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NOTES

Hydrogenation of Benzene on Supported Platinum Catalysts

Platinum, supported on various high surface area carriers like alumina, silica–alumina, kieselguhr and carbon, is used extensively for various reactions such as reforming of petroleum, oxidation of carbon monoxide, hydrogenation of olefins in the liquid phase, etc. All these reactions may be divided into two categories, namely, those whose specific rate (rate per unit surface area of metal) depends only on the number of platinum atoms exposed on the surface of the carrier ("structure insensitive" or "facile" reactions) and those whose specific rate depends not only on the total number of exposed Pt atoms but also on the presence of a certain preferred configuration of these Pt atoms ("structure sensitive" or "demanding" reactions) (*1*, *2*). Recently, radial electron distribution, electron microscopy and hydrogen–oxygen titration techniques have been applied simultaneously to characterize the structure of Pt crystallites dispersed to various extents on alumina and silica–alumina carriers (*3*). The hydrogenation of benzene on these catalysts has also been studied and is now reported.

The Pt supported catalysts were obtained from various commercial sources (*3*). The Pt dispersion (the fraction of Pt atoms exposed on the surface of Pt crystallites) was obtained according to the procedure proposed by Benson and Boudart (*4*) with a stoichiometry of 3 hydrogen atoms/Pt atom. Hydrogenation experiments were conducted in a flow reactor using 1 ml of catalyst (<40 mesh). Care was taken to eliminate diffusion effects. The catalysts were reduced in a flow (4 liters/hr) of pure, dry hydrogen for 8 hr at 400°C before use. All runs were conducted at 120°C and atmospheric pressure, and with a hydrogen:benzene ratio of 8. The products were analyzed by gas chromatography.

Table 1 summarizes the metal dispersion and catalytic properties of the catalysts. The reaction was found to be zero order with respect to the partial pressure of benzene under the reaction conditions employed. As may be seen from Table 1, the hydrogenation activity, expressed as the turnover number (i.e., the number of benzene molecules hydrogenated per second per exposed Pt atom, which was determined from H_2–O_2 titration) is independent of both the crystallite size of Pt and the nature of the carrier. Aben, Platteeuw and Stouthamer (*5*) have also observed a similar result.

From X-ray scattering experiments, it was deduced earlier (*3*) that in the top

TABLE 1
METAL DISPERSION AND CATALYTIC ACTIVITY OF SUPPORTED Pt CATALYSTS

Catalyst	Wt % Pt	Support	%, Dispersion[a]	Turnover no.[b]
099A	0.795	SiO_2–Al_2O_3	12.67	2.75
065A	0.760	SiO_2–Al_2O_3	34.57	2.09
059A	0.772	SiO_2–Al_2O_3	46.27	2.62
099B	0.750	SiO_2–Al_2O_3	51.20	2.77
059E	0.731	SiO_2–Al_2O_3	54.93	4.21
103A	0.639	Al_2O_3	20.80	2.98
103B	0.738	Al_2O_3	78.13	3.82

[a] Values taken from Ref. (*3*).

[b] Turnover number is defined as molecules of benzene hydrogenated per second per exposed Pt atom.

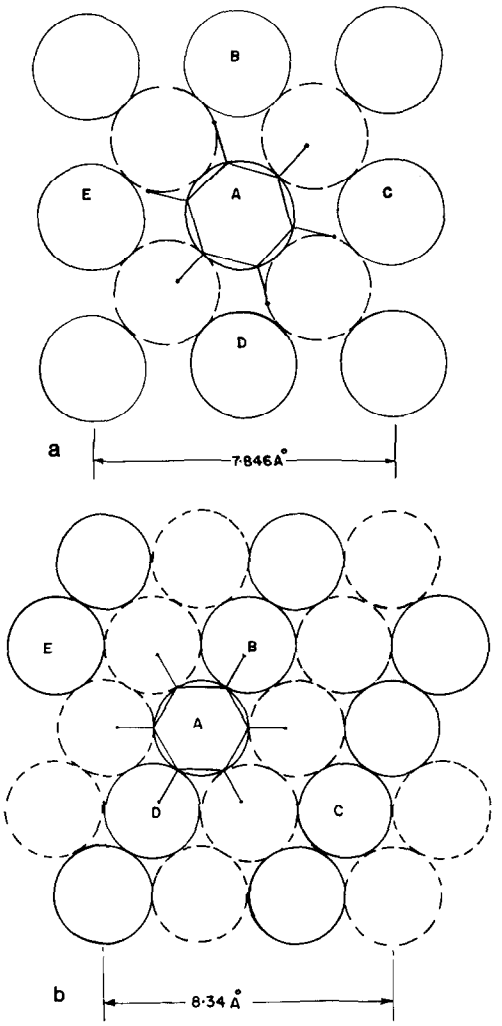

FIG. 1. Distribution of surface Pt atoms in (100) and (111) planes of Pt crystallites, respectively. The vacancies are indicated as broken circles. The orientation of an adsorbed benzene molecule is also indicated.

two surface layers of Pt crystallites, the metal atom:metal vacancy stoichiometric ratio corresponds to a value of 1:1. Figure 1a and b show a plausible vacancy distribution for (100) and (111) planes of Pt crystallites, respectively, which satisfy this ratio. The "flat" adsorbed position of a benzene molecule is also indicated in Fig. 1. The absence of crystallite size effects in benzene hydrogenation (Table 1) means that the edge and corner Pt atoms are equivalent to the face atoms as sites for the reaction. This may be understood from Fig. 1a and b. Each benzene adsorption site (Pt atom A) is surrounded by vacant sites. Structurally, these face atoms are therefore similar to those at crystallite edges and corners in that both types of atoms (face as well as edge and corner) present an almost isolated Pt atom (relatively free of the electronic and steric influences of neighboring atoms) to the adsorbed benzene molecule. This structural equivalence causes their similar reactivity in the hydrogenation reaction.

Moreover, adsorption of a benzene molecule on Pt atom A will exclude simultaneous adsorption of another benzene molecule on metal atoms B, C, D and E (Fig. 1a). Thus, on the average, at least 5 Pt atoms are expected to be involved in one hydrogenation step. In fact, Aben, Platteeuw and Stouthamer (*5*), applying the theory of absolute reaction rates to their data had arrived at a similar result. The present model accounts also for the "*ortho* effect" in benzene-D_2 exchange processes (*6*). This arises due to the steric hindrance between bulky substituents in the *ortho* positions and Pt atoms B and/or C. "Severe" deactivation occurs when one bulky group interacts with Pt atoms B or C. "Complete" deactivation results when two bulky groups interact with both Pt atoms B and C.

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