

The Surface Properties of the Platinum Metals

A REVIEW OF THE SECOND SURFACE SCIENCE CONFERENCE

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An international conference on surface science was held at the Cavendish Laboratory, University of Cambridge, in March. More than ninety papers were presented, covering a very broad range of topics in surface science. This review concentrates only on those contributions particularly concerned with the platinum metals.

Surface science is a rapidly developing field and the organisers of the Second European Surface Science Conference (ECOSS 2) faced an unenviable task in whittling down the 300 submitted papers to a manageable number for consecutive presentation at a four-day meeting. Nevertheless, the conference succeeded admirably in its aim to "stress novel topics in the physics and chemistry of surfaces from both a fundamental and a technological point of view".

In his opening address, Professor David Tabor of the University of Cambridge gave a general historical survey of surface phenomena, from the earliest records of Babylonian times to the most sophisticated experimental probes of the present day. In addition he discussed some of the rather elusive factors that determine the areas of academic research and the fashions which encourage one area in preference to another. The present sub-discipline of Surface Science concentrated too exclusively, he thought, on the clean solid surface and on solid-gas interactions, and he called for more attention to be paid to solid-solid and solid-liquid interactions.

Professor G. A. Somorjai, of the University of California, Berkeley, reviewed the many surface science techniques which are taking catalysis from the realm of empiricism to that of high technology. Somorjai's group at the

Lawrence Berkeley Laboratory has developed special instrumentation to couple the low pressure environment necessary for the application of most of these techniques to the high pressure conditions essential for practical catalysis. Different reaction mechanisms via short-lived intermediates become possible in an industrial reactor as opposed to a high-vacuum experimental chamber. Model studies using well characterised surfaces have revealed the special importance of surface irregularities (steps, kinks and point defects) where heats of chemisorption may be a factor of two different from the clean surface. Examples from hydrocarbon conversion and carbon monoxide hydrogenation reactions demonstrated the high bond-breaking activity of kink sites on platinum, and Somorjai demonstrated the power of selectively blocking different types of irregularities with surface additives to control the rate and product distribution of surface reactions.

The theme of co-adsorption was extended by R. J. Madix of Stanford University. Madix has examined the effects of adsorbed sulphur, carbon and oxygen on the adsorption and reaction of CO, H₂, CH₃OD, H₂CO and HCOOH on a platinum surface. These surface reaction modifiers generally weaken the chemical interactions of the adsorbate with the surface, resulting in lower binding

energies of the molecular species. In contrast, less reactive metals, such as copper and silver, show pronounced enhancement of surface bonding due to adsorbed oxygen.

E. Umbach and his co-workers at the Technische Universität, München presented a multimethod study of the adsorption states of NO on ruthenium (001). The methods included measurements of photoemission spectra, work function changes, thermal desorption and low energy electron diffraction. The various molecular and dissociated adsorption states, their regions of existence and their interconversion have been investigated. The results are quite similar to the behaviour of CO on tungsten (110).

Vibrational Techniques

Several papers described vibrational spectroscopic methods for surface studies. The applications of i.r. ellipsometric spectroscopy were reviewed by M. J. Dignam, University of Toronto. Different vibrational peaks characterise different adsorption sites of CO on a platinum surface, and sometimes even the number of adjacent CO molecules may be identified from the vibrational frequency. In the complementary technique of high resolution electron energy loss spectroscopy, reviewed by H. Ibach of KFA Jülich, vibrational energies are detected from the energy loss of scattered electrons; information about the adsorption site is provided by the number and symmetries of energy-loss modes and A. M. Baro, also from Jülich, demonstrated the application to hydrogen on platinum (111).

The interaction of CO with rhodium was reported by A. Leger and his colleagues from Paris, using yet another vibrational technique, inelastic electron tunnelling spectroscopy. This is similar to Ibach's method, but instead of scattering electrons directly off a metal surface one looks for excitations of a molecular sample in an insulating barrier between two metals. The inelastic energy loss of electrons tunnelling through the barrier shows up as a sudden change in gradient of the

current versus voltage curve at the onset energy.

T. E. Madey and his co-workers at the National Bureau of Standards and at the Fritz-Haber Institute in Berlin reported electron stimulated desorption ion angular distribution (ESDIAD) experiments to verify the bonding configuration of CO on the rather open palladium (210) surface. The relative yields of O⁺ and CO⁺ ions are sensitive to the bonding mode and indicate that at low coverages bridge-bonding can occur between palladium atoms in the first and second layers, so that the axes of adsorbed CO molecules are inclined away from the surface normal by about 18°.

Atomic and molecular beam scattering experiments were reviewed by G. Ertl of the Institut für Physikalische Chemie, München. The dynamics of reactive and non-reactive scattering of (electronic ground-state) gases from solid surfaces provide information on the sticking probability and mean surface residence time, as well as on the kinetics and mechanism of heterogeneous catalytic reactions. Ertl discussed in particular the interactions of CO and O₂ with palladium and platinum surfaces. He also introduced as a new surface spectroscopic tool the electron emission accompanying the scattering of electronically excited species at metal surfaces; for example the electron energy distribution following bombardment of a CO covered palladium surface with excited helium atoms allows identification of the valence levels of the adsorbate, just as in photoemission spectroscopies.

T. Engel, of I.B.M. Zürich, reported molecular-beam relaxation and isotopic exchange experiments which show that the water formation reaction between hydrogen and oxygen molecules on palladium (111) proceeds via a Langmuir-Hinshelwood mechanism. The rate-determining step is OH formation from adsorbed oxygen and hydrogen atoms. In an excess of hydrogen the kinetics are dominated by the transport of atomic hydrogen between the bulk metal and the surface; in excess oxygen, diffusion of

hydrogen into the bulk is blocked by adsorbed oxygen, and the reaction rate is reduced.

Several papers were concerned with the detailed atomic arrangement at clean surfaces of platinum group metals. G. Comsa, of KFA Jülich, has scattered helium atoms from a clean platinum surface cut at a small angle to the (111) plane and found direct evidence for an upward bending of the terrace planes of atoms in the vicinity of the downward steps. J. Küppers, München, described work on the recrystallisation of the iridium (100) surface into a (5×1) superlattice while G. Allan, Lille, reported theoretical studies of the atomic relaxation at a platinum surface.

Two papers recorded quantum mechanical

calculations of the interaction between platinum and chemisorbed species. D. W. Bullett and E. P. O'Reilly of the Cavendish Laboratory described theoretical studies to compare and contrast CO chemisorptive bonding at surfaces with the bonding of CO to metal atoms in cluster carbonyl molecules such as Pt₃(CO)₆ and Os₆(CO)₁₈. Embedded cluster calculations to model the chemisorption of hydrogen on palladium and platinum were presented by J. P. Muscat of Imperial College.

The proceedings of ECOS 2 will be published by North Holland in a special issue of *Surface Science*, and the third European Conference on Surface Science will be held in Cannes in September 1980.

The Future Availability of the Platinum Metals

Civilisation as we know it today is highly dependent on the use of metals that exist only in finite amounts, and which therefore must be used in a responsible way. In recognition of this fact a conference entitled Future Metal Strategy, organised by The Metals Society, was recently held in London to provide an international forum for the discussion of many of the vital factors that may influence the supply and utilisation of a number of the more important metals during the next twenty years. In one of the papers, by Dr. J. E. Hughes, Deputy Managing Director of Johnson Matthey & Co Limited, Dr. G. J. K. Acres, Manager of the Johnson Matthey Research Centre, and Miss M. T. Herbert, the future supply and demand situation for the platinum group metals was reviewed.

The authors explained that over 98 per cent of the world's output of the platinum group metals is obtained from just three countries, South Africa, Canada and the U.S.S.R., while no less than 65 per cent of the total output of platinum alone is mined from the Merensky Reef of the Bushveld Igneous Complex in South Africa. Existing reserves, that is the known deposits at present being mined, are believed to contain sufficient platinum to last for some 150 years.

When considering both the present and the future availability of the platinum group metals it is most important to remember that

the amounts of palladium, rhodium, iridium, osmium and ruthenium mined are directly proportional to the output of platinum in the case of the South African production, or of nickel in the case of Canadian and Russian material. This is because at present prices it is not economic to mine for them as principal products. The current production of platinum group metals from the Merensky Reef is approximately 93,000 kilograms per year, the composition including: platinum 60, palladium 25 and rhodium 4 per cent.

In addition to the platinum deposits of the Merensky Reef, platinum group metals also occur at two other horizons in the Bushveld Igneous Complex. These are the Upper Chrome Group and the Platereef, and although they are largely unexplored and unmined it is estimated that, if the metals can be extracted economically, the total resources could then last for 400 years.

The usefulness of the platinum group metals to industry is based on their unique properties, including catalytic activity, high melting points and chemical inertness over wide ranges of temperature. Existing and future applications include such topical areas as energy generation and conservation, fertiliser production and pesticide manufacture, pharmaceutical preparation and anti-cancer therapy, the control of noxious emissions and the cathodic protection of ships and other steel structures.