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Selectivity of Platinum and Platinum–Nylon Catalysts

Catalysts composed of platinum on nylon supports exhibit unique selectivities in hydrogenation of benzene (*1–3*). Even though slight amounts of cyclohexene may be detected in some platinum-catalyzed hydrogenations—as reviewed by Balandin (*4*)—the catalytic selectivity for production of cyclohexene rather than cyclohexane is much higher for the platinum–nylon catalysts than for other platinum catalysts (*1–3*). Harrison and Rase (*1*) suggested that the high selectivity for cyclohexene production could be explained at least partially by a geometric interpretation, with supporting electron microscopic evidence which I supplied. Dini *et al.* (*3*) suggested, however, that "geometric effects invoked by Harrison and Rase could not be an entirely valid explanation for the observed selectivities, and that a different interpretation might apply." They discounted the geometric effects because (a) they found the platinum in their catalysts to be in the form of a complex and (b) they found that there was no appreciable difference in qualitative selectivities of catalysts prepared from nylons with differing amide group repeat distances.

The question as to whether geometric effect determines the selectivity of platinum–nylon catalysts is important not only for this specific catalyst. It also becomes important in that comparison of platinum with platinum–nylon catalysts allows evaluation of Balandin's multiplet theory (*4*) of heterogeneous catalysis for the same reaction.

I would like to point out that the experimental results of Dini *et al.* (*3*) do not disprove that a geometric effect is a determinant for the selectivity of platinum–nylon catalysts. Boudart (*5*) has reported that for benzene hydrogenation with platinum catalysts composed of crystallites in the 15- to 50-Å size range the activity per unit surface area does not depend on the degree of dispersion of the metal. Thus the low activity of the platinum–nylon catalysts (*1, 2*) must not be due simply to disorder caused by dispersion of the platinum into small crystallites. It would seem extremely unlikely, on the other hand, that the nylon would not exert some electronic influence on dispersed platinum, whether in the form of crystallites, complexes, or atomic dispersion.

I would like to suggest that atomic dispersion of platinum on the nylon surface in an ordered manner at amide group loci results in a completely different benzene hydrogenation mechanism consistent with the experimental results published to date. The sextet theory propounded by Balandin (*4*) for platinum-catalyzed hydrogenation of benzene involves a configuration as shown in Fig. 1.

The "sextet" includes six adsorption sites—three for π bonding of benzene to platinum and three corresponding sites for chemisorption of hydrogen. The π bonding of benzene to platinum has been reported by Palazov (*6*). The important distinction between platinum and platinum–nylon can be seen by comparison of Figs. 1 and 2.

If the platinum is atomically dispersed at amide linkages the differences are essentially the same—no matter which nylon is used. These differences and probable con-

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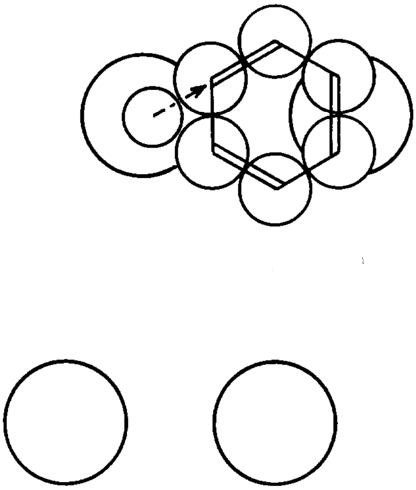

FIG. 2. Physical arrangement of benzene and hydrogen on platinum–nylon 66 symbolized as in Fig. 1.

sequences are as follows:

(1) Benzene can be π bonded to three platinum atoms on the platinum metal and only to one on the platinum–nylon. As a result the benzene should be much more strongly adsorbed on the platinum metal and the electron withdrawal from the benzene ring should be much greater for the metal.

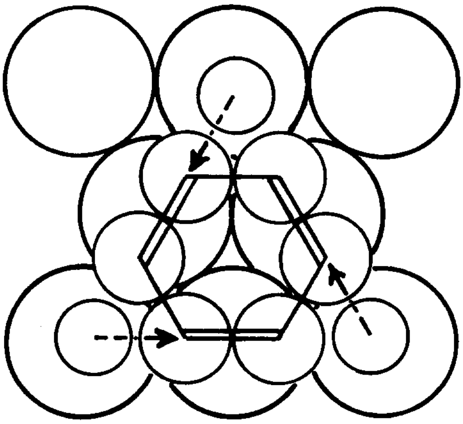

FIG. 1. Physical arrangement of benzene and hydrogen on (111) face of platinum. Large circles represent platinum atoms and smaller circles imposed on benzene ring represent carbon atoms. Double bonds represent loci of π bonds between benzene and platinum, while circles with outpointing arrows represent hydrogen atoms reacting with benzene.

(2) Hydrogen can add directly to π-bonded carbon atoms on the platinum metal, whereas this is physically impossible as a surface reaction for the platinum–nylon. In the latter case chemisorbed hydrogen can add only to carbon atoms at bonds conjugated to those involved in the π complex. Thus the hydrogenation would be expected to be slower for the platinum–nylon case. Also the π-bonded double bond left at the cyclohexene stage of hydrogenation is completely inaccessible to chemisorbed hydrogen. Further hydrogenation would not be expected at such sites.

The above consequences for platinum–nylon as compared to platinum, i.e., weaker benzene adsorption, slower reaction, and high selectivity for cyclohexene production, have been shown to be true (*1–3*). It appears very likely that the geometric effect is operative in this reaction.

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