Hydrogenation of Some Condensed-Ring Aromatic Hydrocarbons

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AS A RESULT of extensive research since 1930, the general principles governing aromatic hydrogenation are reasonably well understood today (*4*). However, quantitative data on the catalytic hydrogenation of condensed polynuclear aromatics with commercial catalysts is still quite limited in spite of the importance of ring saturation in connection with certain hydrocarbon conversion processes (*1, 2, 3*). This article describes the effect of temperature on the hydrogenation of naphthalene, phenanthrene, and pyrene over four different catalysts at 1000 p.s.i.g. The principal result of the work was to show the shift, with increasing temperature, from catalyst activity to thermodynamic equilibrium as the controlling factor in the extent of hydrogenation.

EXPERIMENTAL

Catalysts. Properties of the fresh catalysts are given in Table I. Prior to use, the platinum, palladium, and cobalt molybdate catalysts were stabilized against major activity changes by several hydrogenation tests with interposed air regenerations; nickel tungsten sulfide was conditioned with feed, but was not regenerated. The extent to which this procedure affected the activities of the various catalysts was not determined.

Feedstocks. The aromatics were dissolved in *n*-cetane to provide feedstocks containing about 5 weight % of aromatic. Sulfur contents were 0.011, 0.010, and 0.012 weight % and nitrogen contents were 0.004, 0.001, and 0.003 weight % in the naphthalene, phenanthrene, and pyrene feeds, respectively.

Procedure. The experiments were conducted in a conventional, continuous-flow system. The feed and product were analyzed by ultraviolet absorption spectroscopy. In some experiments with naphthalene, partition chromatography was also used in order to obtain a direct measurement of Decalin as well as Tetralin and naphthalene in the product.

Table I. Properties of Hydrogenation Catalysts

Composition, Wt. %	Surface Area, Sq. Meters /G.	Size and Form
0.5 Pd-on-alumina	175	⅛ × ⅛-inch, pills
0.8 Pt., 0.3 Cl, 0.3 F-on-alumina	175	1/16 inch, spheres
3 NiS, 27 WS_2-on-alumina	174	10-/20-mesh, particles
2.5 CoO, 4.5 MoO_3-alumina	173	10-/20-mesh, particles

RESULTS AND DISCUSSION

The results are summarized in Figures 1, 2, and 3, in which the composition of the product, expressed as mole per cent of the charged aromatic, is shown on a cumulative basis as a function of temperature. At the lower temperature levels, hydrogenation appeared to be a function of catalyst activity and differences between the various catalysts were observed. At increasingly higher temperatures, hydrogenation generally increased until catalyst activity was superseded by thermodynamic equilibrium as the controlling factor, although the final equilibrium composition was not necessarily reached. These combined effects resulted in a temperature at which maximum hydrogenation was observed. In all but one case, the maximum occurred between 600° and 700° F.

Pyrene was relatively difficult to hydrogenate in these experiments, apparently because of a combination of low reactivity and less favorable thermodynamics.

Naphthalene Equilibrium. In experiments with naphthalene at temperatures above 750° F., the concentration of naphthalene appeared to approach the equilibrium value, since it was essentially independent of both feed rate and catalyst. Using the data obtained with cobalt molybdate

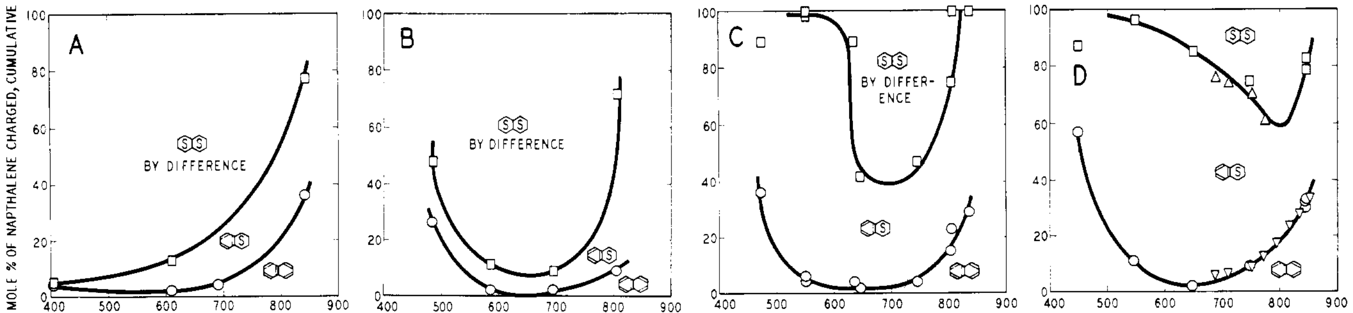

Figure 1. Hydrogenation of naphthalene at 1 LHSV, 1000 p.s.i.g., 180 to 1, H_2 to naphthalene ratio with 5 weight % of naphthalene in cetane

A. Palladium-alumina
B. Platinum-alumina
C. Nickel, tungsten sulfides-alumina
D. Cobalt molybdate-alumina ○□ 1 LHSV; Decalin by difference ▽△ 0.5 LHSV; Decalin by chromatography

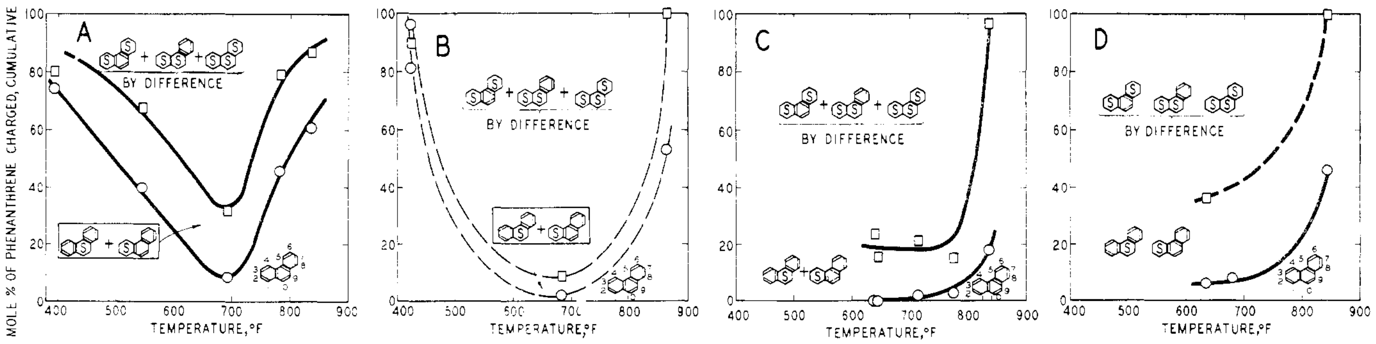

Figure 2. Hydrogenation of phenanthrene at 1 LHSV, 1000 p.s.i.g., 280 to 1, H_2 to phenanthrene ratio with 5 weight % of phenanthrene in cetane

A. Palladium-alumina
B. Platinum-alumina
C. Nickel, tungsten sulfides-alumina
D. Cobalt molybdate-alumina

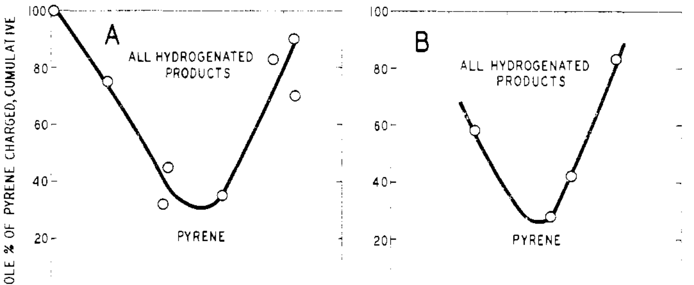

Figure 3. Hydrogenation of pyrene at 1 LHSV, 1000 p.s.i.g., 280 to 1, H_2 to pyrene ratio with 5 weight % of pyrene in cetane

A. Platinum-alumina
B. Cobalt molybdate-alumina

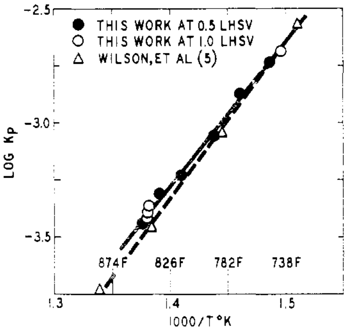

Figure 4. Equilibrium constants for naphthalene-tetralin-hydrogen

catalyst, values of the thermodynamic equilibrium constant K_p were calculated by the expression:

$$K_p = (N_{C_{10}H_{12}}/N_{C_{10}H_8} \times N^2_{H_2}) \times 1/P^2_{atm} \times 1/\gamma^2_{H_2}$$

Any Decalin in the system was included with the Tetralin and the mole fraction of hydrogen was assigned a value of 1.0.

These values are compared with those reported by Wilson (5) (Figure 4). The authors' values correspond to slightly lower concentrations of naphthalene at the higher temperatures.

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Received for review November 25, 1960. Accepted September 19, 1961. Division of Petroleum Chemistry, Symposium on Catalysts and Catalytic Cracking, 138th Meeting, ACS, New York, N. Y., September 1960.