

The Platinum Metals in Catalysis

PAPERS PRESENTED AT INTERNATIONAL CONGRESS

A wide range of reactions, studied from both theoretical and practical points of view, was discussed at the International Congress on Catalysis held in Philadelphia in September. Extending over five days, and attracting some eighty papers, the Conference was organised by the Catalysis Clubs of Philadelphia and Chicago, the National Science Foundation, the University of Pennsylvania and the International Union of Pure and Applied Chemistry. The platinum metals were employed as catalysts in many of the investigations described, and significant results were reported on the lesser-known catalytic properties of rhodium and ruthenium.

Smith and Thompson (1) found, for instance, that rhodium had an important advantage over platinum as a catalyst in the hydrogenation of methoxybenzenes. Anisole, the three dimethoxybenzenes and 1, 2, 3, trimethoxybenzene were hydrogenated over both Adams' platinum catalyst and 5 per cent rhodium on alumina, and it was found that rhodium could hydrogenate the aromatic ring with far less cleavage of the methoxy groups (6-18 per cent) than that caused by platinum (40-60 per cent). The amount of cleavage was found to increase linearly with temperature for each catalyst, except in the case of anisole where the change with temperature was quite small or negligible. The discovery that rhodium, particularly at lower temperatures, can catalyse the reduction of the aromatic nucleus with only slight cleavage of the methoxy groups should be of importance in organic syntheses. The rate constants for the hydrogenation with pure platinum oxide were only two to three times greater than with 5 per cent rhodium catalysts, indicating that rhodium must have a greater activity per unit weight than platinum.

Hydrogenation was therefore attempted with pure rhodium oxide, but no reaction occurred, due probably to the conditions being insufficient to reduce the oxide to the metal form.

The use of rhodium and ruthenium as catalysts in liquid-phase hydrogenation by Gilman and Cohn (2) emphasises their superiority over palladium and platinum for certain specific reactions. Carrier-based rhodium catalysts should find a large scale application in the reduction of substituted aromatic ring systems; the hydrogenation of rings containing alkyl-, hydroxyl- or carboxyl substituents was stoichiometric, and in no case was any evidence of cleavage found. Substituent groups on a heterocyclic nucleus are similarly immune from cleavage in rhodium catalysed hydrogenation, and unsubstituted heterocyclic compounds such as pyrrole and pyridine, which had resisted previous attempts at catalytic hydrogenation over nickel, were easily reduced in the presence of rhodium catalysts.

Ruthenium in Hydrogenation

A ruthenium catalyst consisting of 5 per cent metal on either activated alumina or charcoal was found to be specific for the hydrogenation of the carbonyl group in aliphatic aldehydes and ketones under atmospheric conditions. With this catalyst preferential reduction of the carbonyl group in the presence of an olefinic linkage occurs, so that in certain instances unsaturated alcohols can be obtained. Ruthenium is also especially effective in the conversion of sugars to polyhydroxy alcohols. At elevated temperatures and pressures the disaccharides, sucrose and lactose, are both hydrolysed and reduced giving dulcitol, sorbitol and mannitol. Maltose

is not hydrolysed and is only reduced with difficulty using large amounts of catalyst, the product being maltitol. The hydrogenation of dextrose was studied in detail and the reaction rate was found to increase sharply with pressure. These investigations show ruthenium to be of particular interest as a catalyst for the reduction of saccharides.

Oxidation Catalyst Films

An interesting paper by Adey and Calvert (3) describes the preparation of an oxidation catalyst coating suitable for deposition on non-porous surfaces such as metals. This has been commercially applied in the coating of resistance wire, which is then wound into an electrically energised coil giving the catalyst in a convenient form for bringing to activation temperature. This film is more active as an oxidising catalyst than a straight deposit of platinum, has a longer life and is less subject to poisoning. It has already found commercial use as a unit for deodorising the steam and grease from electric ovens; it is placed in the oven-vent and oxidises the gases as they pass over it.

Evaporated metallic films were used as catalysts by Anderson and Kemball (4) in their work on the catalytic exchange and

deuteration of benzene. They used films of palladium and platinum (among others), the most extensive results being obtained with these two metals because it was found that on these surfaces the exchange and deuteration reactions occurred simultaneously.

Influence of Atomic Character

A contribution to the problem of the nature and extent of a relationship between catalytic activity and position in the periodic table (character of the metal bond) was submitted by Amano and Parravano (5) who used alumina-supported ruthenium, rhodium, platinum and palladium as catalysts in the vapour-phase hydrogenation of benzene. Catalytic activity was found to be in the order $Rh > Ru > Pt > Pd$; with the exception of palladium, this sequence is in accord with the behaviour previously established for compact metals and films.

Reforming Catalysts

In a paper dealing with the basic activity properties of reforming catalysts Weisz and Prater (6) attempted to correlate the two basic functional activities of dual-function catalysts to their performance in naphtha reforming. Catalyst samples of different platinum activity were prepared, and also

References

- 1 H. A. SMITH and R. G. THOMPSON A Study of the Catalytic Hydrogenation of Methoxybenzenes over Platinum and Rhodium Catalysts.
- 2 G. GILMAN and G. COHN The Action of Rhodium and Ruthenium as Catalysts for Liquid-Phase Hydrogenation.
- 3 W. M. ADEY and W. R. CALVERT The Preparation and Use of an Oxidation Catalyst Film for Non-Porous Supports.
- 4 J. R. ANDERSON and C. KEMBALL Catalytic Exchange and Deuteration of Benzene over Evaporated Metallic Films in a Static System.
- 5 A. AMANO and G. PARRAVANO The Vapour-Phase Hydrogenation of Benzene on Ruthenium, Rhodium, Palladium and Platinum Catalysts.
- 6 P. B. WEISZ and C. D. PRATER Basic Activity Properties for Pt-type Reforming Catalysts.
- 7 G. C. BOND and J. ADDY The Reaction of Cyclopropane and of Propane with Deuterium over Metals of Group VIII.

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those in which the activity of the support was varied by altering its composition. Catalytic reaction tests were devised for measuring each of these activities separately, and the results indicate that above a certain critical platinum activity the reforming power of the catalyst depends on the "acidic" activity provided by the promoted support.

Pumice-supported palladium, rhodium, platinum and iridium were used by Bond and

Addy (7) in an investigation into the reaction of cyclopropane and propane with deuterium. The order of activity for both reactions was found to be Rh > Pt > Pd; however this may have no basic significance since it was measured per unit weight of metal instead of per unit surface area. Preliminary results were obtained for iridium and its behaviour was expected to be closely similar to that of rhodium.

Cathodic Protection of Naval Vessels

In a paper on "Navy Experimental Work with Cathodic Protection" presented to the National Association of Corrosion Engineers (*Corrosion*, 1956, 12, 18-24), Irving D. Gessow describes the work done by the United States Navy Bureau of Ships on the cathodic protection of ships' hulls. Impressed current systems using graphite rod anodes are satisfactory for the external protection of inactive ships, and may increase the docking interval from five to seven or eight years.

No clear evidence is yet available as to the economic advantage of the general use of cathodic protection for active ships, but work has been concentrated principally on destroyers and submarines, where the pitting of plates may have serious consequences. Both sacri-

ficial and impressed current systems have been fitted; magnesium anode sacrificial systems are relatively heavy and require replacement in two years or less while impressed current systems with either graphite or platinum-clad anodes are lighter and more permanent but are higher in first cost. One destroyer and one submarine have been fitted with platinum-clad anodes. The submarine installation appears very successful; results from the destroyer installation were not available at the time the paper was prepared, but it is understood that an inspection of the destroyer after fourteen months of service showed that the anodes were clean and bright and apparently performing satisfactorily, while in general the hull was in excellent condition.

One of seven platinum-clad anodes installed on the hull of a destroyer. Each anode has a platinum sheath 0.005 inch thick on a silver alloy rod 50 inches long

