THE STRUCTURE OF MIXED HYDROGENATION CATALYSTS

Humbert Morris
Northwestern University, Evanston, Illinois

Benzene can be reduced to cyclohexane by hydrogen only in the presence of a catalyst. Ipatieff, Corson and Kurbatov[1] have shown that pure copper is ineffective as a catalyst, producing measurable reduction only at high temperatures and pressures. They have also shown that small amounts of nickel in the copper make it active as a catalyst. Where there is as little as 50 parts per million of nickel, in 90 seconds contact time at 225° C., they obtain 4% hydrogenation. Ipatieff, Corson and Kurbatov also found that these nickel-activated copper catalysts experienced an irreversible deactivation when they underwent prolonged heating at 400° C.

Nickel is ferromagnetic, but it is readily soluble in copper, and dilute solutions of nickel in copper are not ferromagnetic.[2] Thus, magnetic measurements can show whether a copper-nickel system consists of mixed crystals or of a solid solution of nickel in copper, or of both a solution and mixed crystals. Dr. P. W. Selwood and the writer have therefore made parallel measurements of ferromagnetism and catalytic activity in an effort to determine the nature of the change that reduced the activity of the catalyst.

The first samples of purified copper tested were strongly ferromagnetic owing to ten parts per million of iron. It was necessary further to purify this copper because the ferromagnetic effects due to any activating nickel would have been obscured by the iron. Copper containing less than one part per million of iron was finally obtained by electrolysis. This copper was made by electrolysis from c.p. copper sulfate. The deposit was dissolved in redistilled nitric acid and again electrolyzed. Copper purified in this way was found to be inactive in the hydrogenation of benzene, confirming the results of Ipatieff and Corson, and contradicting those of Pease and Purdum[3], who claimed that copper prepared from c.p. copper oxide was an active hydrogenation catalyst. This purified copper was activated with 1% of nickel. Nickel nitrate solution was stirred into a slurry of copper hydroxide. It was dried, decomposed by heating, and reduced by hydrogen at 200° C. This catalyst effected 60% reduction of benzene in 30 seconds at 175°. This active catalyst was strongly ferromagnetic. The ferromagnetism of the catalyst shows that the nickel is not in solution in the copper. The catalyst must consist of mixed crystals of copper and nickel.

The catalyst was then heated at 350° for two hours, and again tested for catalytic activity and ferromagnetism. It was found to be only one third catalytically effective as before, and only one third as ferromagnetic.

It may be concluded from these results that the catalyst loses its activity because it forms a solid solution of nickel and copper. That is, that thermal deactivation consists of a process of diffusion of the nickel into the copper.

The catalytic activity was measured by an apparatus designed and built by Ipatieff and Corson. Hydrogen gas was purified by passing it successively over (1) copper gauze at 550°C. in a quartz tube; (2) through lead acetate solution; (3) potassium hydroxide; and (4) drying tubes. It was then passed into benzene at 25°C. in a thermostat, and finally over the catalyst. The gas was then passed through traps cooled in dry ice to catch the benzene and cyclohexane.

The magnetic susceptibility was measured by the Gouy method.[4] The sample tube was hung from one pan of a micro balance above an electromagnet, so suspended that the middle partition was in the center of the magnetic field. One end of the tube was evacuated and the catalyst packed into the other end. The tube was weighed with no magnetic field. Then the magnet was turned on and the tube weighed again. The apparent change in weight was proportional to the magnetic susceptibility.

REFERENCES

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