

Third International Congress on Catalysis

THE ROLE OF THE PLATINUM METALS IN HETEROGENEOUS CATALYTIC REACTIONS

The Third International Congress on Catalysis, organised most efficiently by the Royal Dutch Chemical Society, took place in Amsterdam from July 20 to 25. It was attended by 828 active members from 31 countries including 141 from the USA, 29 from the USSR, and 115 from Great Britain. Of the ninety-eight papers presented, twenty-seven refer to the use of the platinum group metals as catalysts, and these are reviewed here.

In order to restrict the scope of the meeting, two themes had been selected by the organising committee: these were (i) Selectivity in Catalytic Reactions, and (ii) the Molecular Description of Catalytic Reactions. In addition to a full programme of discussion of the papers, there were six general lectures that covered some of those aspects of catalysis not included in the main themes. Two of these lectures of particular interest to those working with the platinum metals were those by Professor R. S. Nyholm on the structure and reactivity of transition metal complexes and by Professor J. Halpern on developments in homogeneous catalysis.

The proceedings of the Congress will be published by the North Holland Publishing Company, Amsterdam.

For the purpose of this short review, the papers of greatest interest have been classified under the headings: (i) Catalytic Reforming, (ii) Aromatic Ring Reduction, (iii) Reduction of Other Unsaturated Groups, and (iv) Miscellaneous Processes.

Catalytic Reforming

Six papers were concerned with catalysts for the reforming of hydrocarbons and the related mechanisms of reactions. J. A. Rabo, V. Schomaker and P. E. Pickert, of Union Carbide, described a technique for ion-

exchanging a calcium Y zeolite with $[\text{Pt}(\text{NH}_3)_4]^{2+}$ to give after reduction a Pt content of $\frac{1}{2}$ per cent. This catalyst was resistant to poisoning by thiophen. The same zeolite on impregnation with H_2PtCl_6 to give after reduction the same Pt content was rapidly poisoned by thiophen. They concluded that the Pt in the former catalyst was atomically dispersed.

Another novel procedure was described by A. G. Goble and P. A. Lawrance of the British Petroleum Company Ltd. These authors showed that treatment of a $\text{Pt}/\text{Al}_2\text{O}_3$ catalyst with carbon tetrachloride vapour at 300°C resulted in the chlorination of surface hydroxyl groups, and that the resulting catalyst could isomerise n-hexane even at room temperature with remarkably high selectivity.

H. J. Maat and L. Moscou (Ketjen N.V.) showed that increasing the platinum crystallite size by sintering led to a decrease in dehydrocyclisation activity, accompanied by an increase in isomerisation activity. V. Haensel, G. R. Donaldson and F. J. Riedl of Universal Oil Products, reported that methylcyclopentene was a primary intermediate product in the conversion of methylcyclopentane to benzene over $\text{Pt}/\text{Al}_2\text{O}_3$, and that cyclohexene could be detected in the dehydrogenation of cyclohexane to benzene at high space velocities. Its yield was greatly increased on

partially poisoning the catalyst with tert-butyl mercaptan. Kh. M. Minachev and G. V. Isagulyants (U.S.S.R.) were however unable to detect cyclohexene in the dehydrogenation of cyclohexane over Pd/Al₂O₃ at 480°C. S. Khoobiar, R. E. Peck and B. J. Reitzer, of the Illinois Institute of Technology, studied the kinetics of cyclohexane dehydrogenation over Pt/Al₂O₃ in an isothermal reactor, and they suggested that although reaction was initiated on the catalyst pellets it was probably propagated on the surface of the added 'inert' alumina.

Aromatic Ring Reduction

Five papers were devoted to the problem of the mechanisms of the hydrogenation and exchange of benzene and its methyl derivations over the platinum group metals and emphasis here also was on the role of olefinic intermediates.

S. Siegel and V. Ku (University of Arkansas) have detected them during the liquid-phase hydrogenation of the xylene isomers: concentrations varied between 0.02 and 0.7 mole per cent. They conclude that virtually every saturated molecule formed passes through the desorbed olefin stage. F. Hartog, J. H. Tebben and C. A. M. Weterings, of Dutch State Mines, studied the hydrogenation of benzene over platinum, palladium and ruthenium catalysts, using both hydrogen and deuterium, with full product analysis in the latter case. They concluded that C₆X₆ and C₆X₇ species (X=H or D) were common intermediates for both hydrogenation and exchange, and that cyclohexene was an intermediate, but even in the most favourable case, which is ruthenium, only about 1 per cent desorbs from the surface. The paper presented by R. J. Harper and C. Kembell (The Queen's University, Belfast) dealt with the exchange and hydrogenation of p-xylene over films of platinum, palladium and tungsten. Exchange of the methyl groups was the most rapid process, followed by the slower ring exchange and hydrogenation processes. No olefinic intermediates were

detected in this work. H. A. Smith and W. E. Campbell, of the University of Tennessee, measured the rates of reduction of benzene and a series of methylbenzenes alone and in competition over Rh/Al₂O₃, and from their results were able to calculate the relative strengths of adsorption of the molecules.

K. Hirota and T. Ueda (Osaka University) observed that in the exchange of p-xylene with D₂O, platinum and palladium catalyse the exchange of both ring and methyl hydrogens; iridium, ruthenium and rhodium do so less efficiently, while nickel and cobalt can only exchange the methyl hydrogens.

Reduction of Other Unsaturated Groups

Comparatively few papers were devoted to the hoary old problem of the mechanism of the hydrogenation of olefins catalysed by the platinum group metals. J. Turkevich, F. Nozaki and D. Stamires (Princeton University), in what was widely agreed to be one of the most impressive papers of the Congress, examined the electron spin resonance of Pd/Al₂O₃, and on this basis proposed a donor-acceptor model for catalytic hydrogenation. J. L. Carter, P. J. Lucchesi, J. H. Sinfelt and D. J. C. Yates (Esso Research and Engineering Co) studied the hydrogenation of ethylene over Pt/Al₂O₃ and concluded that migration of active intermediates occurred between the Pt and Al₂O₃ centres. G. V. Smith and J. A. Roth (Illinois Institute of Technology) investigated the addition of deuterium to dimethylitaconate and its isomers, and obtained evidence for an intramolecular hydrogen transfer. G. C. Bond and J. S. Rank (Johnson Matthey and Co Ltd) showed that the rate of double-bond migration in 1-pentene relative to its rate of hydrogenation was similar for palladium on a number of supports, and for Pd/C in a number of solvents. They also studied the liquid-phase hydrogenation of the pentynes and pentadienes using platinum, palladium, ruthenium, rhodium and iridium catalysts, and obtained product distributions. J. J. Phillipson, P. B.

Wells and D. W. Gray, of the University of Hull, studied the gas-phase hydrogenation of 2-butyne using platinum, rhodium and iridium supported on alumina, and discussed reaction mechanisms in detail.

Miscellaneous Processes

Two interesting papers concerned the mechanism of the hydrogen-oxygen reaction. V. Ponec, Z. Knor and S. Černý (Czechoslovak Academy of Science) followed the chemisorption of hydrogen and of oxygen, and their interaction, on films of rhodium, palladium, nickel and molybdenum by electrical conductivity changes. S. Z. Roginsky (Institute for Chemical Physics, Moscow) summarised a great deal of published work, chiefly concerning the isotope effect in this reaction.

J. R. Anderson and N. J. Clark, of the University of Melbourne, studied the reactions of hydrogen cyanide on evaporated films of platinum, palladium and a number of other metals. Kobozev, Krilova and Shashkov, of the Moscow State University, investigated

the exo-electron emission of platinum on several supports: this novel and simple technique merits further application.

Conclusions

The limitations imposed by the organisers of the Congress on its scope resulted in an overall impression of a strong 'academic' flavour: only the general lecture by Professor Borekov on the theoretical bases of selection, preparation and use of industrial catalysts served partially to restore the balance. In the papers reviewed here, there were two recurrent themes, first, the detection and description of reaction intermediates, using a variety of techniques and approaches, and secondly the role of the support, with particular reference to the possible activation of the support by the metal, for which concept there is now much indirect evidence. It remains to be seen to what extent these issues are clarified before the next Congress, which it is hoped will be held in the Soviet Union in 1968.

G. C. B.

Effect of Rhodium on the Gold-Platinum System

Those gold-platinum alloys used for the manufacture of spinning jets in the production of viscose rayon have for many years been modified by small additions of rhodium, which appeared to broaden the miscibility gap and assist age-hardening. A recent X-ray study by Raub and Falkenburg (1) has shown that approximately 2 atomic per cent of rhodium completely eliminates the gold rich solid solution which normally contains 20 per cent or more of platinum. Although rhodium also reduces the solubility of gold in platinum, the effect is not so pronounced, and platinum rich solid solutions extend right across to the rhodium corner of the diagram.

Although Raub had earlier predicted the basic instability of the rhodium-platinum solid solutions it was found that heat treatments extending up to four years at 600°C failed to produce any evidence of separation. The binary gold-rhodium system was also examined. At the peritectic temperature of 1068°C saturation concentrations of the

terminal solid solutions were found to be 1.5 atomic per cent of rhodium and 0.3 atomic per cent of gold.

In 1951, Grube, Schneider and Esch (2) attributed some additional lines on the diffraction pattern of a gold rich gold-platinum solid solution to an ordering reaction based on the Au-Pt composition. No other workers have hitherto detected these lines. Raub and Falkenburg, however, developed similar "sideband" structures simply by annealing the alloys for 1,000 hours in the solid solution region. The lattice parameter of this additional face-centred cubic phase increased rapidly with platinum content. This behaviour cannot easily be explained by an ordering reaction and will require further investigation.

A. S. D.

References

- 1 E. Raub and Günter Falkenburg, *Z. Metallkunde*, 1964, **55**, (7), 392-397
- 2 G. Grube, A. Schneider and M. Esch, *Heraeus Festschrift*, 1951, 20