

Second International Congress on Catalysis

The growing importance of catalysis in the chemical industry has been recognised by the organisation of a series of International Conferences, the first being held in Philadelphia in 1956. At the second Conference, arranged in Paris in July by the Société de Chimie Physique and the Institut Français du Pétrole, over 600 representatives attended. This review deals with those of the papers describing work carried out with the platinum metals.

Of the 143 communications presented at this Congress, some sixty dealt with the adsorptive and catalytic properties of metals, the remainder dealing with metal oxides, acidic catalysts, and some aspects of homogeneous catalysis. Of these sixty, about one-third referred specifically to metals of the platinum group; it is clear that for many fundamental and applied studies, nickel is still the favoured metal, while a few papers dealt with the catalytic properties of iron, cobalt, copper and zinc.

The chemisorption of hydrogen and oxygen on platinum black was studied by Aston and his associates at 0°C and below (1): their technique of "thermal titration", which has recently been described in *J. Amer. Chem. Soc.* (23), involves the addition of hydrogen to a surface covered by oxygen, and *vice versa*, and the measurement of the subsequent heat changes. The adsorption of benzene on alumina-supported platinum reforming catalysts was studied by determining the response of the effluent composition to transient changes in the benzene-nitrogen or benzene-hydrogen feed gas; gas-liquid chromatography was used for this purpose (2).

Several papers were devoted to catalytic hydrogenation and related problems. One of the simplest conceivable systems, the exchange of one hydrogen isotope adsorbed on a metal with another in the gas phase, was studied by Borekov and Vassilevitch (3) using platinum films at low temperatures.

By observing the relative rates of hydrogenation of pairs of the xylenes over platinum in acetic acid, it was concluded that the order of the adsorption of the three isomers is: ortho > meta > para (4). The hydrogenation of derivatives of furan has been studied using platinum, osmium, iridium, ruthenium and rhodium, all supported on charcoal and using skeletal palladium and platinum (5).

Remarkable synergistic (co-operative) phenomena were observed when mixed palladium-ruthenium catalysts were employed for liquid-phase hydrogenation (6). Thus, for example, while neither 5 per cent platinum or ruthenium on charcoal is active for the hydrogenation of nitropropane, a catalyst consisting of 2.5 per cent of each metal was satisfactorily active. Similar results were obtained with nitriles and with pyridine. This synergistic effect was said to be due to the ability of one metal to hydrogenate an intermediate which would strongly adsorb on, and hence poison, the other.

In the hydrogenation of acetylene and its derivatives (7, 8), highly selective formation of olefins was achieved in the initial stages using alumina-supported palladium, and the reduction could be caused to stop entirely at the olefin stage by selective poisoning by dimethylsulphide (7) or mercury vapour (9).

The state of platinum in supported catalysts was the subject of several papers, which should be compared with those recently summarised in *Platinum Metals Review* (24).

In a typical alumina-supported reforming catalyst, the platinum was shown to be very highly dispersed (10), and evidence was adduced to show that the dehydrocyclisation activity of a related catalyst was associated with an irreducible platinum complex formed from chloroplatinic acid and the support (11). The corresponding palladium complex was rapidly reduced. The possibility of using silica-alumina molecular sieves, e.g. de-cationised Linde type Y, as supports for reforming catalysts was demonstrated (12). The kinetics of reforming processes were discussed (13), and the reactions of polymethylcyclopentanes over alumina-supported platinum were reported (14).

Gray and his associates (15) described the isomerisation of *n*-pentane over alloys of the platinum metals supported on eta-alumina; the combinations used were Pt-Rh, Pd-Rh, Pt-Ir, Pt-Ru, Os-Pt and Pt-Re. In most cases, an alloy of a certain composition showed an activity greater than that of either of the components separately; this composition corresponded to that having exactly one *d*-band vacancy per atom. The phenomenon, which was especially marked in the Pt-Ru system, is reminiscent of that described in reference (6), but the two are probably unrelated.

Three papers were devoted to catalytic

oxidation. The rearrangement of surface atoms during the oxidation of methane by air over incandescent platinum, 10 per cent Rh-Pt and 25 per cent Ir-Pt was demonstrated, and the suggestion made that the catalyst initiates some homogeneous reaction (16). Radioactive rare gas ions introduced into platinum by ion bombardment are released when the hydrogen-oxygen reaction is performed, again showing the rearrangement of surface atoms (17). The oxidation of carbon monoxide in the presence of palladium-gold alloys has been investigated (18); the activation energy is about 2 Kcal/mole⁻¹ for 100 to 60 per cent gold, and about 30 Kcal/mole⁻¹ for 60 to 0 per cent gold.

The activity sequence for some of the platinum metals in formic acid decomposition is (19):



This reaction has also been observed by infra-red spectroscopy to occur over supported platinum at -60°C (20).

Finally, attention should be drawn to two theoretical papers, one (21) emphasising the role of surface geometry, and the other (22) the importance of the latent heat of sublimation of the catalytic metal. It is very doubtful whether either approach by itself will materially assist the progress of the science of catalysis.

G. C. B.

References

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| 2 | R. C. Pitkethly and A. G. Goble .. | The adsorption of benzene on supported platinum catalysts |
| 3 | G. K. Borekov and A. A. Vassilevitch | Mécanisme de l'échange isotopique de l'hydrogène sur les dépôts minces de platine |
| 4 | H. A. Smith and C. P. Rader .. | Competitive catalytic hydrogenation of the xylenes on platinum |
| 5 | N. I. Chouikine and I. F. Belsky .. | Les transformations catalytiques dans la série furannique |
| 6 | P. N. Rylander and G. Cohn | Liquid-phase hydrogenations with platinum-ruthenium and palladium-ruthenium catalysts |
| 7 | W. M. Hamilton and R. L. Burwell, Jr. | Hydrogenation of dimethylacetylene on palladium catalysts |
| 8 | G. C. Bond, J. Newham and P. B. Wells | The selective hydrogenation of unsaturated hydrocarbons |
| 9 | G. C. Bond and P. B. Wells | The poisoning of a palladium catalyst by mercury vapour |
| 10 | G. A. Mills, S. Weller and E. B. Cornelius | The state of platinum in a reforming catalyst |

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| 11 | K. W. McHenry, R. J. Bertolacini, H. M. Brennan, J. L. Wilson and H. S. Seelig | The nature of platinum dehydrocyclisation catalyst |
| 12 | J. A. Rabo, P. E. Pickert, D. N. Stamiros and J. E. Boyle | Molecular sieve catalysts in hydrocarbon reactions |
| 13 | P. B. Weisz | Principles of polystep catalytic conversion and the transformation of hydrocarbons |
| 14 | F. G. Gault and J. E. Germain .. | Conversion des polyméthylcyclopentanes sous pression d'hydrogène sur des catalyseurs au platine |
| 15 | T. J. Gray, N. G. Masse and H. G. Oswin | Isomerisation catalysis with supported metal alloys |
| 16 | P. Bussière, P. Dévoré, B. Domanski and M. Prettre | Propriétés du platine incandescent et mécanisme des oxydations catalytiques à son contact |
| 17 | C. Jech | Release of radioactive inert gases from surface-labelled platinum during catalytic reactions |
| 18 | A. G. Daghish and D. D. Eley .. | The carbon monoxide-oxygen reaction on palladium-gold alloys |
| 19 | W. M. H. Sachtler and J. Fahrenfort | The catalytic decomposition of formic acid vapour on metals |
| 20 | R. P. Eischens and W. A. Pliskin .. | Infra-red study of the chemisorption and decomposition of formic acid |
| 21 | A. A. Balandin | On the theory of heterogeneous catalysis of hydrogenation and dehydrogenation reactions |
| 22 | G. C. A. Schuit, L. L. van Reijen and W. M. H. Sachtler | Regularities in the catalytic activities of metals |

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| 24 | | <i>Platinum Metals Rev.</i> , 1960, 4 , 92 |

SENSITIVE ELEMENTS FOR LEAK DETECTION

The sensitive elements, sometimes called Ozotron valves, manufactured by Associated Electrical Industries Limited, are devices for the detection of minute concentrations of halogen ions in the atmosphere. They take advantage of the unique property of a hot platinum surface of ionising halogens and their compounds.

The valve, which is open to the atmosphere, comprises an anode indirectly heated to about 800°C, surrounded by a cold cathode—both electrodes being made of platinum. A voltage of about 230 d.c. is applied between anode and cathode and in normal conditions a small standing current is passed by the valve. If, however, halogen or halogen compounds such as freon or trichlorethylene are present in the atmosphere, ionisation occurs at the surface of the anode and the ions produced flow across the cathode, thus appreciably increasing the current. Applications of this device are principally in leak detection. For example, a tank may be tested by filling it with a halogen gas. A fan is arranged to suck gas through the Ozotron, which is mounted behind a short nozzle. Should the tank leak at any point, halogens will be detected immediately the nozzle is brought to that point. The overall sensitivity of the equipment is such that it can detect one part of halogen per 1,500,000 parts of air.

