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(8) For the correlation coefficients in Figures 1 and 2 and the entropy correlations, the aminopyridine and 2,6-di-*tert*-butylpyridine points were omitted.

(9) See ref 1d, pp 156–166.

(10) The data now available for alkyl substituted pyridines show hydrophobic solvation effects; see ref 4d and L. Sacconi, L. Paoletti, and M. Ciampolini, *J. Am. Chem. Soc.*, **82**, 3828 (1960). Such solvation effects in the neutral pyridines may also be considered to be present in the pyridinium ions and to cancel in the overall thermodynamic cycle, so that $\Delta H^\circ_{\mathrm{ext}}$ and the deviations from unit slope in Figures 1 and 2 reflect the electrostatic solvation effects in the pyridinium ions resulting from addition of the proton (see ref 4d).

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Isomerization on Metals. Correlation between Metal Particle Size and Reaction Mechanisms

Sir:

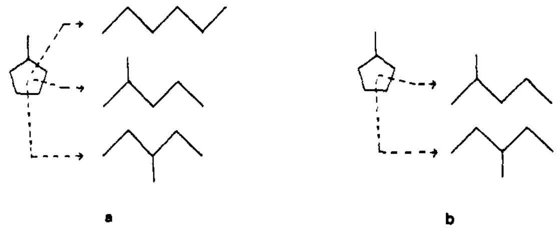


Figure 1.

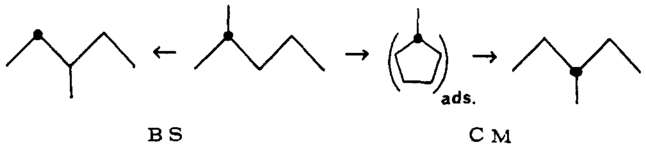


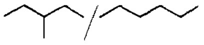
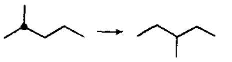
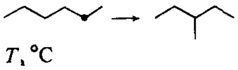
Figure 2.

Hydrogenolysis of methylcyclopentane and isomerization of hexanes on platinum belong to the class of catalytic reactions wherein the selectivity of the reaction depends upon the metal particle size. Previous work has shown that platinum-alumina catalysts of extremely high and low dispersion ($\bar{d}$ = 15 and 180 Å, respectively) behave in a very different way in these reactions. For example, nonselective hydrogenolysis of methylcyclopentane takes place on highly dispersed 0.2% Pt-Al_2O_3 catalyst with an almost equal chance of breaking all five cyclic carbon-carbon bonds (Figure 1a). On the other hand, the CH_2-CH_2 bonds are selectively ruptured on 10% Pt-Al_2O_3 of low dispersion (Figure 1b).[1] Moreover, labeling experiments have shown that isomerization of 2-methylpentane to 3-methylpentane proceeds almost exclusively according to a "cyclic" mechanism (CM) on the 0.2% Pt-Al_2O_3 catalyst, while the contribution of the alternative "bond shift" (BS) mechanism is predominant on 10% Pt-Al_2O_3 (Figure 2).[2]

We report in this note some preliminary results concerning the existing correlation between the metal particle size and the relative contributions of the various mechanisms (cyclic or bond shift for isomerization, selective or nonselective for methylcyclopentane hydrogenolysis). A set of seven Pt-Al_2O_3 catalysts with a mean metal particle size (d_H) ranging from 10 to 200 Å was prepared. The continuous change of metal dispersion, *a*, defined by the ratio between superficial and total platinum atoms and obtained from hydrogen chemisorption measurements, was effected by changing (1) the metal content of the catalyst from 0.2 to 10% and (2) the dehydroxylation state of the alumina; calcinating an extremely pure alumina described elsewhere[3] at 600 °C during 1-200 h modified the concentration of the superficial hydroxyl groups and also the size of the metal particles in the supported catalysts obtained by impregnation with chloroplatinic acid and reduction.

The following three reactions were studied as a function of d_H. (1) Hydrogenolysis of methylcyclopentane, from the ratio *r*, 3-methylpentane over *n*-hexane, are calculated the relative contributions of the selective and nonselective mechanisms. (2) Isomerization of 2-methylpentane-*2*-^{13}C

Table I

Catalysts	Pt %	2.25	8.5	8.4	7.1	4.1	2.5	0.2
	on Al_2O_3[a]	A	A	B' 10 h	B' 210 h	B' 210 h	B' 210 h	A'
	Cl %	0.5	0.85	0.6	0.75	0.6	0.6	0.2
Characterization	*a* = H/Pt	0.05	0.07	0.12	0.35	0.55	0.70	1.0
	d_H (Å)	170	120	70	24	16	12	8.5
Methylcyclopentane	*r* = 	3.2	2.4	1.3	0.7	0.4	0.4	0.4
Hydrogenolysis at 220 °C	Selective mech %	85	80	64	37	0	0	0
% of cyclic mechanism in isomerization		25	16	20	16	30	62	84
		48	55	—	67	—	83	100
	T, °C	285	254	254	254	254	254	300

[a] A and A' represent two batches of commercial alumina with decreasing superficial OH content. B'_{nh} an alumina A' which has been calcinated at 600 °C in air during *n* hours.

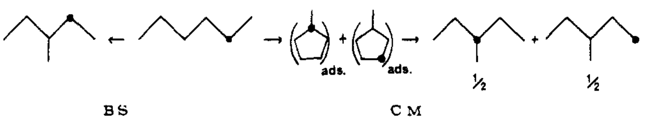


Figure 3.

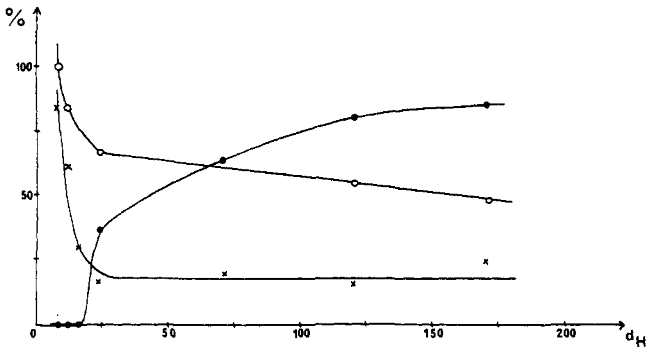


Figure 4. Contributions of the various mechanisms in: (a) isomerization of 2-methylpentane to 3-methylpentane, ×; (c) of *n*-hexane to 3-methylpentane, ○ (percent of cyclic mechanism); (b) hydrogenolysis of methylcyclopentane, ● (percent of selective hydrogenolysis).

into 3-methylpentane allows a distinction between the cyclic and bond shift mechanisms to be made (Figure 2). (3) Isomerization of *n*-hexane-*2*-^{13}C into 3-methylpentane is considered in order to determine the contribution of the cyclic mechanism in chain shortening (Figure 3).

The results are summarized in Table I and Figure 4, where the percentages of selective hydrogenolysis (curve b) and of cyclic mechanisms in isomerization (curves a and c) are plotted as a function of d_H. d_H, which is related to hydrogen chemisorption measurements, is conventionally calculated from the dispersion a by using the relationship $a \times d_H = 8.5$ which holds when assuming cubic crystallites.

An important and common feature of curves in Figure 4 is the break which appears at a dispersion of 0.5 (d_H = 20 Å). In addition, the following observations can be made. (1) The ratio r in methylcyclopentane hydrogenolysis is decreased continuously to a limiting value of 0.4 which characterizes a pure nonselective mechanism. (2) The percentage of cyclic mechanism in the isomerization of 2-methylpentane to 3-methylpentane remains constant ($\simeq$20%) during a large dispersion range (a = 0–0.5) and then increases sharply without, however, reaching 100, even for the most dispersed catalysts. (3) For the isomerization of *n*-hexane to 3-methylpentane, the percentage of cyclic mechanism increases continuously from 50 to 100% with a definite break around a dispersion of 0.5. (4) The chlorine content remains practically constant throughout the series of catalysts from d_H = 170 Å down to d_H = 12 Å. The observed changes in mechanisms should then be explained by a particle size effect and not by a bifunctional effect due to the presence of chlorine on the carrier.

Observation 3 is directly connected with 1 and 2. Due to the principle of microscopic reversibility the change from nonselective to selective hydrogenolysis of methylcyclopentane when increasing the metal particle size implies a change from a "nonselective" cyclic mechanism to a "selective" cyclic mechanism of isomerization which does or does not allow the interconversion between *n*-hexane and methylpentane. Therefore the continuous decrease of the percentage of cyclic mechanism in the isomerization of 3-methylpentane into *n*-hexane (Figure 4c) is accounted for by two effects: (1) the change in nature of the cyclic mechanism from nonselective to selective at low and medium dispersion; (2) the disappearance of the bond shift mechanism at very high dispersion.

From the above results, some deductions can be made concerning the nature of the sites. First of all, any interpretation according to the "mitoedrical" theory[4] should be ruled out. If one assumes[5] that the cyclic mechanism takes place on the corner and edge atoms of the crystallites, while also assuming that the face atoms are responsible for the bond shift mechanism, one should observe a *continuous decrease* of the percentage of cyclic mechanism when increasing the particle size, especially in the range 20–50 Å. On the contrary, the contribution of cyclic mechanism remains constant beyond 20 Å which clearly shows that the sites responsible for bond shift and cyclic mechanism are topographically similar, i.e., both involve or do not involve edge atoms. Since extremely dispersed catalysts are very active for isomerization, we believe that both types of isomerization sites include edge atoms.

Secondly the value of the mean particle size below which the "bond shift" isomerization disappears, 20 Å, is very close to the one corresponding to the disappearance of the B_5 sites in the model of the incomplete cubooctaedron.[6] It is therefore tempting to identify the sites associated with the bond shift and "nonselective" cyclic mechanisms with B_5 sites and isolated edge atoms, respectively. However, the absence of a sharp discontinuity in curve a is most probably due to a spread in the particle size distribution; this suggests that the size of the smallest particles in the catalysts with a dispersion larger than 0.5 is less than 20 Å. Therefore another hypothesis should be put forward. One possibility might be the intervention in highly dispersed catalysts of pseudocrystals (icosaedron for instance), with a C_5 symmetry axis,[7] on which the bond shift mechanism could not take place any more. The verification of such an assumption requires a careful determination, by electron microscopy and other techniques, of the *lower* limit of the crystallite size in the highly dispersed catalysts (a > 0.5). Similarly the progressive change from the nonselective to the selective mechanism of methylcyclopentane hydrogenolysis when the dispersion is smaller than 0.5 suggests the existence of a limiting size of the metal particles, larger than 20 Å, below which the selective mechanism disappears. In this case the determination of the *upper* limit of the crystallite size in the metal particle distribution would allow one to identify more precisely the sites associated with the nonselective and the selective hydrogenolysis.

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