JOURNAL OF CATALYSIS **21**, 250–253 (1971)

LETTER TO THE EDITORS

Comments on a Dispersion Effect in Hydrogenolysis of Methylcyclopentane and Isomerization of Hexanes over Supported Platinum Catalysts

Several years ago, Barron *et al.* (*1*, *2*) demonstrated that the isomerization of *n*-hexane or methylpentanes and the hydrogenolysis of methylcyclopentane over platinum–alumina catalysts involved a common intermediate of cyclopentane structure. The cyclic mechanism of isomerization by dehydrocyclization and ring opening was also shown to be important over platinum films, together with the bond shift mechanism discovered by Anderson and Baker (*3*), Anderson and Avery (*4*), and discussed by Boudart *et al.* (*5*).

During their work, the French authors noticed very large differences between the concentrated and dispersed platinum-on-alumina catalysts (5–20% and 0.2–1.5%, respectively), as far as the product distributions were concerned; they interpreted these differences by an effect of the metallic particle size (*2*, *6*, *7*).

In a recent issue of this Journal (*8*), Dautzenberg and Platteeuw repeated the experiments of Barron *et al.* Over two platinum–alumina catalysts (with 0.5 and 1% of metal on the carrier) they obtained in hydrogenolysis or isomerization exactly the same product distributions as the French workers, although their catalysts were prepared from platinous tetrammine hydroxide instead of chloroplatinic acid and with a reduction temperature of 500°C instead of 200°C. They did not extend their study to the concentrated catalysts. They claimed, however, that the very large difference of selectivity observed by Barron *et al.* for hydrogenolysis and isomerization between the dispersed and concentrated catalysts was related to a difference of chlorine content due to the mode of preparation, and not to a particle size effect.

We wish to report here some results, so far kept unpublished, which show that in no case the chlorine content and more generally any dual function mechanism may account for the differences observed between the 0.2 and 10% platinum–alumina catalysts.

Hydrogenolysis of methylcyclopentane and isomerization of 2-methylpentane, have been studied over various platinum catalysts at 200–340°C under 1 atm of hydrogen, by using the pulse microreactor technique. The catalysts used included:

Three different batches of Pt–Al_2O_3, 10%, prepared by impregnation of an inert alumina with chloroplatinic acid, platinous tetrammine chloride, and platinous tetrammine hydroxide, respectively.

10% Pt–SiO_2 and 10% Pt–pumice catalysts.

0.2% Pt–Al_2O_3 catalysts prepared from chloroplatinic acid.

A batch of 0.2% Pt–Al_2O_3 catalyst prepared with an alumina which has been previously acidified by gaseous HCl at 200°C.

For the preparation of all these catalysts the reduction temperature was kept below or equal to 200°C and the hydrogen flow rate equaled 8 ml/mn.

The initial product distributions for hydrogenolysis and isomerization are characterized by the ratio *n*-hexane over 3-methylpentane (r). The values of r at various temperatures are represented in Fig. 1.

1. The plots r (T) are obviously distributed in two regions. One region of lower values corresponds to the 10% platinum catalysts the second one with higher values correspond to the 0.2% platinum catalysts.

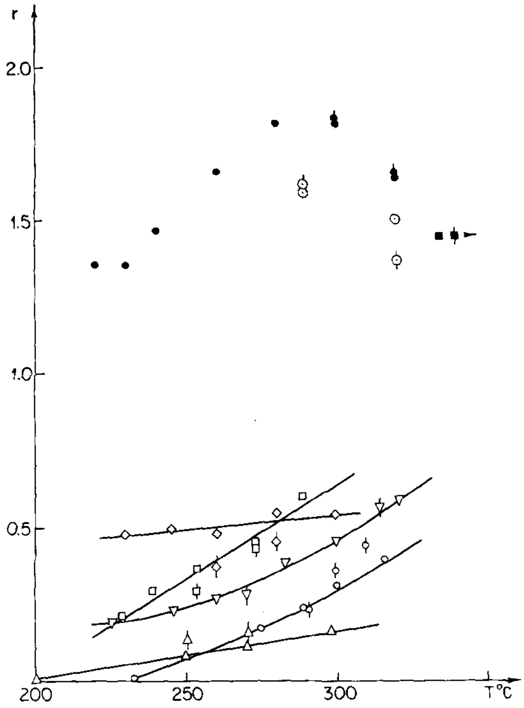

FIG. 1. Hydrogenolysis and isomerization over various platinum catalysts: r (T) plots: Pt–Al_2O_3 10% (a) prepared from chloroplatinic acid: hydrogenolysis of methylcyclopentane (○); isomerization of 2-methylpentane (○⃒); (b) prepared from $Pt(NH_3)_4Cl_2$: hydrogenolysis (△); isomerization (△⃒); (c) prepared from $Pt(NH_3)_4(OH)_2$: hydrogenolysis (□); isomerization (□⃒). Pt-pumice 10% prepared from chloroplatinic acid: hydrogenolysis (▽); isomerization (▽⃒). Pt-Silica 10% prepared from chloroplatinic acid: hydrogenolysis (◇); isomerization (◇⃒). Pt–Al_2O_3 0.2% prepared from chloroplatinic acid: hydrogenolysis (●); isomerization (●⃒). Pt–Al_2O_3 0.5% [Ref. (*8*)] prepared from $Pt(NH_3)_4(OH)_2$: hydrogenolysis (■); isomerization (■⃒). 0.2% Pt over acidified alumina: hydrogenolysis (⊙); isomerization (⊙⃒).

2. The amount of chlorine does not affect much the product distributions, since the three batches of 10% Pt–Al_2O_3 catalyst behave very similarly.

3. The carrier has also very little influence.

4. The alkane distribution is not modified at all when the alumina has been previously chlorinated. The isomerization rate, however, is divided by a factor of 20 to 100; and at 320°, the hydrogenolysis of methylcyclopentane is accompanied by the formation of benzene (1.8% of benzene vs 6.5% of C_6 paraffins).

As complementary experiments, the contact reactions of *n*-hex-1-ene and of methylcyclopent-1-ene over acidified alumina were studied with the same pulse technique between 250 and 500°:

1. From 350° up to 500°, the isomerization of methylcyclopentene to cyclohexene by ring enlargement is the only observable reaction with this material.

2. The isomerization of hex-1-ene is noticeable only from 270°.

3. This isomerization yields 2-methylpentenes and 3-methylpentenes in approximately equal amounts. The ratio r' of the hydrocarbons with 2-methylpentane and 3-methylpentane structures obtained over an acidic catalyst is then very different from the ratio r' obtained over platinum catalysts, which are included between 2 and 4 (Table 1).

The above results clearly rule out any speculation about a possible chlorine effect on the product distribution of hydrogenolysis and isomerization *in the temperature range envisaged* (220–350°); they show also that the dual function mechanism does not intervene at such low temperatures.

We still believe that the observed differences between the concentrated and the dispersed catalysts are due to a difference in the particle size. We do not mean by a "particle size effect" that the distribution is *directly* related to the size of the

TABLE 1
HYDROGENOLYSIS AND ISOMERIZATION OVER VARIOUS CATALYSTS

	Hydrogenolysis of methylcyclopentane over:					
		10% Pt–Al_2O_3 from:				
	0.2% Pt–Al_2O_3 from $PtCl_6H_2$	$PtCl_6H_2$	$Pt(NH_3)_4Cl_2$	$Pt(NH_3)_4(OH)_2$	10% Pt–pumice	10% Pt–SiO_2
T (°C)	300	300	250	254	250	245
r′	2.15	3.5	3.10	3.36	3.2	2.73
	Isomerization of n-hexane over:				Isomerization of hex-1-ene over Al_2O_3 + HCl	
	0.2% Pt–Al_2O_3 from $PtCl_6H_2$	10% Pt–Al_2O_3 from $PtCl_6H_2$				
T (°C)	300	300		T (°C)	300	
r′	2.2	3.5		r′	0.91	

platinum crystallites; we mean that two types of sites (or defects) are present on the surface and that their concentration is determined by the size of the metal particles.

The existence of the two types of sites was clearly demonstrated as early as 1957 in the first paper on this subject *(6a)*. It was shown then that two product distributions for the hydrogenolysis of methylcyclopentane are obtained: one for *all* the catalysts with a metal content lower than 1%; the other one for *all* the catalysts with a metal content higher than 3%.

One type of sites (A), existing on the dispersed catalysts, is responsible for the nonselective mechanism of hydrogenolysis. A recent tracer study using carbon 13 *(9)* shows that sites (A) are associated with a pure cyclic mechanism of isomerization. We believe that sites (A) involve a very limited number of platinum atoms (possibly one).

The second type of sites (B), present on the concentrated catalysts, determine a selective hydrogenolysis. Tracer studies show that on these sites isomerization occurs according to both cyclic and bond shift mechanisms *(9, 10)*. We believe that sites (B) consist of several contiguous superficial atoms.

The crystalline part, in our view, does not play a role by itself, but only as a kind of carrier of the active sites: when a stable catalyst, either of type A or of type B, is heated at more than 500°, in such conditions that the size of the crystallites is increased, the catalytic activity decreases steeply, but the product distributions remain constant.

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Received November 24, 1970