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Active Centers of Platinum–Silica Catalysts in Hydrogenolysis and Isomerization of *n*-Pentane

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A study has been made of the different factors liable to influence the dispersion of platinum deposited on silica by ion exchange and its activity in hydrogenolysis and isomerization of *n*-pentane. The parameters investigated are the active metal loading and the reduction and calcination temperatures.

The first two parameters have very little influence on the dispersion and selectivity but an oxidizing treatment (calcination) causes a considerable increase in the mean diameter of the crystallites.

When the mean diameter of the crystallites increases from about 10 to 150 Å the hydrogenolysis turnover number decreases by a factor of 10 but the isomerization turnover number remains appreciably constant.

A quantitative correlation is found between the hydrogenolysis–isomerization ratio and the proportion of low coordination-number atoms located at the corners and edges of the platinum crystallites, assumed to be cubic or octahedral.

INTRODUCTION

The last decade has seen a great deal of research devoted to the hydrogenolysis and isomerization of saturated hydrocarbons catalyzed by noble metals and especially by platinum. Most of this research has sought either to determine the mechanism leading to a rearrangement or a breaking of carbon chains or else to link the rates of these reactions to the mean diameter of metal crystallites or, more generally speaking, to the geometric structure of the metallic deposit. Mention can be made of research on the hydrogenolysis of ethane (*1, 2*), butane (*3, 4*), cyclopentane (*5, 6*) and hexane (*7*), as well as research on the isomerization of neopentane (*8*) and hexane isomers (*7, 9–13*). These different research projects have generally led their respective authors to classify such reactions in the category of "demanding reactions" according to the classification recommended by Boudart *et al.* (*14*).

An examination of these different projects, however, has led us to single out two special points that deserve further experimental work. The first one is the relative behavior of hydrogenolysis and isomerization reactions when the diameter of the catalytic metal crystallites varies. This point appears to have been systematically studied only by Anderson and Shimoyama (*15*) in the hydrogenolysis of *n*-hexane and 2- or 3-methylpentane. The second one is the quantitative identification of the active centers that catalyze these demanding reactions.

In attempting to elucidate these specific points, we have undertaken a kinetic study of the hydrogenolysis and isomerization of

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n-pentane on catalysts of the platinum–silica type. Platinum was chosen because it is one of the rare metals capable of simultaneously bringing about the hydrogenolysis and isomerization of *n*-pentane. As for silica, its choice as a support resulted from the fact that it is inactive under test conditions, and the transformations observed could therefore be ascribed solely to the action of the metal.

Once the nature of the catalyst has been defined, the respective influence on both the state of metal dispersion and catalyst activity of various parameters of preparation have been determined; these parameters are the type of impregnation, the amount of active metal and the calcination and reduction temperatures.

Two methods of preparing platinum–silica catalysts were used in this study. The first one employed ion exchange between an impregnation solution and a support. This method, when applicable, is known to result in a very good microscopic dispersion of the metallic precursor, as has been proven by research on the depositing of platinum (*16–18*) or palladium (*19, 20*) on silica. An analysis of such interactions between support and solute as well as the discovery of exchange equilibria were the subject of a previous paper (*21*). The second impregnation method was the most conventional one and was mainly used for the sake of comparison. It is based on the absence of any exchange between the support and the metallic salt dissolved in the impregnation solution.

To sum up, the present experimental study of the hydrogenolysis and isomerization of *n*-pentane over platinum deposited on silica has the following three complementary aspects:

Analysis of the influence of preparation parameters on crystallite size;

Simultaneous analysis of the apparent kinetics of the hydrogenolysis and isomerization reactions over platinum;

Interpretation of the experimental findings in terms of correlations between the kinetic findings and the structural properties of the metallic deposit.

EXPERIMENTAL METHODS

A. MATERIALS

Phillips "pure grade" *n*-pentane used in the present study was previously distilled to eliminate traces of cyclopentane and to lower the isopentane content to less than 0.1% mol.

Hydrogen, nitrogen and helium were "U" quality pure gases from "L'Air liquide." They were further purified by a Deoxo treatment followed by water adsorption of a 3 Å molecular sieve.

The platinum–silica catalysts were prepared from a Rhône-Poulenc silica and a chloroplatinic acid solution supplied by Compagnie des Métaux Précieux.

B. CATALYST PREPARATION

Before any preparation, the silica support having a particle size of between 1.6 and 2.8 mm was refluxed with concentrated nitric acid for 16 hours, washed until all trace of acid was eliminated and then dried and calcined in air at 600°C for 3 hr. After this treatment, the support had a specific area of 260 m^2/g, a pore volume of 1 cm^3/g and a sodium content of 0.23% by weight.

The first series of catalysts, namely the "cation exchanged" catalysts, were prepared by an exchange between silica and a Keller's-complex ammonia solution (*21*). The volume of the solution to be exchanged was between 5 and 10 times the pore volume of the support, and the concentrations of Keller's complex and ammonium chloride were adjusted as a function of the platinum content required in the final catalyst.

This mode of impregnation by exchange has two advantages.

i. It theoretically creates an atomic dispersion of platinum on the surface of the support.

ii. The presence in the impregnation solution of a suitable concentration of free ammonium ions enables the metal-carrying ion to be dispersed over the entire surface area of the silica and thus prevents any concentration gradient between the outside and middle of the particle.

As soon as exchange equilibrium is obtained, the catalyst is washed with distilled water and then dried in air at 120°C for 16 hr. After that it is treated in various atmospheres (nitrogen, air, hydrogen) and at different temperatures (200–700°C) under conditions that vary from one formula to another because one of the objectives of this study was precisely to analyze the influence of such heat treatments on the structure of the metallic deposit.

The second series of catalysts was prepared by the simple wetting of a known weight of support with a volume of chloroplatinic acid solution equal to the pore volume of the support. The chloroplatinic acid concentration of the solution was adjusted to obtain the desired platinum content in the final catalyst. The catalyst was then dried and reduced *in situ* in a hydrogen flow of 5 liters/hr at 410°C for 6 hr prior to kinetic or chemisorption measurements. These catalysts, with which no exchange occurs between the impregnation solution and the support, will be called "impregnated catalysts."

C. CATALYST CHARACTERIZATION

Three different methods were used to evaluate the state of dispersion of the metal. They were carbon monoxide chemisorption, electron microscopy and X-ray diffraction. This latter method could be used only in the case of crystallites larger than 30–40 Å.

1. CO Chemisorption

Chemisorption measurements were made under dynamic conditions, at 25°C, by a chromatographic method (*22*). The catalyst sample weighing about 1 g was dried, calcined and reduced under conditions identical to those used for the parallel kinetic studies. It was then desorbed for 1 hr at 400°C under a helium flow of 3 liters/hr. It was checked that the desorption time and temperature were sufficient to eliminate the hydrogen chemisorbed on the metallic surface upon completion of the reduction and that the silica support did not chemisorb the carbon monoxide under the operating conditions.

CO chemisorption is a way of measuring the total number of accessible metal atoms on the crystallite surface provided the stoichiometry of this chemisorption is known. In this study, a stoichiometry coefficient metal/gas equal to 1.15 was chosen with reference to the work by Dorling and Moss (*23*).

To estimate the mean size of the crystallites from chemisorption data, the relation existing between this size and the percentage of surface metal atoms must be determined from various hypotheses concerning the geometry of these crystallites. In this project, we limited ourselves to cubic and octahedral models representing the stable elementary crystallographic planes of the platinum, i.e., planes (100) and (111), respectively.

Cubic model. The crystallites were likened to cubes having 5 exposed faces, with the sixth being in contact with the support. For a given sample, all the crystallites were also assumed to have the same mean size (l). On the basis of these assumptions, we obtained the following equations giving the number of atoms located in the corners (N_c), on the ridge (N_a), on the faces (N_f), on the surface (N_s) and in the volume (N_v) as a function of a multiple n of the length a of the unit cell of platinum (a = 3.92 Å):

$$N_c = 8,$$

$$N_c + N_a = 12n - 4,$$

$$N_s = N_c + N_a + N_f = 10n^2 + 2n + 1,$$

$$N_v = 4n^3 + 6n^2 + 3n + 1.$$

In calculating N_c, N_a, and N_s, we took into consideration the atoms located on the ridge of the face of the crystal in contact with the solid.

The value of N_s was obtained directly by applying the following formula:

$$N_s = \frac{V_{\mathrm{CO}} \cdot t \cdot N}{22.4 \times 10^3}$$

where

N	the Avogadro number
t	the adsorption stoichiometry, taken as 1.15
V_{CO}	the volume of chemisorbed CO expressed in ml/g of catalyst.

The following formulas can also be used to determine the dispersion (D) of the metal defining the percentage of atoms accessible to carbon monoxide:

$$N_v = \frac{P \cdot N \times 10^{-2}}{M}$$

and

$$D = \frac{N_s}{N_v} = \frac{V_{\mathrm{CO}} \cdot t \cdot M}{P \cdot 22.4 \times 10} = \frac{10n^2 + 2n + 1}{4n^3 + 6n^2 + 3n + 1},$$

in which M is the atomic mass of the metal and P the mass percentage of platinum deposited on the silica support.

The latter equation thus links n with the volume of chemisorbed CO for a cubic representation of the crystallites and can be used to determine their mean size l, by the equation $l = n \cdot a = 3.92n$.

Octahedral model. If instead of a cubic configuration we assume an octahedral configuration representative of the (111) planes of platinum, we obtain the following equations by using formulas proposed by various authors (*5*, *24*, *25*) but corrected to account for the assumption adopted that the face of the octahedron in contact with the support is not accessible to CO:

$$N_c = 6,$$

$$N_a + N_c = 12n - 6,$$

$$N_s = \tfrac{1}{2}(7n^2 + 3n + 2),$$

$$N_v = \tfrac{1}{3}(2n^3 + 6n^2 + 7n + 3),$$

$$\frac{V_{\mathrm{CO}}}{P} = \frac{3}{2} \cdot \frac{7n^2 + 3n + 2}{2n^3 + 6n^2 + 7n + 3}$$

with

$$l = \frac{a(2)^{\frac{1}{2}}}{2} \cdot n.$$

2. Electron Microscopy

Electron microscope examination of the "ion-exchanged" and "impregnated" catalysts which contained more than 1 wt% of platinum were made with a Siemens Elmiskop 1 apparatus.

The samples were prepared in the following manner:

A small amount of catalyst was crushed in an agate mortar. The fine part was placed in suspension in ethylene glycol. A drop of this suspension was placed on a support membrane made up of a carbon film produced by the vacuum evaporation of heated graphite electrodes. After drying in a flow of warm air, the support and sample were set in place inside the microscope and then examined by transmission.

The mean size of the metallic particles was then determined directly from photographs obtained by measuring the diameter of a large number of crystallites and by using the following formula expressing the surface mean diameter l_s:

$$l_s = \frac{n_i l_i^3}{n_i l_i^2},$$

in which n_i represents the number of crystallites having a diameter l_i.

3. X-Ray Diffraction

The mean size of the metallic particles was also determined from X-ray diffraction diagrams obtained with a Philips PW 1010 apparatus, by measuring the width of diffraction lines at half height and then applying Scherrer's formula. Like electron microscopy, this technique provides direct access to the size of the crystallites, but it nevertheless has the disadvantage of not being sensitive to particles smaller than 30 Å. This means that the values obtained by this method may be higher than those deduced from CO chemisorption results.

4. Comparison of All Three Methods

Without wishing to anticipate the results that are presented below, it can already be said that the mean crystallite diameter values given in Tables 3 and 4 and calculated by the three different techniques generally agree with one another. However, for our general interpretation we will use the simplest method which enabled us to make the greatest number of measurements, i.e., the selective chemisorption of carbon monoxide.

D. KINETICS STUDIES

The kinetic analysis of the hydrogenolysis and isomerization of *n*-pentane on platinum was made under dynamic conditions at atmospheric pressure. The catalyst (2 g), diluted by 16 g of quartz having exactly the same grain size, was placed in the middle of a quartz reactor 1 cm in diameter, then reduced during 6 hr in a hydrogen flow of 5 liters/hr. Experiments were then made at temperatures between 210 and 380°C under the following standard conditions:

partial pentane pressure	44 mbar,
partial hydrogen pressure	460 mbar,
total gas flowrate	20 liters/hr.

The reaction temperatures were measured by an iron–constantan thermocouple placed in a thermometric well located in the middle of the catalytic bed. The reactant flowrates were controlled by a syringe micropump for *n*-pentane and by two rotameters for hydrogen and helium. This latter gas was injected solely to change the partial pressures of the reactants during the kinetic analysis of the transformation.

A relatively special reactant injection system (*6*) was used to prevent leaks between the body of the syringe and the piston caused by the volatility of the pentane (bp = 35.5°C). The water filled syringe pushes the *n*-pentane contained in an intermediate flask toward an acetone/dry ice trap and then toward the reactor. The role of the trap is both to steady the injection by preventing too fast a volatilization of the hydrocarbon and to decrease its water content.

The reaction products, i.e., paraffinic hydrocarbons containing 1 to 5 carbon atoms, were separated by gas chromatography at 50°C in a 3-m column made up of 20% squalane deposited on 80–100 mesh firebrick and were than analyzed by a flame ionization apparatus.

RESULTS

A. Kinetics of Isomerization and Hydrogenolysis Reactions of Pentane

Kinetic measurements were performed at low conversion rates (0.5–5%) after the catalyst had been warmed up for 4–5 hr. Under such conditions, the only reactions observed on a catalyst of the platinum–silica type were hydrogenolysis of *n*-pentane to methane, ethane, propane and butane, isomerization to isopentane, and cyclization to cyclopentane.

Preliminary tests were made to see whether the reactions observed were effectively due solely to activation by the metal. For example, the neutrality of the silica support was checked by injecting 1-pentene on the support alone under the reaction conditions. Up to 450°C, no isomerization of the carbon skeleton was observed. The only reaction noted was a position isomerization of the double bond to the 2 *cis*- and *trans*-pentenes.

A prior check was also made by varying the catalyst weight (0.5–5 g) at a constant space velocity and then by varying the grain size of the catalyst particles (0.5–4 mm) to see that the outside and inside mass-transfer phenomena did not disturb the chemical kinetics.

The X_H, X_I, and X_C conversions, respectively, due to hydrogenolysis, isomerization and cyclization, were calculated on the

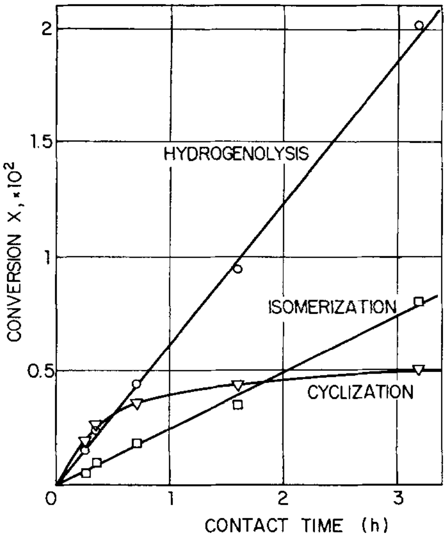


FIG. 1. Conversions of *n*-pentane as a function of contact time $\theta = W/F$ over a Pt–SiO$_2$ exchanged catalyst at 282°C under standard conditions. W = catalyst weight (g); F = pentane flowrate (g/hr).

basis of a carbon balance according to the following equations:

$$X_H = \frac{C_1 + 2C_2 + 3C_3 + 4C_4}{C_1 + 2C_2 + 3C_3 + 4C_4 + 5C_5} = \sum_{j=1}^{4} jC_j \Big/ \sum_{j=1}^{5} jC_j, \quad (1)$$

$$X_I = \frac{5Ci_5}{C_1 + 2C_2 + 3C_3 + 4C_4 + 5C_5} = 5Ci_5 \Big/ \sum_{j=1}^{5} jC_j, \quad (2)$$

$$X_C = \frac{5Cc_5}{C_1 + 2C_2 + 3C_3 + 4C_4 + 5C_5} = 5Cc_5 \Big/ \sum_{j=1}^{5} jC_j. \quad (3)$$

Figure 1 shows how the different reaction products evolve at 282°C as a function of contact time defined by the reciprocal of WHSV (pentane weight per catalyst weight·hour). The curve representing the conversion of *n*-pentane into cyclopentane can be seen to curve inwards and to level off at low WHSV. A simple theoretical calculation enables us to attribute this phenomenon to a thermodynamic limitation of the cyclization reaction under the experimental conditions used (about 0.5% conversion when P_{H_2} = 460 mbar, P_{C_5} = 44 mbar and T = 282°C).

Only the initial specific rates of hydrogenolysis and isomerization, V_H and V_I, will thus be followed because they can be determined quite simply by applying the following equations:

$$V_H = \frac{d(X_H)}{d\left(\frac{W}{F}\right)} = \frac{X_H F}{W}, \quad (4)$$

$$V_I = \frac{dX_I}{d\left(\frac{W}{F}\right)} = \frac{X_I F}{W}, \quad (5)$$

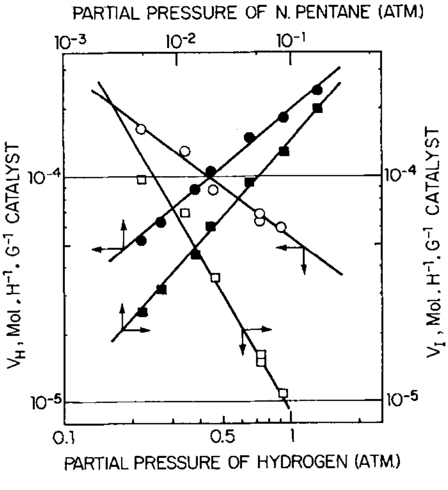


FIG. 2. Rates of isomerization (■) and hydrogenolysis (●) as a function of the partial pressure of pentane: 283°C; P_{H_2} = 0.456 atm; Pt–SiO$_2$ exchanged catalyst (1.26 wt% Pt). Rates of isomerization (□) and hydrogenolysis (○) as a function of the partial pressure of hydrogen: 282°C; P_{C_5} = 0.044 atm; Pt–SiO$_2$ exchanged catalyst (0.62 wt% Pt).

where

W	catalyst weight in g
F	molar flowrate of *n*-pentane in mol/hr
V_H and V_I	rates in mol/hr g of catalyst.

Figure 2 gives the results of a series of tests showing the respective effects of partial pressures of hydrogen (P_{H_2}) and pentane (P_{C_5}) on the initial hydrogenolysis and isomerization rates. These results obtained with 1.26% Pt/SiO$_2$ exchanged catalyst and presented in logarithmic coordinates show that V_I and V_H can be expressed by a formal kinetic equation of the type:

$$V = K \cdot P_{H_2}{}^{n} \cdot P_{C_5}{}^{m}, \tag{6}$$

in which n and m are the apparent orders with relation to hydrogen and pentane. The values of n can be seen to be negative for both reactions, while the values of m are positive. Table 1 tentatively gives the values of these apparent orders for several platinum–silica catalysts that differ from one another either by their active metal content or by their preparation method. An examination of these results then led us to present the activities in terms of rate rather than in terms of rate constant on account of the variations of n and m.

B. Influence of Heat Treatments in Hydrogen and Nitrogen

This influence was studied on catalysts prepared by cation exchange. The exchange between a tetrammine platinum(II) chloride solution and silica produces a catalyst precursor in which the active species is always found to be included in a Pt(NH$_3$)$_x^{2+}$ cation, even after drying at 120°C for 16 hr. Therefore, the complex must be reduced in order to bring out the metallic platinum.

In most catalytic tests, the choice of reduction in hydrogen at 410°C for 6 hr meets the following two purposes:

The need to reduce catalysts at a higher temperature than the reaction temperature (210–380°C) so as to prevent any subsequent change in the structure of the metallic deposit inside the reactor;

The need to eliminate as much as possible the decomposition gases from the precursor salts. These gases are liable to contaminate the catalyst (i.e., ammonia for cation-exchanged catalysts and chlorine for impregnated catalysts).

However, it has not been determined whether these reduction conditions are the optimum ones, and we felt that it was important to study their influence on both crystallite size and catalytic activity. Three cation-exchanged catalysts with 1.26, 1.45, and 5.12% platinum were thus prepared

TABLE 1

Apparent Orders of Reaction[a]

% Pt	Type	T_{calc} (°C)	T_{red} (°C)	l(Å)[b]	T_{reaction} (°C)	S[c]	n_H	n_I	m_H	m_I
1.26	Exchanged	120	410	14.5	283	0.40	−0.75	−1.75	0.42	0.58
5.12	Exchanged	120	410	11	263	0.30	−0.85	−1.52	—	—
5.12	Exchanged	700 nitrogen	660	17	271	0.13	−0.65	−1.42	—	—
8.20	Impregnated	120	410	172	290	2.85	−1.85	−1.85	—	—

[a] $V_I = k_I P_{H_2}{}^{n_I} P_{C_5}{}^{m_I}$; $V_H = k_H P_{H_2}{}^{n_H} P_{C_5}{}^{m_H}$.

[b] Mean crystallite diameter calculated from V_{CO} (octahedral configuration).

[c] Selectivity equal to the ratio of isomerization rate/hydrogenolysis rate.

TABLE 2

Influence of Treatments in Hydrogen or Nitrogen

% Pt	Calcination temp in nitrogen (°C)	Reduction temp in H_2 (°C)	V_{CO} (ml/g catalyst)	D	l(Å)[a]	Temp range examined (°C)	$V_H \times 10^2$[b]	$V_I \times 10^2$[b]	$S = V_I/V_H$	$R \times 10^2$[c]
1.26	—	410 (6 hr)	0.71	0.56	14.5	245–310	0.90 1.33	0.58 0.54	0.65 0.40	50.5
1.26	—	500	0.63	0.50	17	245–310				
1.26	—	590	0.70	0.55	15	245–310				
1.26	620 (3 hr)	410	0.74	0.59	14	— —	—	—	—	—
1.45	—	200	0.91	0.63	12	240–310	2.10	0.54	0.26	50.9
1.45	—	410	1.10	0.76	8.5	240–310	2.22	0.60	0.27	50.1
1.45	—	600	0.99	0.68	10.5	240–310	—	—	—	–
1.45	700 (3 hr)	410	0.87	0.60	13.5	240–310	—	—	—	–
5.12	—	410	3.45	0.67	11	215–285	1.98	0.59	0.30	58.8
5.12	700 (6 hr)	660	2.62	0.51	17	215–285	1.28	0.71	0.32	58.4

[a] l calculated from V_{CO} (octahedral model).

[b] Specific rates expressed in mol hr^{-1} g^{-1} of platinum.

[c] R defined by Eq. (8).

TABLE 3

Effect of Loading on Metal Dispersion

Pt (wt%)	V_{CO} (ml/g catalyst)	D	l (Å)				Temp range examined (°C)	$V_H \times 10^4$[e]	$V_I \times 10^4$[e]	$S = \frac{V_I}{V_H}$	$R \times 10^2$[f]
			—[a]	—[b]	—[c]	—[d]					
Exchanged catalysts											
0.40	0.18	0.45	16.3	19.8	—	—	260–320	0.82	0.23	0.28	49.4
0.45	0.39	0.87	4.5	6.0	—	—	270–320	0.60	0.17	0.29	52.3
1.26	0.71	0.56	11.9	14.5	—	$\leqslant 25$	245–310	1.13 1.68	0.74 0.68	0.65 0.40	50.5
1.45	1.10	0.76	6.7	8.5	—	$\leqslant 25$	240–310	3.22	0.88	0.27	50.1
3.11	1.85	0.59	11.0	13.5	—	—	230–300	5.79	1.69	0.29	54.3
5.12	3.45	0.67	9.0	11.0	—	$\leqslant 30$	215–285	10.15	3.02	0.30	58.8
5.50	3.23	0.59	11.0	13.5	—	—	215–285	16.20	2.43	0.15	65.6
Impregnated catalysts											
0.24	0.05	0.20	46	55	100	—	320–360	0.03	0.03	1.00	58.7
0.80	0.10	0.125	73	88	100	85[g]	300–340	0.09	0.14	1.54	67.0
2.40	0.32	0.13	69	82	120	—	— —	—	—	—	—
8.20	0.54	0.065	138	172	200	167[h]	270–320	0.27	0.72	2.85	66.0

[a] l calculated from V_{CO} assuming a cubic configuration.

[b] l calculated from V_{CO} assuming an octahedral configuration.

[c] l measured from the X-ray values.

[d] l measured from electron microscope photographs.

[e] Specific rates at 282°C expressed in mol. hr^{-1} g^{-1} catalyst.

[f] R defined by Eq. (8).

[g] Metal size distribution = 10–160 Å with arithmetic mean diameter of 40 Å.

[h] Metal size distribution = 10–210 Å with arithmetic mean diameter of 66 Å.

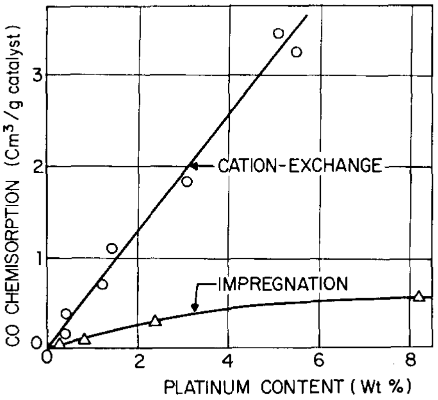


FIG. 3. Variation of the carbon monoxide chemisorption vs metal content of Pt–SiO_2 catalysts; cation-exchanged method (○), impregnation method (△).

for the purpose of studying the effect of treatment conditions in hydrogen or nitrogen. The results are given in Table 2. For a given amount of metal, it was found that the metallic surface of the catalyst varied only very little as a function of pretreatment conditions in hydrogen and nitrogen. A catalyst with 5.2% platinum, treated in nitrogen for 6 hr at 700°C and then in hydrogen for 6 hr at 660°C, still has a dispersion of 0.51 which can be compared with the value of 0.67 for the same catalyst treated under much milder conditions, i.e., for 6 hr in hydrogen at 410°C. This variation corresponds to a very slight enlargement of the crystallites whose size changes from about 11 to 17 Å.

Whereas dispersion of the metal varies only very slightly as does the isomerization rate and the distribution R of the hydrogenolysis products, Table 2 also shows that the hydrogenolysis rate and the selectivity S vary in a more significant way.

S and R are defined, respectively, by the following equations:

$$S = \frac{V_I}{V_H} = 5Ci_5 / \sum_{j=1}^{4} jC_j = \frac{5Ci_5}{C_1 + 2C_2 + 3C_3 + 4C_4}, \qquad (7)$$

$$R = C_2 + C_3 / \sum_{j=1}^{4} C_j = \frac{C_2 + C_3}{C_1 + C_2 + C_3 + C_4}. \qquad (8)$$

The important fact revealed by this series of tests is thus that platinum, once it has been reduced to a metallic state, appears to have difficulty in migrating to the surface of the support in a reducing or inert atmosphere. Kinetically, the temperatures applied are probably too low and the treatment times too short for this migration to become extensive. On the other hand, it is not impossible that a "qualitative reorganization" takes place and involves platinum transfers over very short distances. Such a reorganization would result in reducing the concentration in the structural defects of the platinum crystals and in varying the relative proportion of the different crystallographic planes on the metallic surface. This hypothesis would explain the variations observed in the activity and selectivity, even though the metallic surface, as determined by CO chemisorption, remains practically constant. Moreover, some authors have observed such a qualitative sintering by treatment in a vacuum or reducing atmosphere of catalysts made up of Pt deposited on Spheron (*8*) or by exchanged palladium on silica–alumina (*26*).

C. Influence of the Platinum Content and the Preparation Method

Two series of catalysts were prepared, with the platinum content being varied from one catalyst to the other. The catalysts were prepared in the first series by cation exchange using Keller's complex, in the second series by chloroplatinic acid impregnation. The results concerning the identification of the metallic deposit, the specific activity and the selectivity of the catalysts are grouped in Table 3. They illustrate the superiority of the method of

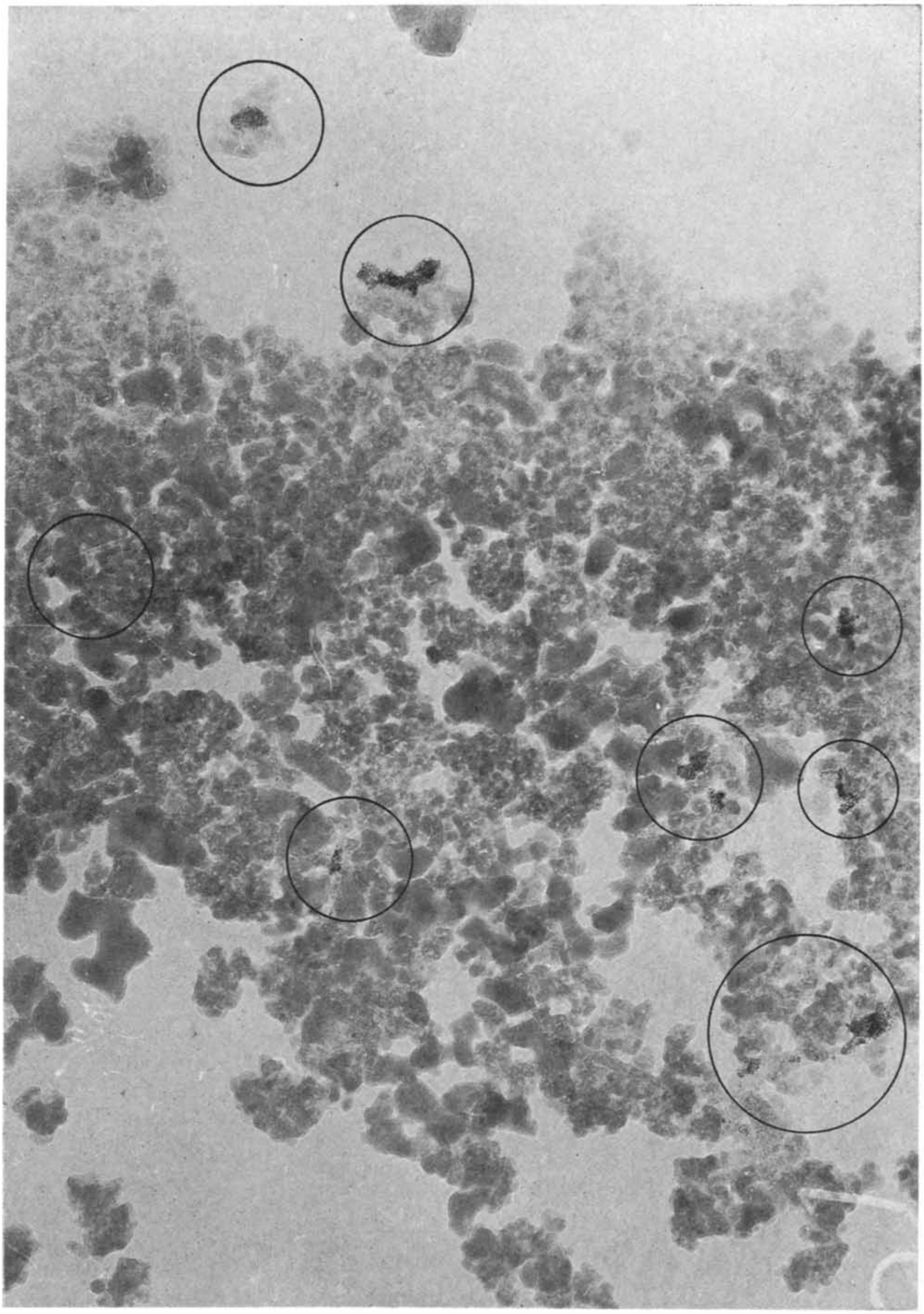


Fig. 4. Electron micrograph of a 1.45 wt% cation-exchanged platinum–silica catalyst. Magnification 90,000×.

using ion exchange when a good dispersion of the metal is desired. This advantage appears even more clearly in Fig. 3 which shows the volumes of chemisorbed CO as a function of platinum content. Although the calculated dispersions vary from 0.45

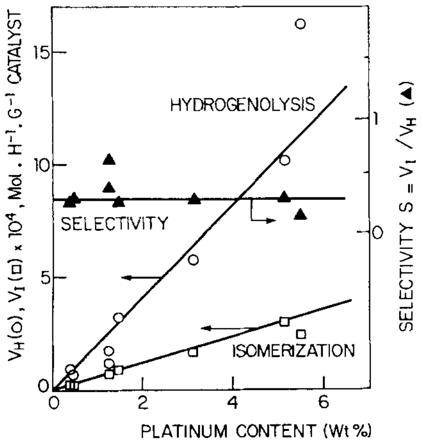


FIG. 5. Activity and selectivity of platinum cation-exchanged catalysts. Effect of the platinum content on the hydrogenolysis and isomerization rates of *n*-pentane at 282°C.

to 0.87 when going from one cation-exchanged catalyst to another, it can be seen that, within the reproducibility and repeatability limits of the preparation methods, the volume of chemisorbed CO representative of the accessible surface area varies linearly with the metal content up to an amount of 5.5%. This value, moreover, corresponds to the maximum amount that can be exchanged under the conditions applied with the silica support that we used. It is also somewhat surprising to note that there was no atomic dispersion when the impregnation mechanism involves an ion exchange. However, this can be explained on the basis of electron microscopy observations (Fig. 4) which showed that preferential zones existed on the surface of the silica, probably as a result of a heterogeneity of the support. During the exchange, the $Pt(NH_3)_x^{2+}$ cations became concentrated in preferential zones and then, by reduction, generated zero-valence metallic atoms that were thermodynamically not very stable and bunched together in each preferential zone to form small-size stable crystallites.

On the other hand, for catalysts prepared by H_2PtCl_6 impregnation without any ion exchange, it was found that the metallic surface area did not increase proportionally with the metal content. The crystallites are larger the larger the metal content. In this case, the elementary stage governing the final dispersion state of the metal is probably the crystallization of chloroplatinic acid in the pores of the silica as was clearly explained by Dorling *et al.* (*16*).

On the basis of these data and for the sake of studying solely the influence of the platinum content on the activity and selectivity of catalysts, we chose catalysts prepared by ion exchange because this method makes it possible, when the metal content is increased, to maintain the same state of dispersion.

Variations of the initial hydrogenolysis rates as a function of temperature permitted us to determine the apparent activation energies; these varied from 30 to 34 kcal/mol and are similar to those of the isomerization reaction.

The activity and selectivity of different catalysts compared at the same temperature (282°C) are given in Fig. 5 according to platinum content. Both the hydrogenolysis and isomerization rates can be seen to be more or less proportional to the amount of metal in the catalysts. This results in a selectivity *S* defined in relation to the two rates V_I and V_H, thus making it relatively constant and equal to 0.29. It should be pointed out in this regard that the hydrogenolysis rate undergoes fluctuations that are difficult to interpret on the basis of just this single series of tests. However, as shown below, these fluctuations are actually very slight compared with those observed when the crystallite diameter is deliberately made to vary in large proportions. To sum up, increasing the number of the platinum crystallites of equivalent mean size on the surface of the silica has no appreciable effect on the specific activity and selectivity of such catalysts in hydrogenolysis and isomerization reactions of *n*-pentane.

TABLE 4

Effect of Calcination Temperature

% Pt	T (°C)		V_{CO} (ml/g catalyst)	D	l (Å)				Temp range examined (°C)	$V_H \times 10^{2e}$	$V_I \times 10^{2e}$	$S = \frac{V_I}{V_H}$	$R \times 10^{2f}$
	Calcination 3 hr	Reduction 6 hr			—[a]	—[b]	—[c]	—[d]					
1.45	25	410	0.98	0.67	9	11	—	$\leqslant 25$	—				
1.45	25-acetone	410	0.96	0.66	9	11	—	$\leqslant 25$	—				
1.45	120	410	1.10	0.76	6.7	8.5	—	$\leqslant 25$	240–310	2.22	0.60	0.27	50.1
1.26	120	410	0.71	0.56	12	14.5	—		245–310	0.90	0.59	0.65	50.5
										1.33	0.54	0.40	
1.45	260	410	0.78	0.54	13	15.5	—		— —	—	—	—	—
1.26	350	410	0.48	0.38	20	25	—		255–315	0.47	0.42	0.90	55.7
1.26	520	410	0.17	0.13	69	82	100		275–325	0.13	0.25	1.96	68.0
1.26	600	410	0.13	0.10	92	112	110	117[g]	300–345	0.02	0.049	2.46	74.3
1.26	700	410	0.08	0.06	148	185	180	183[h]	345–375	0.0017	0.0054	3.21	73.7

[a] l in Å, calculated from V_{CO} (cubic model).

[b] l in Å, calculated from V_{CO} (octahedral model).

[c] l determined from the X-ray values.

[d] l measured from electron microscope photographs.

[e] Specific rates at 282°C expressed in mol. hr^{-1} g^{-1} Pt.

[f] R defined by Eq. (8).

[g] Metal size distribution = 40–170 Å with arithmetic mean diameter of 100 Å.

[h] Metal size distribution = 60–300 Å with arithmetic mean diameter of 126 Å.

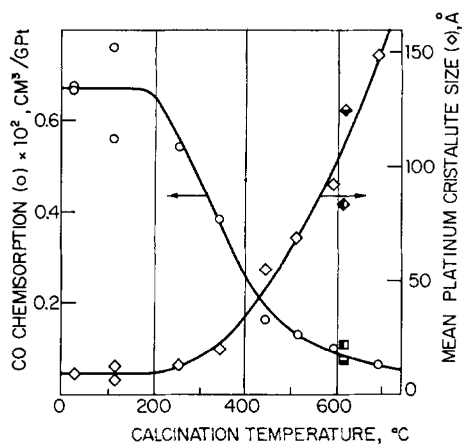


FIG. 6. CO chemisorption (○) and platinum crystallite size (◇) as a function of calcination temperature in air for exchanged catalysts (1.26 or 1.45 wt% Pt). (◘, ◆) catalyst reduced at 600°C during 3 hr before the calcination step. (◧, ◆) catalyst treated in nitrogen at 620°C during 3 hr before the calcination step. Mean crystallite size (◇) calculated from CO chemisorption (cubic model).

D. Influence of the Calcination Temperature

Two methods can be used to vary the mean diameter of the metallic crystallites. One is calcination in air (*16, 20, 26*), and the other, as we have already seen, is variation of the platinum content of catalysts prepared by impregnation without any interaction of the solution with the support used. We mainly made use of the former technique for varying crystallite diameter and studying its influence on the specific hydrogenolysis and isomerization rates of *n*-pentane.

Platinum–silica catalysts were thus prepared by cation exchange, calcined in air in a muffle furnace for 3 hr at various temperatures, and then reduced in a 5 liters/hr hydrogen flow at 410°C for 6 hr. The influence of calcination time in air at constant temperature on the kinetics of sintering, although of great interest, was not investigated.

The results concerning the characterization of catalysts and their specific activities are reported in Table 4. The variation in the volume of chemisorbed carbon monoxide vs calcination temperature (Fig. 6) reveals highly extensive sintering of the metallic deposit. The metallic surface of the deposit decreases steadily above 200°C, and at the same time the mean diameter of the platinum crystallites increases to a value of about 150 Å at a calcination temperature of 700°C. The effects of heat treatment in oxygen can also be seen if the catalyst has undergone a prior heat treatment in an inert reducing atmosphere so that the ammine complex has already been changed into metal. Two catalysts prepared by ion exchange and then treated, one in hydrogen at 600°C and the other in nitrogen at 620°C for 3 hr, show a platinum dispersion of about 0.60%, corresponding to a mean crystallite diameter of about 10 Å (cubic model). After such a treatment, if they are also made to undergo

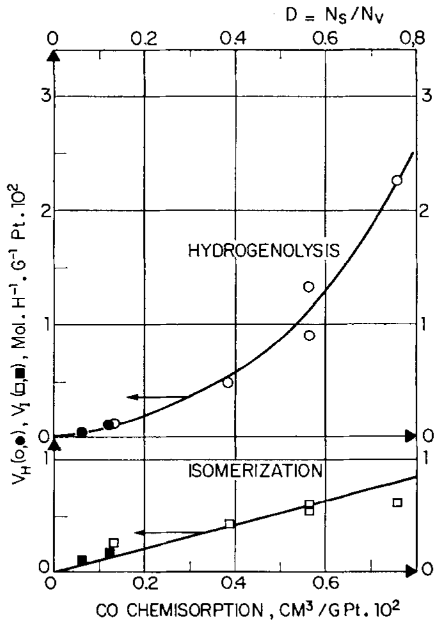


FIG. 7. Variation of the rates of hydrogenolysis and isomerization with the mean crystallite size of Pt–SiO_2 catalysts. (○, □) cation exchanged catalysts (1.26 or 1.45 wt% Pt) calcined at different temperatures and described in Table 4. (●, ■) impregnated catalysts with variable platinum content (0.80–8.20 wt% Pt) and described in Table 3.

calcination in the presence of air at 620°C, the same effects were found as those caused by direct calcination of the freshly impregnated catalyst in air at 620°C. In both cases the mean crystallite diameter is about 110 Å. This rules out the possibility of a sintering mechanism by migration of the ammine cation in oxygen prior to its destruction.

Oxygen is thus probably responsible for the sintering of the platinum, doubtless by enabling the metal to take on a superficial oxidized form that would have much greater ease of migrating to the surface of the silica support and forming large crystallites.

The variation, with temperature, of the hydrogenolysis rates on different air-sintered cation-exchanged catalysts and impregnated catalysts enables us to calculate and compare the activities of different samples at 282°C as a function of the metal dispersion state. The apparent activation energies of both the isomerization and hydrogenolysis reactions vary by about 33 to 40 kcal/mol.

Before looking at the effects of platinum particle size, it should be pointed out that a stable activity was very difficult to obtain especially for low metal surface catalysts, i.e., with exchanged catalysts calcined at 600 and 700°C and with 0.2 wt% platinum impregnated catalyst. Some authors have observed a similar phenomenon for the hydrogenolysis of hexane (*15*, *27*) and for the hydrogenation of ethylene (*28*–30). This phenomenon might be attributed to a self-inhibition of small metal surfaces by unsaturated intermediate products coming from the reaction. As a result, it would probably have been preferable, in order to prevent such apparent effects in crystallite diameter (*31*), to make the kinetic measurements with a constant reactant mass flowrate per unit of platinum surface area. Nevertheless, it is very important to note that, whatever be the decrease of the catalyst activity before reaching a stationary state, the selectivity defined as the ratio between the rates of hydrogenolysis and isomerization does not change during this decrease.

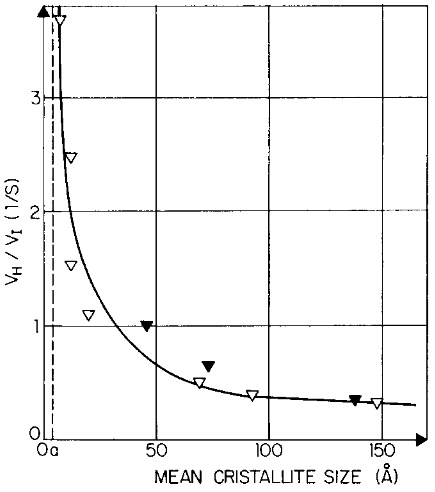


Fig. 8. Variation of the selectivity V_H/V_I with the mean crystallite size of Pt–SiO_2 catalysts. (▽) cation exchanged catalysts (1.26 or 1.45 wt% Pt) calcined at different temperatures and described in Table 4. (▼) impregnated catalysts with variable platinum content 0.24–0.80–8.20 wt% Pt) and described in Table 3.

The curves in Fig. 7 illustrate the variations in the rates of hydrogenolysis and isomerization as a function of catalyst dispersion. An examination of them leads to the following comments:

The rate of isomerization V_I expressed in moles of *n*-pentane transformed into isopentane per hour and per gram of platinum is more or less proportional to the dispersion and hence is apparently not influenced in an appreciable manner by crystallite size despite an apparent leveling off for extensive dispersions.

The rate of hydrogenolysis V_H, also expressed per gram of metal is, on the contrary, considerably more sensitive to the metallic deposit and its decrease does not follow a linear law when the dispersion (*D*) of the metal decreases from 75 to 6%, i.e., when the mean crystallite diameter increases from 7 to 150 Å. The result is that the selectivity defined by the ratio V_H/V_I does not remain constant but decreases as crystallite size increases, as is shown very clearly in Fig. 8.

In order to check that these selectivity variations are not linked to the preparation method, three catalysts were prepared, by chloroplatinic acid impregnation. The varying content of the latter (0.24, 0.80 and 8.20 wt%) served to vary the dispersion of the precious metal without requiring any calcination treatment in air (Table 3). Figure 8 shows that the catalytic performances of these three formulas generally enabled the above-mentioned observations to be made. The above-defined selectivity depends solely on the dispersion of the metal no matter what preparation method is used for varying this dispersion.

DISCUSSION

Analysis of Pt/SiO_2 type catalysts has led to a certain number of important observations with regard to the influence of catalyst preparation conditions on the dispersion of the metallic element:

For catalysts prepared by cation exchange, the variation between 200 and 700°C of the reduction temperature in hydrogen or of treatment in nitrogen brings about no important change in the dispersion of the metal during the 6 hr of treatment. The platinum migration rate in such atmospheres remains very slow. Likewise, for this family of catalysts the dispersion was not appreciably changed when the active metal content was varied from 0.35 to 5.5 wt% after reduction for 6 hr at 410°C.

On the other hand, treatments in an oxidizing atmosphere brought about a considerable change in the dispersion of the metal. Without having been able to check the hypothesis, it was assumed that this enlargement of the crystallites could be attributed to the formation in air of oxidized labile species not connected to the support and capable of migrating on its surface.

With regard to catalysts prepared by chloroplatinic acid impregnation, the deposited metal content had considerable influence on the state of dispersion observed. This effect was probably linked to the crystallization of H_2PtCl_6 in the pores of the silica during the drying phase (*16*).

The experimental results obtained with the isomerization and hydrogenolysis of *n*-pentane with the different catalysts analyzed led us to the following conclusions:

The rate of isomerization appears to be insensitive to the structure of the metallic deposit, i.e., to the size of the crystallites. Apparently it depends solely on the number of accessible platinum atoms N_s. On the basis of this observation, this reaction can thus quite probably be classified among so-called "facile" reactions, using Boudart's terminology.

The rate of hydrogenolysis, on the other hand, does not vary linearly with the number of accessible atoms N_s. This means that the ratio V_H/V_I does not remain constant but decreases by a factor of 10 when the mean crystallite diameter increases from 7 to 150 Å, although without tending toward a value of zero as illustrated by the curve in Fig. 8. Hydrogenolysis of *n*-pentane should thus be catalyzed by specific active centers whose concentration is not proportional to the specific area of the metal. As a result, this reaction can be considered as a "demanding reaction." These results are corroborated by a recent study by Anderson and Shimoyama (*15*) showing on platinum films that the specific hydrogenolysis rates decrease for *n*-hexane, 2- and 3-methylpentane by factors of ~ 10, ~ 2, and >2, depending on the reactant when particle size increases from 15 to 40 Å; at the same time the "isomerization" selectivity (which apparently included a cyclization route) was enhanced.

Following these observations, it was interesting to try to identify these specific active centers responsible for the isomerization and especially the hydrogenolysis of

n-pentane whose rate is enhanced by the widespread dispersion of the metal.

Among various possible hypotheses, we can begin by assuming that the hydrogenolysis is catalyzed by the atoms located on some preferential crystallographic planes. The existence of such preferential sites has already been revealed, in particular by Boudart *et al.* (*8*), who based their work on a crystallographic analysis made on metallic films by Lyon and Somorjai (*32*) and found that the rearrangement of neopentate into isopentane over platinum was enhanced by the (111) planes of the face-centered cubic lattice of platinum. These planes are more thermodynamically stable than (100) and especially (110) planes. In our case, different distribution of crystallographic superficial planes may result either from heat treatments that catalysts undergo or from structural organization of the crystallites under the action of adsorption of n-pentane. The first hypothesis can be reasonably eliminated insofar as similar results have been obtained over equivalent dispersion catalysts resulting from variable calcination or reduction of the sample. On the other hand, considering the nature of our catalysts, we cannot check experimentally the second hypothesis.

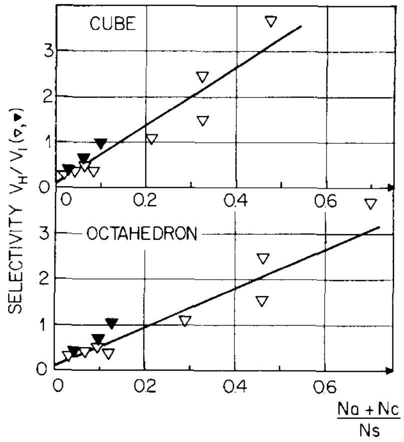
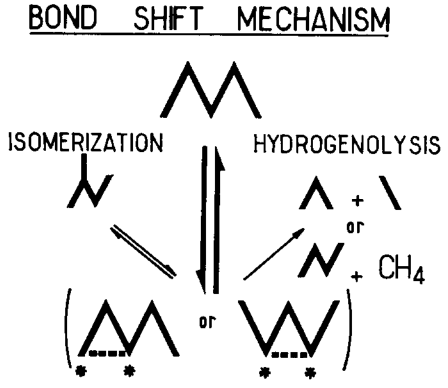


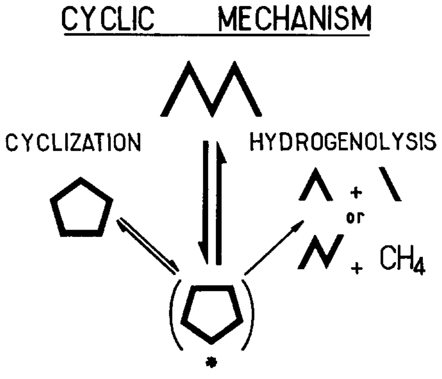
FIG. 9. Correlation between the selectivity V_H/V_I and the proportion of low coordinated atoms of the total platinum surface area defined by $(N_a + N_c)/N_s$. Same symbols as in Fig. 8.

The atoms located at the corners and on the ridges of the metallic crystallites have also been proposed as being the specific active centers because of their weak coordination with the other atoms of the crystallites (*5, 6, 10, 15*). To check the validity of this hypothesis in the case of the hydrogenolysis of n-pentane, the research done by Poltorak and Boronin (*5*), and Van Hardeveld *et al.* (*24, 25*) was taken as a basis for determining the relative proportions of the different families of atoms (corners, ridges, faces) as a function of crystallite diameter. This calculation was done solely with the cubic and octahedral models representative of crystallographic planes (100) and (111), respectively, and an attempt was made to link the V_H/V_I selectivity to the surface percentage of atoms with a weak degree of coordination which are the atoms located at the corners and on the ridges of metallic particles, i.e., $(N_a + N_c)/N_s$. Figure 9 shows that this interpretation quite satisfactorily explains the observed facts and that this is true no matter what geometric model is taken as a reference. However, it should be pointed out that this interpretation is acceptable only as an initial approximation. Indeed, it can be expected that the atoms located in the corners of the crystallites do not have the same activity as those located on the ridges. Nevertheless, the ratio $N_c/(N_a + N_c)$ is still too low, even at dispersions of 60%, to allow these atom types to be clearly differentiated. In addition, the fact of having chosen a CO adsorption stoichiometry that is constant and equal to 1.15 may also be discussed (*23*). Its subsequent variation from 1.0 to 2 is too low with regard to the phenomena observed to change the meaning of the proposed interpretation.

The results may likewise be examined from an essentially mechanistic standpoint. For the hydroconversion reactions, on platinum, of saturated hydrocarbons containing at least 5 carbon atoms, two mechanisms have been proposed. The first, proposed by Avery and Anderson (*4*) under the term "bond shift," involves an unsaturated intermediate product polyadsorbed at 1–3 and capable of being assimilated with a 3-carbon-atom cycle. Once this intermediate has been formed, it may lead, by rearrangement under the effect of hydrogen, to an isomerization or a hydrogenolysis.



The second mechanism proposed by Barron *et al.* (*33*) involves a cyclopentane intermediate probably adsorbed on a single platinum atom, with a mechanism differing from the preceding one which requires the presence of two neighboring metallic atoms.



An examination of these mechanisms shows that the formation of isopentane is not possible by the cyclic method because the isomerization of the cyclopentane intermediate involves merely a movement of the carbon atoms in the carbon chain of *n*-pentane. The isomerization of *n*-pentane may thus be ascribed to the bond shift mechanism. Since the rate of isomerization per unit of platinum surface area is appreciably independent of crystallite size, we can deduce that this mechanism takes place at equal rates on all acceptable atoms no matter what their degree of coordination may be.

The hydrogenolysis reaction of *n*-pentane, on the contrary, involves the two preceding mechanisms. With regard to the contribution by the bond shift mechanism which probably involves the same adsorbed intermediate as in isomerization, we may accept the fact that the rate of hydrogenolysis will also be independent of the degree of coordination of the platinum atoms. The cyclic mechanism should thus be enhanced by the widespread metallic dispersions and the weak coordination dispersion atoms, and would thus appear to be responsible for the greater rate of hydrogenolysis encountered for small crystallites.

This seems in good agreement both with the fact that this cyclic mechanism involves an intermediate adsorbed on a single platinum atom and with the results found by Corolleur *et al.* (*10, 11*) concerning the isomerization of labeled hydrocarbons containing 6 carbon atoms. These authors in effect demonstrated that the two previously mentioned mechanisms made a contribution that was more or less equivalent to the conversion of hexane on a platinum–alumina catalyst with a high active metal content (10%) and small dispersion (crystallites of about 180 Å), whereas the cyclic mechanism was enormously preponderant on a platinum–alumina catalyst with a small content (0.2%) and widespread dispersion of the active element.

It should be pointed out that the isomerization, and hydrogenolysis of *n*-pentane make up a special case. Indeed, as opposed to *n*-pentane, paraffinic hydrocarbons having less than 5 carbon atoms in their linear chain cannot produce the pentane cycle. Their rearrangement is thus governed solely by the bond shift mechanism. On the other hand, C_6 and higher hydrocarbons have a linear chain of at least 5 carbon atoms, they may also become isomerized according to Gault's cyclic mechanism and lead to extensive aromatics formation.

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