# Effect of the Metal Particle Size in Supported Catalysts on the Selectivity and the Reaction Mechanisms

In the hydrogenolysis of methylcyclopentane and isomerization of hexanes, striking differences have been obtained in the *initial* product distributions on concentrated and dispersed supported catalysts (10% and 0.2% platinum on alumina) (*1–3*).

By using hydrocarbons labeled with carbon 13, these differences could be ascertained and the reaction mechanisms determined more precisely (*4, 5*). While a simple cyclic mechanism takes place on a 0.2% Pt–$Al_2O_3$, both bond shift and cyclic mechanisms occur on a 10% Pt–$Al_2O_3$ catalyst. This difference of behavior between the dispersed and the concentrated catalysts was explained by the difference in the size of the metal particles (20 and 200 Å, respectively).

Dautzenberg and Platteuw strongly objected to this interpretation, suggesting that the difference in the product distributions on the dispersed and the concentrated catalysts was due to a difference of acidity of the alumina, resulting from the use of chloroplatinic acid as impregnating salt (*6*). This objection could be ruled out easily, by performing experiments on three different 10% Pt–$Al_2O_3$ catalysts prepared from platinous tetrammine hydroxide, platinous tetrammine chloride, and chloroplatinic acid: *No substantial differences* in the product distributions were observed on the three catalysts (*7*).

In a recent letter to the editors (*8*), Dautzenberg and Platteuw objected again to a particle size effect, claiming that "in the testing procedure of the French workers, the conversions in the pulse reactor system over the 10% Pt catalyst have been too high, (concurrent with too many secondary reactions)". However, experiments with a conversion lower than 5% are reported in the first papers dealing with the dispersion effect (*1, 3*), and, in the study of the isomerization of labeled methylpentanes on 0.2 and 10% Pt–$Al_2O_3$ catalysts (*4, 5*), the conversion was always kept lower than 10%.

Moreover, Dautzenberg and Platteuw claim that the initial distributions on both 0.2 and 10% Pt–$Al_2O_3$ catalysts are the same and that the distributions observed on a concentrated catalyst in our experiments (*2, 5*) are due to secondary successive reactions. If this assumption was correct, the observed distribution of the hexane isomers on the 10% Pt–$Al_2O_3$ catalyst *should be* intermediate between the equilibrium distribution and the initial distribution obtained on a 0.2% Pt–$Al_2O_3$ catalyst. It is clear from Table 1 that this is not the case at all.

Once the objection of a readsorption process is ruled out, it remains to explain the distributions obtained by the Dutch workers in the isomerization of *n*-hexane on Pt–$Al_2O_3$ catalysts (*8*); they obtained on a 10% Pt–$Al_2O_3$ and on a 1% Pt–$Al_2O_3$ catalyst, the same ratio 2-methylpentane/3-methylpentane, $r = 2.0$, very different indeed from the one obtained on the 10% Pt catalyst used in our experiments: $r = 3.5$. We believe that the apparent disagreement between the two sets of results can again be explained by a particle size effect. The 10% Pt catalyst used by Dautzenberg and Platteuw (*8*) is much more dispersed indeed than the 10% Pt catalyst used by Maire and Gault (*3*). Only 50% of the platinum was accessible to X-ray diffraction instead of more than 90% and the mean particle size of the visible part was 80 instead of 200 Å.

We report here some additional data in favor of this interpretation. Several 10% Pt–$Al_2O_3$ and Pt–$SiO_2$ catalysts were prepared in different ways in order to change the average size of the metal crystallites. After impregnation of an inert alumina by

TABLE 1

INITIAL AND EQUILIBRIUM DISTRIBUTIONS OF ISOMERS FROM HYDROGENOLYSIS OF METHYLCYCLOPENTANE ON PLATINUM-ALUMINA CATALYSTS AT 300°C[a]

| Catalysts[b] | 0.2% Pt-$Al_2O_3$ | 10% Pt-$Al_2O_3$ | Equilibrium[c] |
|---|---|---|---|
| $r_1$ = 2MP/3MP | 2.15 | 3.5 | 1.6 |
| $r_2$ = 3MP/$n$-H | 0.55 | 2.8 | 1.15 |
| $r_3$ = 2MP/$n$-H | 1.1 | 9 | 1.8 |

[a] According to refs. *1-3*.

[b] 2MP = 2 methylpentane, 3MP = 3 methylpentane, $n$-H = $n$-hexane.

[c] These equilibrium data have been determined experimentally (*1*).

various salts, the impregnated catalyst was dried and reduced under various conditions. The catalyst was then submitted to a standard treatment by hydrogen at 300°C under 1 atm during 48 hr. The average size of the metal crystallites was then determined by the ratio H/Pt between the number of hydrogen atoms chemisorbed and the number of platinum atoms deposited on the carrier ($d_H$), and, when possible, by the broadening of the X-ray diffraction line ($d_X$). Some differences were observed between $d_H$ and $d_X$ and are easily explained by the fact that in the dispersed catalysts, a fraction of the crystallites cannot be detected by the X-ray method.

For each catalyst, the selectivity in the hydrogenolysis of methylcyclopentane, at 260°C and under 1 atm of hydrogen, was studied by using the pulse microreactor technique, and the isomerization of labeled methylpentanes and $n$-hexanes was investigated on the most characteristic catalysts.

The results, which will be presented in detail in a later publication, may be summarized as follows:

(1) The mean size of the crystallites $d_H$ does not depend too much upon the nature of the impregnating salt.

(2) For a platinum–alumina catalyst, $d_H$ depends strongly upon the hydrogen flow rate and the temperature during the *early* stage of the reduction. The catalysts prepared at the lower hydrogen flow rate (1 ml/min) and the lower temperature (50°C) have the same characteristics as the ones used in our previous experiments (hydrogen flow rate: 8 ml/min; reduction temperature: 1 hr at 100°C, then 48 hr at 300°C). These catalysts have a mean particle size of 200 Å and will be referred to further as *catalysts A*. The catalysts reduced with the higher hydrogen flow rate (200 cm$^3$/min) and the higher temperature (200°C) were highly dispersed with a mean particle size $d_H$ of 60 Å; they are referred to as *catalysts B*.

(3) The catalysts which have been dried for 1 hour in a stream of nitrogen (flow rate 70 ml/min) at 200°C are slightly more dispersed than the catalysts prepared in the usual way, without any drying.

(4) The use of silica instead of alumina as carrier decreases strongly the size of the metal particles; however, the effects of hydrogen flow rate, temperature and drying treatment for a platinum-silica catalyst are the same as for a platinum-alumina catalyst. The increase of particle size when drying the unreduced catalyst had already been observed by Dorling and Moss (*9*).

TABLE 2

SELECTIVITY IN HYDROGENOLYSIS OF METHYLCYCLOPENTANE AT 260°C AS A FUNCTION OF METAL PARTICLE SIZE

| Catalysts | 10% Pt-$Al_2O_3$ A | 10% Pt-$SiO_2$ A | 10% Pt-$Al_2O_3$ B | 10% Pt-$SiO_2$ B | 0.5% Pt-$Al_2O_3$ A |
|---|---|---|---|---|---|
| H/Pt | 0.04 | 0.18 | 0.38 | 0.57 | 0.97 |
| $d_H$ | 185 | 44.5 | 23.5 | 15 | 12 |
| $d_X$ | 200 | 103 | 65 | —[a] | —[a] |
| $r_2$ = 3MP/$n$-H | 4.6 | 1.46 | 0.80 | 0.55 | 0.42 |
| $r_1$ = 2MP/3MP | 3.30 | 2.79 | 2.70 | 2.52 | 2.49 |

[a] Undetectable.

(5) The selectivity in hydrogenolysis parallels very closely the magnitude of the particle size. For 23 catalysts samples of various particle sizes, only one minor discrepancy was observed. Some of the results are presented in Table 2; they give a good idea of the very close agreement between the physical methods for determining the metal particle size and the "chemical method" represented by the use of the selectivity in methylcyclopentane hydrogenolysis.

(6) The use of labeled hexanes shows that the isomerization of *n*-hexane to methylpentanes and vice-versa occurs more than 90% of the time according to a cyclic mechanism on any catalyst except on the ones with very large crystallites ($d_H >$ 150 Å). The results obtained by the Dutch workers, who used a catalyst with 80 Å particles are then very easily explained: with such a catalyst, one expects a cyclic mechanism of isomerization of *n*-hexane, with a nonselective ring opening of the cyclic intermediate; i.e., a ratio 2-methylpentane/3-methylpentane very close to 2.

(7) The interconversion between methylpentanes occurs according to a cyclic mechanism *only* for the very highly dispersed catalyst ($d <$ 50 Å). For the catalysts with a higher particle size, the bond shift mechanism is predominant.

All these results demonstrate clearly the existing correlation between the metal particle sizes and the various reaction routes in a catalytic reaction. As already outlined in our previous papers, we mean by particle size effect the influence of the size of the metal particles upon the formation of the various types of "defects" which are responsible for the various reaction mechanisms. In the case of supported metal catalysts, these defects appear during the early stage of the preparation of the reactive surface.

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# Kinetics of Ethane Hydrogenolysis

The kinetics of the catalytic hydrogenolysis of ethane to methane have been investigated on all the Group VIII metals (*1*). A kinetic scheme originally proposed by Cimino *et al.* (*2*), extended to include situations in which adsorption equilibria are not established, was used for the interpretation of the results (*1*). The purpose of the present note is to reinterpret the kinetics in terms of a reaction sequence in which the step involving carbon–carbon bond scission has been revised. The new interpretation has the advantage of giving a much improved fit to the kinetic data,