Comparative Study of Various Platinum Catalysts in Skeletal Reactions of C₆-Hydrocarbons

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Four platinum catalysts, Pt-black, Pt/C, Pt/SiO₂, and Pt/Al₂O₃, have been compared in skeletal reactions of 3-methylpentane (3MP) and methylcyclopentane (MCP), in the presence of various partial pressures of hydrogen. Analogous hydrogen effects (defined as primary and secondary) have been observed for each catalyst. The selectivities could be explained almost exclusively by the influence of hydrogen. The selectivity of isomerization plus C₅-cyclization vs fragmentation increased with increasing hydrogen pressure as did the ratio of saturated vs unsaturated C₆ products. The 2-methylpentane vs n-hexane ratio (2MP/n-H) from both 3MP and MCP exhibited a strong hydrogen dependence (permitting separation of bond shift and C₅-cyclic isomerization as a function of the hydrogen pressure), and significant crystallite size effects were also observed here.

INTRODUCTION

Recent studies of skeletal hydrocarbon reactions have shown that these processes can be reduced to a few elementary steps (C₅-cyclic and bond shift isomerization, hydrogenolysis via multiply adsorbed species) (*1, 2*). Alkene-alkyl and carbene-alkyl insertion has been suggested for cyclization, irrespective of whether a C₅- or C₆-ring is formed (*2*). Another approach proposed C₆-cyclization via hexatriene intermediates (*3*). This process, accordingly, would be essentially different from C₅-cyclization (and C₅-cyclic isomerization) which occur via two mechanisms, one involving associatively adsorbed species (*4*)

and the other (less important) pathway unsaturated intermediates [probably like those suggested in Ref. (*2*)]. They may proceed simultaneously (*5, 6*). Kazansky and Rumyantseva reported selective ring opening of methylcyclopentane as early as 1947 (*7*) over Pt/C. Nonselective ring opening was reported over Pt/Al₂O₃ (*8*). 1,3,3-Triadsorbed (*1*), cyclopropane-type (*9*), or unsaturated (*10*) intermediates have been proposed for bond shift isomerization.

Different product distributions observed under various conditions permit conclusions to be drawn about the elementary steps and the nature of surface intermediates involved in them.

The influence of (i) hydrogen, (ii) crystallite size, and (iii) the support are worth mentioning here.

(i) Hydrogen effects may give information about the possible degree of dissocia-

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219

tion of surface intermediates. Two of the authors (*11*) observed maximum yields for isomerization and C₅-cyclization of *n*-hexane and 2-methylpentane as a function of the hydrogen partial pressure over platinum black. Aromatization of *n*-hexane showed a maximum at lower hydrogen pressures whereas benzene yield from 2-methylpentane (*11*) and 3-methylpentane (*5*) decreased with increasing hydrogen pressures. The above hydrogen effects permit the assumption that aromatization requires intermediates of more unsaturated character than C₅-cyclic reactions (*5, 26*). Benzene formation from isohexanes would proceed via bond shift type dehydroisomerization (*12*), which might involve unsaturated surface intermediates like those proposed by McKervey *et al.* (*10*). Garin and Gault, however, reported a very strong negative hydrogen order for both hydrogenolysis and the two types of isomerization over Pt/Al₂O₃ (*9*). Therefore they suggested deeply dissociated surface intermediates for each process.

C₅-ring opening showed a positive hydrogen order with Pt-black (*12, 26*) and Pt/SiO₂ (*30*). More hydrogen caused more selective ring opening over Pt/C (*13*).

(ii) Very thorough studies with films of various thickness and Pt/Al₂O₃ containing various amounts of metal revealed crystallite size effects. In reactions of C₆-hydrocarbons over small crystallites the formation of a C₅-ring and its nonselective opening predominates (*15–17*). Over large crystallites, ring opening is mainly selective and, in addition, bond shift isomerization occurs (*17–19*). Dautzenberg and Platteeuw (*20*) questioned the existence of a crystallite size effect and stressed instead influence of pretreatment.

(iii) Support effects may manifest themselves with acidic carriers where cyclization and ring opening may proceed both on the metal and the acidic centers simultaneously (*30*). The latter causes selective ring opening in the vicinity of the alkyl substituent

of the C₅-ring which is just the opposite to that observed with Pt-black and Pt/C (*7, 11*). Both hydrogenative and dehydrogenative C₅-cyclization has been reported over Pt-black (*5*) and Pt/Al₂O₃ whereas only the hydrogenative pathway was found over Pt/C (*14*). No final evidence is available as to whether they are support effects or not.

All these factors may manifest themselves simultaneously. Their exact separation is all the more difficult since various laboratories stressed rather one or two of these interdependent phenomena. The amount of surface hydrogen available over metal sites must be influenced by hydrogen spillover being dependent on the support (*21–23*) and on crystallite size (*23*). One may also wonder to what extent the above-mentioned effects (*6, 11, 15–19*) can be attributed eventually to different supports.

A more consistent picture can be hoped for only if systematic studies are carried out with a number of catalysts under conditions which are identical as far as possible. A first attempt in this direction will be described in the present paper. The comparative study of four platinum catalysts, one unsupported and three on various carriers, may hopefully permit us to estimate the role of these various factors. The effect of hydrogen will be emphasized throughout. The extent to which the various postulated mechanisms are consistent with the data presented will also be pointed out.

EXPERIMENTAL

The catalysts used were described elsewhere: 18% Pt/C (*13*), 0.6% Pt/Al₂O₃ (*6, 24*), 5% Pt/SiO₂ (*23*), and Pt-black (*3, 5, 11*). The acidity of 0.6% Pt/Al₂O₃ was decreased by including Na⁺ ions in the catalyst preparation (*34*) [cf. catalyst A in Ref. (*24*)].

Crystallite sizes of platinum (Table 1) were determined from the broadening of

TABLE 1

Some Physical Characteristics of Various Platinum Catalysts

Catalyst	Spec. surface[a] (m² g⁻¹)	Metal surface (m² g⁻¹)		Mean crystallite size (nm)		
		By O₂ chemi-sorption[b]	Calculated from X-ray cryst. size[c]	From X-ray broadening		Calcu-lated from O₂ chemi-sorption
				Of (111) line	Of (200) line	
Pt-black	4	—	9.2	29.0	32.0	—
Pt/C (18%)	415	—	14.0	21.0	19.0	—
Pt/SiO₂ (5%)	280	31.3	21.2	14.0	12.5	8.9[c]
Pt/Al₂O₃ (0.6%)	150	110[d]	56	Undetectable (below 5.0)		2.5[e]

[a] Nitrogen adsorption by BET method.

[b] Assuming an O_2/H_2 stoichiometry of Pt:O = 1:1.

[c] Assuming spherical particles [cf. (27)]. Aggregation of particles observed for Pt-black and Pt/C may result in lower real surfaces.

[d] Other measurement (I. V. Gostunskaya) gave 90 m² g⁻¹ which corresponds to a crystallite size of 3 μm.

[e] Electron microscopy: about 3 nm for Pt/Al₂O₃ and 2 to 10 nm crystallites for Pt/SiO₂.

X-ray diffraction profiles of (111) and (200) planes using a Rigaku–Denki X-ray diffractometer with a copper tube and a nickel filter. Electron microscopy of the two oxide-supported catalysts was carried out using a JEOL 100U transmission electron microscope. It revealed that Pt/Al₂O₃ is rather monodisperse whereas Pt/SiO₂ is a polydisperse system: Crystallites between about 2 and 10 nm were seen over amorphous silica. X-Ray diffraction does not "see" these small particles (32). Metal surfaces have been measured also by oxygen chemisorption using a Sartorius micro-balance.

The runs were carried out in a pulse-microcatalytic system described previously (3, 5) connected to a gas chromatograph with a katharometer. Pure helium, hydrogen, and their mixture (containing 5, 20, 35, and 50% of hydrogen, respectively) were used alternatively as the carrier gas. Comparative kinetic runs have also been carried out in a static circulation apparatus (with Pt-black only) in which different hydrocarbon/hydrogen ratios could be established (26).

Hydrocarbon reagents: 3-methylpentane (3MP) and methylcyclopentane (MCP) were chromatographically pure substances.

The typical temperature of experiments with Pt/C was 300°C (573°K), while the other three catalysts have been compared at 375°C (648°K), these temperature giving approximately similar conversion values and product distributions. Some experiments have also been carried out with Pt-black at 300°C (573°K), in both pulse and circulation systems; apart from this, temperature effects have not been studied.

RESULTS

A. Catalyst Activity

The product spectrum observed is illustrated by typical results in Table 2 obtained at medium hydrogen pressure.

The yields of saturated C₆ products from 3-methylpentane show a rather flat maximum. A monotonic increase in the yields of ring-opening products of methylcyclo-

TABLE 2

Typical Product Compositions Obtained over Various Catalysts[a]

Catalyst (°K)	Reagent	Composition (mole%)				
		$<C_6$	Sat. C_6[b]	Benzene	Olefin	Unreacted
Pt-black	3MP	0.36	1.45	—	0.23	97.96
(0.26 g) 573	MCP	0.25	5.35	—	0.43	93.97
Pt-black	3MP	6.40	4.73	1.01	2.44	85.42
(0.26 g) 648	MCP	5.76	6.19	—	3.06	85.00
PT/C	3MP	3.73	15.31	—	—	80.96
(0.036 g) 573	MCP	1.04	28.24	—	—	70.72
Pt/Al$_2$O$_3$	3MP	1.87	10.84	1.30	3.16	82.83
(0.108 g) 648	MCP	1.44	8.91	—	6.12	83.51
Pt/SiO$_2$	3MP	1.30	2.13	0.45	2.09	94.03
(0.050 g) 648	MCP	0.94	2.71	—	5.61	90.74

[a] Pulse system, 3-μl hydrocarbon pulses into 60 ml min^{-1} carrier gas (20% H$_2$ + 80% He).

[b] Isomers and methylcyclopentane from 3MP; open chain alkanes from MCP.

pentane can be observed with more hydrogen; the absolute yields exceeded those observed from 3-methylpentane. These are illustrated in Fig. 1a and b.

The yield of products with π-bonds (benzene and olefins) is gradually suppressed in the presence of increasing amounts of hydrogen. The same can be stated for hydrogenolysis giving $<C_6$ fragments.
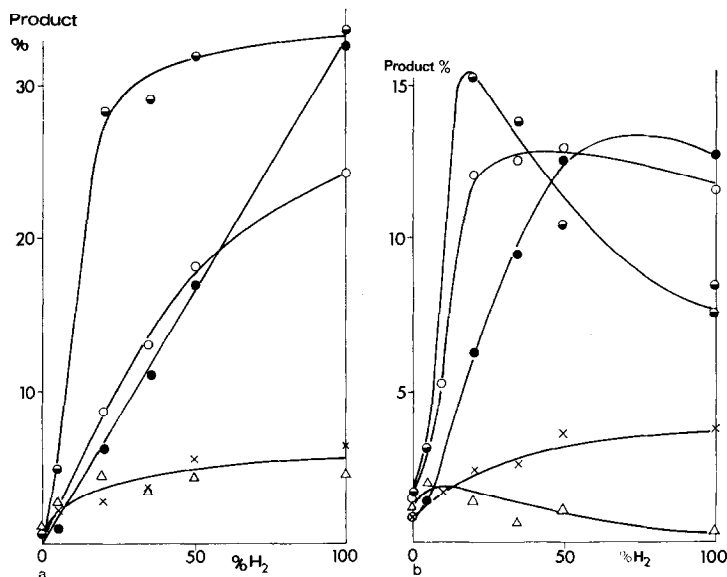

FIG. 1. Yields of saturated C$_6$-products as a function of the hydrogen content of the carrier gas. (a) Starting hydrocarbon; methylcyclopentane; the points represent C$_6$-alkane products of ring opening. (b) Starting hydrocarbon: 3-methylpentane; the data represent the sum of skeletal isomers plus methylcyclopentane. ○, Pt-black, 648°K; △, Pt-black, 573°K; ◐, Pt/C, 573°K; ○, Pt/Al$_2$O$_3$, 648°K; ×, Pt/SiO$_2$, 648°K.

TABLE 3

Selectivity of Saturated C_6-Product Formation $(S_{C_6}\%)^a$ vs Hydrogenolysis
over Various Pt-catalysts

A. Pulse system[b]

Catalyst	Temperature (°K)	Reagent	H_2 content in the carrier gas (%)					
			0	5	20	35	50	100
Pt-black	573	3MP	57	86	80	83	79	—
		MCP	60	82	95	95	96	94
	648	3MP	16	22	43	71	72	68
		MCP	8	32	56	72	80	87
Pt/C	573	3MP	82	89	81	77	80	86
		MCP	58	94	91	92	94	98
Pt/SiO$_2$	648	3MP	64	60	59	62	67	64
		MCP	—	77	78	80	85	84
Pt/Al$_2$O$_3$	648	3MP	63	87	85	80	86	82
		MCP	43	89	86	89	90	95

B. Circulation system[c]

Catalyst	Temperature (°K)	Reagent	p_{H_2} (Torr)					
			35	50	75	100	180	300
Pt-black	573	3MP	90	90	90	92	92	94
		MCP	—	96	—	98	99	99
	633	3MP	25[d]	28	63	72[e]	83	—

[a] $S_{C_6} = \sum$ saturated C_6 products$/\sum$ saturated C_6 products $+ \sum <C_6$ fragments$) \times 100$.

[b] For conditions see footnotes to Table 2; S_{C_6} calculated from product mole% values; since all platinum catalysts broke the C_6 molecules into two parts, the error caused by not considering the mole number increase did not alter the relative order of various catalysts, although it influenced the numerical values.
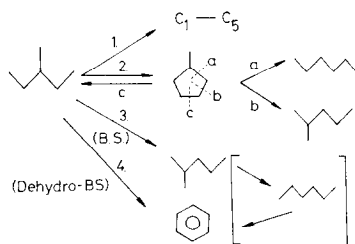
[c] Hydrocarbon pressure $p_{HC} = 5$ Torr; catalyst, 0.157 g Pt-black; contact times, 10 min for 3MP and 5 min for MCP. S_{C_6} values calculated from true reaction rates (26).

[d] 2 at 20 Torr.

[e] at 125 Torr.

B. Catalyst Selectivity

The reaction possibilities are shown in Scheme 1. With a considerable fraction of

unreacted hydrocarbon in the effluent, selectivity data within the total conversion may provide more useful information. The values were calculated in a way somewhat different from that used in an earlier paper by Karpinski and Clarke (25), namely, benzene was taken by itself and C_5-cyclics were added to saturated C_6-isomers. This corresponds to the classification of the scheme proposed according to the hydrogen sensitivity of various reactions. These show a similar picture for all catalysts which is analogous to that reported earlier for platinum black (11, 12, 26).
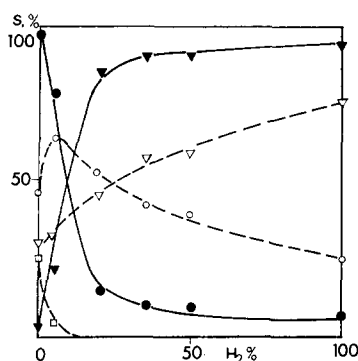
Three types of selectivity have been

FIG. 2. The selectivities for various classes of C_6-products from 3-methylpentane. T = 573°K. ●, MCP, Pt/C; ▼, isomers, Pt/C; ○, MCP, Pt-black; ▽, isomers, Pt-black; □, benzene, Pt-black.

studied:

(i) The "saturated C_6-selectivity" (S_{C_6}) is characteristic of the ratio of saturated C_6 products (i.e., the ratio of Reaction *2* to Reaction *1* in the scheme) vs fragmentation. Table 3 shows that selectivity values for MCP are higher than those for 3MP. A very characteristic drop of S_{C_6} was observed with Pt-black at 633–648°K in the lower hydrogen pressure region, both in the pulse and the circulation system.

(ii) The percentage distribution of various C_6 products of skeletal reactions of 3MP are shown in Fig. 2 (573°K) and Fig. 3a–c (648°K). This gives the relative role of Reactions *2* ($a + b$) and *4*. Any possible contribution of Reaction *3* (see

later) is added to ($a + b$). Results obtained with Pt-black in a circulation apparatus (Table 4) show a similar hydrogen pressure dependence to those depicted in Figs. 2 and 3a.

(iii) The ratio of 2MP/n–H within the C_6 saturated alkane (i.e., the ratio of reactions *b* and *a*) products from 3MP and MCP have been summarized in Fig. 4. Figure 5 compares these values determined in the pulse and circulation apparatus as a function of the logarithm of the hydrogen/hydrocarbon pressure ratio at 573°K [the average hydrocarbon/carrier gas ratio within the pulse was taken to be roughly 1:10 after Ref. (*26*)]: In spite of the very large differences between contact times surprisingly similar results are obtained.

DISCUSSION

The main conclusions will be drawn on the basis of the *selectivity* measurements. An attempt will be made to interpret our results in terms of *hydrogen effects* as far as possible, regarding the influence of support material and metal dispersion as having only a less important (but, as will be seen later, not negligible) influence. This is supported also by the fact that at 648°K any eventual dual character of the carrier ought to have manifested itself (*1*) but such indications have not been found. Also, different experimental conditions gave similar results.
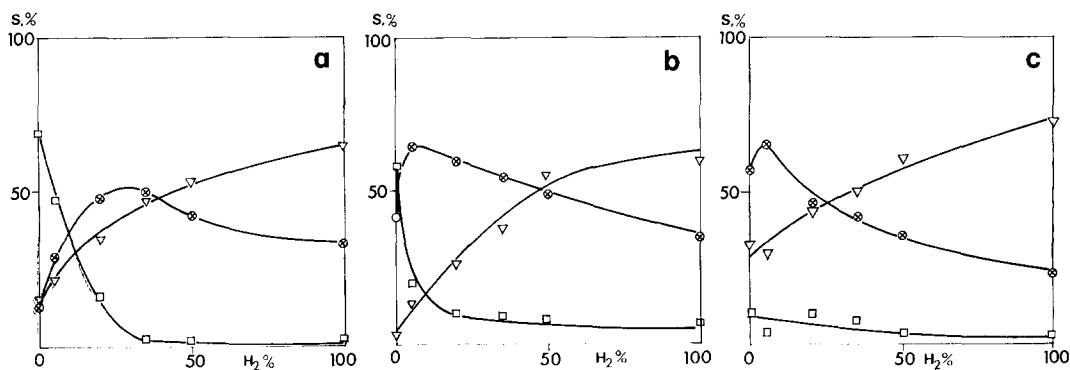

FIG. 3. The selectivities for various classes of C_6-products from 3-methylpentane. T = 648°K, a, Pt-black; b, Pt/SiO₂; c, Pt/Al₂O₃. The symbols have the same meaning as in Fig. 1.

TABLE 4

Selectivities (Percent) for Various Classes of Skeletal C_6-Products from
3-Methylpentane[a] on Pt-black

Temperature (°K)	Selectivity for	p_{H_2} (Torr)							
		20	35	50	75	125	180	300	500
573	Isomers	14	29	38	59	72	75	81	—
	MCP	82	70	61	41	28	25	19	—
	Benzene	4	1	1	Trace	Trace	0	0	—
633	Isomers	3	3	7	11	29	50	—	85
	MCP	0	13	19	57	59	46	—	13
	Benzene	97	84	74	32	12	4	—	2

[a] Circulation system, see footnote c to Table 3.

Two types of hydrogen effects will be distinguished: The actual dependence of any factor on hydrogen pressure will be called the *primary* hydrogen effect. The different behavior of various catalysts at similar hydrogen pressure will be called *secondary* hydrogen effects. For example, the fact that C_5-cyclization selectivity of 3MP has a maximum as a function of hydrogen pressure is a primary hydrogen effect (Fig. 3a–c). The position of these maxima and the actual selectivity observed there is catalyst dependent and therefore is due to secondary hydrogen effects.

One important primary hydrogen effect on product yields is that isomerization and C_5-cyclization of 3MP with zero or positive hydrogen balance has maximum yields at medium hydrogen pressures (Fig. 1a) as opposed to MCP ring opening proceeding with hydrogen uptake: For this, yields increase up to 1 atm hydrogen (or eventually further).
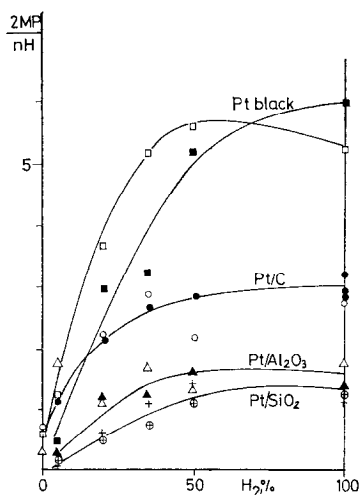
The primary hydrogen effects on various

FIG. 4. The ratio of 2-methylpentane/n-hexane from both 3MP and MCP over four catalysts, as a function of the hydrogen pressure. Pt-black, 648°K: □, 3MP; ■, MCP; Pt/C, 573°K: ○, 3MP; ●, MCP; Pt/SiO₂, 648°K: +, 3MP; ⊕, MCP; Pt/Al₂O₃, 648°K: △, 3MP; ▲, MCP.
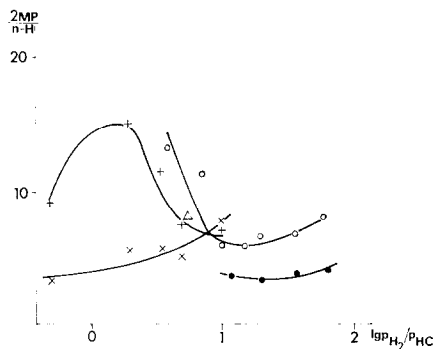

FIG. 5. The 2-methylpentane/n-hexane ratio from 3MP and MCP as a function of the logarithm of hydrocarbon/hydrogen pressure ratio. T = 573°K. +, 3MP, ×, MCP (pulse system, $p_{av..HC}$ 100 Torr); ○, 3MP; ●, MCP (static system, p_{HC} = 5 Torr); △, 3MP (static system, p_{HC} = 30 Torr).

selectivities indicate:

Type (i) selectivity (Table 3) is approximately constant with Pt-black at lower temperature and with Pt/C. It increases with increasing hydrogen pressures in all other cases. This indicates a more dissociated surface species for hydrogenolysis than for saturated C_6 formation. The former is generally accepted (1, 2) but the latter statement contradicts the interpretation of Garin and Gault (9).

Type (ii) selectivity (Figs. 2 and 3 and Table 4) shows a very rapid decrease of benzene formation and an increase of saturated C_6 selectivity with increasing hydrogen content in the carrier gas. Within the latter group, the relative amount of MCP predominates at lower hydrogen pressure, corresponding to the above statement about the individual reactions. Increasing isomerization selectivity may correspond to decreasing absolute yields (Figs. 1 and 3). The observation of opposite hydrogen effects on benzene and MCP formation is rather in favor of the hypothesis that these two types of cyclization require different intermediates (3, 5); of them that of C_5-cyclization must be less dissociated. These may be associative type species suggested by Liberman (4) where surface hydrogen may enter into the flatly adsorbed surface complex leading to C_5-ring opening/closure.

Type (iii) selectivity (Figs. 4 and 5) is influenced by different hydrogen concentration very markedly. Therefore, not only crystallite size but also surface hydrogen concentration must be important for the selective or nonselective character of C_5-ring opening. This effect is reported here for the first time.

Secondary hydrogen effects must be connected with the variation of the actual surface hydrogen concentration at the metallic sites. It would be very difficult to predict its value from independent measurements; it is just the value of various reaction selectivities which may be used as indicators to estimate surface hydrogen availability. MCP ring opening is the best indicator reaction because its yield responds the most sensitively to hydrogen pressure changes and this response has a monotonically increasing character (Fig. 1b). According to Type (ii) selectivity of MCP, the catalysts can be arranged into the following order with respect to the decreasing amount of hydrogen available:

$$Pt/C > Pt\text{-black } (573°K) > Pt/Al_2O_3$$
$$> Pt/SiO_2 > Pt\text{-black } (648°K).$$
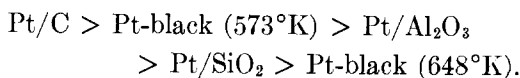
It should be recalled that hydrogen spillover with Pt/C has been found to be much more significant than with Pt/Al_2O_3 (22) which, in turn, showed higher spillover effect than Pt/SiO_2 (23). The position of Pt-black indicates that the hydrogen supply "retained" on its surface (28) may be comparable at 573°K with that observed with supported catalysts. With Pt/C, the retained hydrogen at zero hydrogen pressure is sufficient to promote the formation of saturated C_6 products. Thus, the maximum for MCP yield would be shifted to (hypothetical) hydrogen pressures below zero.

On the basis of Type (i) selectivity, practically the same order is obtained. The equal selectivities with Pt/C and Pt-black at 573°K may be attributed to the former having a higher number of low coordination sites favorable for fragmentation (1) and this effect may have compensated for the difference in hydrogen supply.

In spite of the definite positive hydrogen effect on the selective type C_5-ring opening, the value of the 2MP/n-H ratio under hydrogen-rich conditions is governed by another regularity and is decreasing in the following order:

$$Pt\text{-black } (573°K) \gtrsim Pt\text{-black } (648°K)$$
$$> Pt/C > Pt/Al_2O_3 > Pt/SiO_2.$$
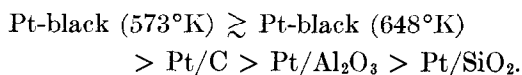
Ring opening involving acidic centers of the support would decrease the 2MP/n-H ratio to below unity (29, 30). This cannot be the case since silica has been reported

to be nonacidic (29); Pt/C, on the other hand, is acidic (31). The differences between "acidic" and "nonacidic" Pt/Al$_2$O$_3$ (24) (the latter being our catalyst) have been reported not to exceed those observed here between alumina-supported and silica-supported metals. It has to be assumed, therefore, that the above order is determined by crystallite size effects (supported also by the relative similarity of the ratios observed with Pt-black in 1 atm H$_2$ at two temperatures). This effect [maybe due to the different origin and supports of our catalyst as opposed to the various Pt/aluminas of essentially the same preparation (17)] manifested itself in a much larger range of particle size than reported previously. The order of Pt/Al$_2$O$_3$ and Pt/SiO$_2$ is reversed owing to the presence of very small particles of Pt/SiO$_2$ not "seen" by X-ray profile broadening (32) but detected by electron microscopy. Also, the influence of other (e.g., electronic) support–metal interactions (so far not clearly defined) cannot be excluded, either, with very small crystallites. The discrepancy between metal surfaces determined by X-ray line broadening and oxygen chemisorption (Table 1) confirms the presence of such particles in Pt/SiO$_2$.

As far as the reaction mechanisms are concerned, the values of the 2MP/n-H ratio from both 3MP and MCP are rather close to each other: This has been taken as a good evidence of the predominance of C$_5$-cyclic skeletal isomerization (8, 33). Pt-black is the only catalyst where significantly more 2MP is formed from 3MP than from MCP, indicating that the importance of bond shift isomerization (which can form 2MP but no n-H in a single step) is not negligible. This is in agreement with the findings of Gault's school whose results predict most pronounced bond shift isomerization with large crystallites (16–18). The difference manifests itself in the low hydrogen pressure region (Fig. 5, left-hand side). This

indicates that bond shift is favored by low surface hydrogen concentrations, maybe because unsaturated surface intermediates are involved in it (10). These intermediates may form benzene at low hydrogen concentration (12) and isomers with more hydrogen present (5). Bond shift isomerization is not particularly sensitive to the variation of the hydrogen pressure, as shown by the small amounts of 2,2-dimethylbutane formed from 3MP throughout the whole hydrogen pressure range (5). The C$_5$-cyclic pathway, however, is accelerated very much by adding more hydrogen to the system [cf. also Refs. (5, 11)]. The overall isomer yields on the left-hand side of Fig. 5, i.e., in the bond shift region, are lower by nearly two orders of magnitude than at higher hydrogen pressures where the C$_5$-cyclic pathway predominates.

It is not clear which experimental parameter may have caused the apparent contradiction between the hydrogen effects reported by Garin and Gault (9) and our present results. At the same time, the existence of their deeply dissociated surface intermediates (9) cannot be denied [as shown by our previous data on "dehydrogenative" C$_5$-cyclization (5, 6)]. Our results are not sufficient, either, to exclude C$_6$-cyclization in a way (2, 25) we attributed here to C$_5$-ring formation only.

To sum up, the considerable effect of the hydrogen pressure on the selectivities of hydrocarbon transformations over various platinum catalysts has been illustrated. All samples studied show the same tendencies. Minor differences can be explained by secondary hydrogen effects, i.e., by the different surface hydrogen coverages of various samples, at the same pressures. Most selectivity values can be interpreted adequately in terms of hydrogen effects only. The selectivity of C$_5$-ring opening, however, requires the assumption of crystallite size effects, too. No definite support effects have been observed, although benzene formation over oxide supported plati-

num may also have occurred partly via dual function catalysis.

This does not mean that we should deny crystallite size or support effects, but it has to be pointed out that these may manifest themselves indirectly, by governing the hydrogen concentration on the metal surface. When evaluating crystallite size effects one must be sure that the "state" of various catalysts as far as surface hydrogen is concerned is analogous.

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