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On the Effect of Metal Particle Size on the Isomerization of *n*-Hexane Over Supported Platinum Catalysts

In a recent publication (*1*) we reported that the relative initial formation of 2-methylpentane and 3-methylpentane, when *n*-hexane was passed over inert-alumina-supported platinum catalysts, was independent of the amount of supported platinum used, 0.5 and 1.0 wt %. Since the same result was obtained over these catalysts after they had been subjected to a reduction treatment at various severities, by which the platinum particles had sintered to various degrees, it was suggested that the isomerization behavior is independent of metal particle size. The relative formation of 2-methylpentane and 3-methylpentane from *n*-hexane was in close agreement with that observed by Barron *et al.* (*2*) and Maire *et al.* (*3*) for their 0.2 wt % Pt-on-alumina catalyst, but was in striking contrast with the value given by these authors for their 10 wt % Pt-on-alumina catalyst.

Because of our vivid interest in the possible existence of particle-size effects on platinum-catalyzed reactions and in order to remove some doubt which might still exist as to the above statement (*5*), we have extended our experiments using catalysts containing a higher loading of platinum. A UOP-type alumina (surface area, 180 m^2/g, pore volume, 0.73 ml/g) was used as the starting material. This product was steamed to remove chlorine and subsequently calcined for 3 hr at 850°C, followed by a treatment with an aqueous solution of Na_2CO_3 and a final calcination for 3 hr at 500°C (0.5 wt % Na in final catalyst). After this treatment, the carrier was essentially inert for skeletal isomerization and cyclization of hexenes, as well as for ring opening of methylcyclopentane at temperatures up to 500°C. Catalysts were prepared containing 1, 5, and 10 wt %. The metal was placed on the support via impregnation of an aqueous solution of $Pt(NH_3)_4(OH)_2$ as described previously (*1*). The final treatment prior to use comprised a calcination in air for 3 hr at 500°C, followed by a treatment *in situ* for 16 hr with atmospheric hydrogen at ca. 400°C. X-Ray diffraction analyses of the 10 wt % Pt catalyst showed that about 50% of the total platinum was present as particles larger than 30 Å. The average particle size of the visible fraction was about 80 Å.

No platinum particles could be detected

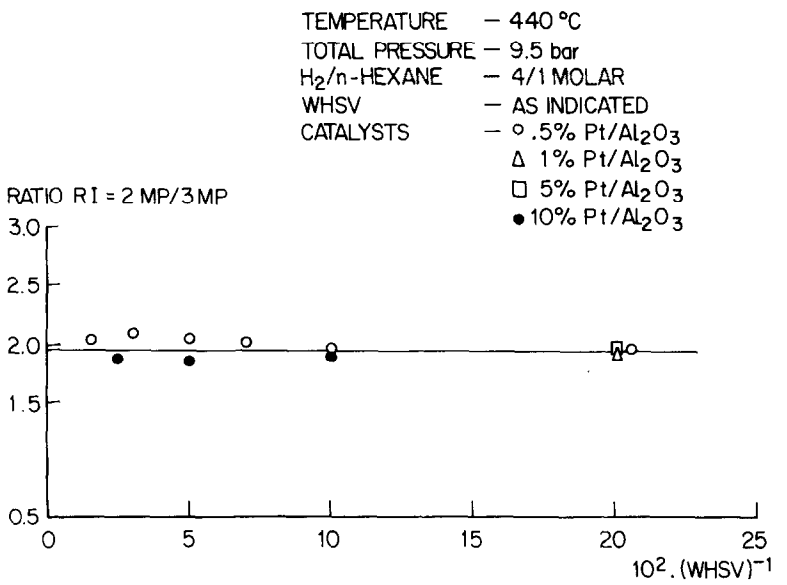

FIG. 1. Ratio of hexane isomers formed from *n*-hexane as a function of space velocity over various support platinum catalysts.

by electron microscopy or X-ray diffraction in the 1 wt % Pt sample, indicating a particle size less than 10 Å.

The isomerization experiments were carried out in the same way as described previously (*1*). Reactions were performed at various space velocities. As before, we observed that, although at each condition the catalyst suffered from a rather heavy decline, the 2-methylpentane/3-methylpentane ratio turned out to be independent of catalyst age. The results in Fig. 1 show that the initial relative formation of 2-methylpentane and 3-methylpentane from *n*-hexane is actually independent of platinum loading (from 0.5 to 10 wt % Pt) and hence of metal particle size. It is interesting to note that the 2-methylpentane/3-methylpentane ratio of ca. 2 was fully confirmed in a recent publication by Anderson *et al.* (*4*) at conversions of *n*-hexane of less than 5% over platium films varying from ultrathin to continuous thick polycrystalline films.

Previously we suggested that the large deviation observed by Barron *et al.* (*2*) for their 10 wt % Pt catalyst could be due to the mode of preparation, which might have introduced some bifunctionality.

Another, probably more important, cause of the discrepancies is related to the testing procedure of the French workers. It is felt that the conversions in the pulse reactor system over the 10 wt % Pt catalyst have been too high (concurrent with too many secondary reactions), which leaves some doubt as to the reliability of the extrapolation to zero conversion.

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