dispersion for the SiO_2–IonX catalysts. The computed values of S(ac/cis) are given in Table II. They vary by a factor of 50 with, in general, S(ac/cis) increasing with increasing dispersion. Other factors are involved since S(ac/cis) is larger on Pt/Al_2O_3 than on Pt/SiO_2 and Pt/Filtros is again somewhat out of line. Similarly. S(cp/ac) in competition between cyclopentene and the acetylene varies from about 50 with highly dispersed Pt/Al_2O_3 to about 1000 for 7-SiO_2–IonX, with reaction of the acetylene being again relatively favored on catalysts of high dispersion (large edge/face ratio) and on catalysts supported on alumina.[23]

Effect of Initial Layer of Oxide on Platinum. Exposure of platinum to oxygen rapidly forms a layer of chemisorbed oxygen atoms which is rapidly reduced by hydrogen at room temperatures. Evidence for this is provided by the hydrogen titration of chemisorbed oxygen[7] and by substantial evidence from surface chemical physics.[24] Therefore, stored catalysts are covered with at least a monolayer of oxygen, and the catalysts of high dispersion are essentially PtO/support. We assume that prolonged storage of the catalyst in air does not lead to the formation of oxide not reducible by the pretreatment in the reactor with hydrogen at 20 °C. N_{cp} and N_{ac} did not depend upon time since preparation of the catalyst over several months nor upon the period of pretreatment between 15 min (the usual period) and 70 min.

We have further assumed that the dispersion appropriate to calculate N's for catalyst "rereduced" at room temperatures is that of catalyst heated in hydrogen at 300 °C and then in helium to 450 °C during the course of measuring the dispersion. One may question the validity of this assumption particularly for catalysts which start as PtO/support. Heating the catalyst to 300 °C in hydrogen, 450 °C in helium, and cooling in helium before insertion into the reactor did not change N_{cp} for 109-Al_2O_3–PtCl nor 24-Al_2O_3–PtCl. Whatever the nature of the crystallites of platinum formed by "rereduction" with hydrogen at 20 °C, the crystallites are formed reproducibly since reproducibility in measuring N's and selectivities was excellent.

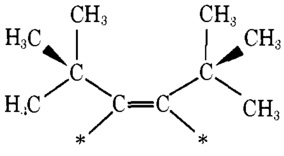
Hydrogenation of 3-Hexyne. Some support for concern about the morphology of platinum crystallites on highly dispersed catalysts was obtained from the results of hydrogenating 3-hexyne on highly dispersed Pt/Al_2O_3. The rate of reaction of 3-hexyne increased continuously during a run and cyclopentene or 3-hexyne injected subsequently was hydrogenated more rapidly than in the original injection. For example, with 41.6 mg of 109-Al_2O_3–PtCl, initial rates of hydrogen absorption in cm^3 per min upon the following successive injections were: cyclopentene 5.06, 3-hexyne 1.57, cyclopentene 6.48, 3-hexyne 2.04, 3-hexyne 2.12, cyclopentene 7.20. Some samples of Pt/Al_2O_3 and Pd/Al_2O_3 behaved similarly with *nor*bornene.[25] Product distributions from hydrogenation of 3-hexyne were unaffected by the increases in rate. 84-Al_2O_3–$PtNO_2$ behaved similarly and even 24-Al_2O_3–PtCl exhibited increases in the rate of hydrogenation of cyclopentene, but the increases were only one-half as large and those for 3-hexyne were negligible. Because of this phenomenon we have not entered a value for N_{3ene} for 109-Al_2O_3–PtCl in Table I. No such phenomenon was observed in 54-SiO_2–IonX and 7-SiO_2–IonX.

We do not think that the effect of 3-hexyne results from production of differing kinds of carbonaceous residues on the surface of platinum. Thus, in the sandwich technique, cyclopentene, another unsaturated hydrocarbon, cyclopentene, the hydrogenation of cyclopentene was zero order in the third run from its beginning and of the same rate as in the first run except as noted above. Further, as may be seen in Figure 2, transition from a rate characteristic of 3-hexyne to one characteristic of 3-hexene occurred in less than 1 min. The small kink seen in the transition region was observed in all cases, and it must represent a period during which the adsorbed layer on platinum changes from one characteristic of 3-hexyne to one characteristic of 3-hexene. Most of the kink occupies only 0.25 min. Thus, the platinum surface seems to have no memory of its previous exposure to various hydrocarbons except for the case of 3-hexyne on Pt/Al_2O_3 and particularly on the more highly dispersed ones.

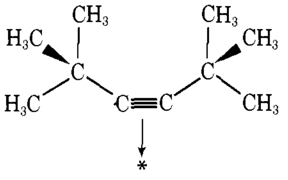
We suggest that the phenomenon involving highly dispersed

Pt/Al_2O_3 and 3-hexyne results from reconstruction of the platinum particles to ones giving higher rates.

Nature of Adsorbed Di-*tert*-butylacetylene. According to current views, the acetylene is adsorbed to form one of the following two forms or some composite of both. X-ray structures of various molecular complexes of acetylenes make it unlikely that a linear π complex exists. The diadsorbed alkene and the bent π complex have similar geometries and similar considerations apply to both forms. There are two types of steric interactions which raise the energy of adsorbed di-*tert*-butylacetylene relative to adsorbed 3-hexyne: steric repulsions between the *tert*-butyl groups and surface atoms of platinum: steric repulsions between the two *tert*-butyl groups amounting to about 9 kcal per mol in diadsorbed alkene.[22] If this number is smaller in the bent π complex, the adsorbate–surface interaction would be larger.[26] Adsorption at edge atoms either as diadsorbed alkane or π complex should involve less adsorbate–surface repulsion than adsorption on the more densely packed crystal planes. If the cis-ene can adsorb with the plane of the double bond inclined to the surface, its adsorbed form should exhibit less adsorbate–surface interaction than in the case of adsorbed di-*tert*-butylacetylene and adsorbed trans-ene and its adsorption at edge atoms would be relatively less favored. Norbornene competes very effectively with other hydrocarbons in hydrogenation reactions.[27] Here, too, the plane of the double bond must be inclined to the plane of the surface.



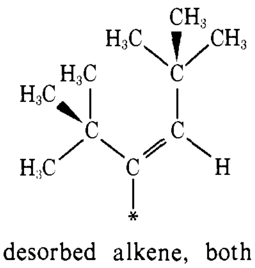
diadsorbed alkene

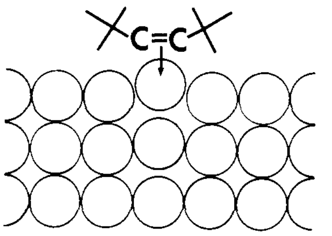


bent π complex

The marked increase in S(ac/cis) and S(cp/ac) with increasing dispersion accords with the view that the sticking probability of the acetylene is relatively much larger at edge atoms vs. atoms in more densely packed planes if one assumes, as would seem likely, that in catalysts of higher dispersion the platinum crystallites are smaller and hence have a larger ratio of edge atoms to those in planes.

However, the rate of hydrogenation of the acetylene appears to be at least as large at face atoms as at edge atoms since N_{ac}/N_{cp} is close to unity on the catalysts of low dispersion and smaller on those of high dispersion (Pt/Filtros excepted). How can this be? We suggest that two factors may be involved. First, the lower heat of adsorption of the acetylene vs. 3-hexyne may actually lead to an increase in rate since, beyond a certain point, increase in the heat of adsorption will lead the adsorbed species to have low reactivity. In particular, in reaction of adsorbed di-*tert*-butylacetylene to monoadsorbed olefin and of that to desorbed alkene, both steps should result in reduction of adsorbate–surface interaction and augmentation of rate vs. the corresponding situation with 3-hexyne. Secondly, the strength of the adsorption bond will tend to pull face platinum atoms above the plane of a face in the case of bulky adsorptives. This may serve significantly to reduce the total energy as compared with the case in which the atoms of platinum stay in the surface plane. We suggest that di-*tert*-butylacetylene adsorbed on face atoms looks something like the following:





The diadsorbed alkene form would be similar but here two atoms of platinum would be raised above the surface. Some version of this semiextractive chemisorption may be rather common in surface chemistry, and it probably overlaps the "corrosive" chemisorption of Boudart.[28] The vibrational amplitudes of atoms normal to faces (at least in the case of nickel[29] but presumably also with platinum) is larger for a surface atom than for a bulk atom and this effect should facilitate raising a surface atom above a surface plane. We see no evidence for the alternative possibility that the acetylene and other unsaturated hydrocarbons adsorb and react upon projecting atoms of some hydrocarbon layer on the surface of platinum.

Possible Surface Contamination. A few rather small effects of support have been noted but the effect of Filtros as a support is so large that we omitted Pt/Filtros from the correlations with dispersion presented earlier in this paper. With respect to N_{ac}/N_{cp}, N_{hyne}/N_{cp}, S(ac/cis), and the product distribution in the hydrogenation of the acetylene, Pt/Filtros usually behaved as if it had a much higher dispersion than that measured. These effects might arise from the surface of the platinum crystallites becoming contaminated with inorganic material which migrates from the support. Some information relating to this possibility results from a study of the effect of silylating three of our catalysts with hexamethyldisilazane (Table III). With Pt/SiO_2, the determined %C corresponds to a monolayer of $(CH_3)_3SiO$- on the silica but the fall of N_{cp} was small, from 15.7 to 13. Thus, neither hydrogen spillover nor supply of olefin to platinum via migration from silica significantly influences the rate of hydrogenation.[18] Silylation changed the product distribution in the hydrogenations of the acetylene and of 3-hexyne only a little, but N_{ac}/N_{cp} fell substantially in all cases and S(cp/ac) increased. It seems probable that the changes result from the deposition of small amounts of contaminants on the surface of the platinum.[18] A highly dispersed contaminant should eliminate more sites for a bulky reactant like the acetylene than for a small one like cyclopentene.

These results suggest that Pt/Filtros may be anomalous because of some migration of impurities to the surface of platinum during the preparation of the catalyst and that further migration occurs during treatment at high temperatures. Such a phenomenon does not appear to occur on Pt/SiO_2 and Pt/Al_2O_3 because N_{ac}/N_{cp} increases during treatment at high temperatures with these catalysts whereas it decreases with Pt/Filtros. It should be noted that the alumina (Catapal) is of high purity and that the silica is of relatively high purity but that the manufacturer reports Filtros to contain 3.86% Na_2O, 2.07% CaO, 0.48% MgO, and 0.21% Al_2O_3 in addition in SiO_2.

Maurel et al.[30] have observed a phenomenon which may be related to that just described: sulfate on the alumina or added hydrogen sulfide plus sulfur dioxide can cause Pt/Al_2O_3 catalysts to manifest the appearance of structure sensitivity as judged by the relative rates of hydrogenation of benzene, isotopic exchange between benzene and deuterium, and hydrogenolysis of cyclopentane. We have seen no sign of such an effect of sulfate on our Pt/Al_2O_3 catalysts, but Catapal is reported to be 99.99% pure after calcination to remove the carbon content.

However, there is another factor which may contribute to the anomalous behavior of Pt/Filtros. Unlike the other catalysts, Pt/Filtros cooled in hydrogen gave a value of N_{cp} only 0.7 that of the catalyst cooled in helium. A similar difference between cooling this catalyst in hydrogen vs. helium was observed in the hydrogenation of ethylene at temperatures below 0 °C.[31] This may be the manifestation of a higher solubility of hydrogen in large particles of platinum than in small ones.

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Silicon Substitution for the Stabilization of Silicenium Ions

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Abstract: Systems have been examined in which a silicenium ion, if produced by hydride transfer ($R_3Si{-}H + (C_6H_5)_3C^+\ ClO_4^-$), would be stabilized inductively by tetravalent silicon attached directly to the electron-deficient silicon. The systems examined in this fashion (triphenylsilane, methyldiphenylsilane, pentaphenyldisilane, pentamethyldisilane, and tris(trimethylsilyl)silane) all exhibited hydride transfer in CH_2Cl_2 or CH_3CN/1,4-dioxane at −20 to −30 °C, by observation of the production of $(C_6H_5)_3C{-}H$ and (after reaction with $NaBD_4$) of recovered $R_3Si{-}D$. The NMR spectrum of methyldiphenylsilane after reaction with $(C_6H_5)_3C^+\ ClO_4^-$ and prior to reaction with $NaBD_4$ showed loss of the methyl doublet and the Si–H multiplet and appearance of a methyl singlet and a C–H peak. None of the systems exhibited conductance prior to reaction with $NaBD_4$. On the basis of the lack of conductance and the common behavior of all systems, including those such as $(C_6H_5)_3SiH$ known not to produce silicenium ions, we conclude that the intermediates in these reactions have the covalent structure $R_3Si{-}O{-}ClO_3$ or are tight ion pairs. Free silicenium ions are not produced, and silicon substitution offers no special stabilization under these conditions.

Trivalent, positively charged silicon (R_3Si^+) has been an elusive chemical species.[2] Although there is evidence from appearance potentials and mass spectral fragmentation that silicenium[3] ions exist in the gas phase,[4] evidence in the condensed phase is very rare. The chemistry of silicon is characterized by coordination expansion rather than contraction because of the availability of low-energy d orbitals. Thus, pentavalent siliconium[3] ions have been prepared and studied.[5]

Traditional attempts to stabilize silicenium ions have been through p_π–p_π ($C \rightarrow Si^+$) donation, which has been successful in carbenium ion chemistry ($C \rightarrow C^+$). There are two drawbacks to this approach. First, carbon is more electronegative (2.55) than silicon (1.90), so that a carbon substituent automatically destabilizes a silicenium ion inductively. Second, p_π–p_π overlap between carbon and silicon is considerably poorer than between carbon and carbon because of the differences in orbital dimensions. Thus, phenyl should have at best a poor stabilizing effect through conjugation and at worst a destabilizing effect through induction. A more viable approach we felt was to choose substituents on silicon that can offer inductive stabilization and to ignore conjugative substituents that stabilize carbenium ions. The types of substituents we have examined to date contain silicon as the atom attached to the silicon that will bear charge in the silicenium ion ($R_3Si{-}Si^+$). The principal stabilizing influence of the silicon substituent is intended to be electrostatic induction of charge. It is also possible that σ delocalization, which has been established to