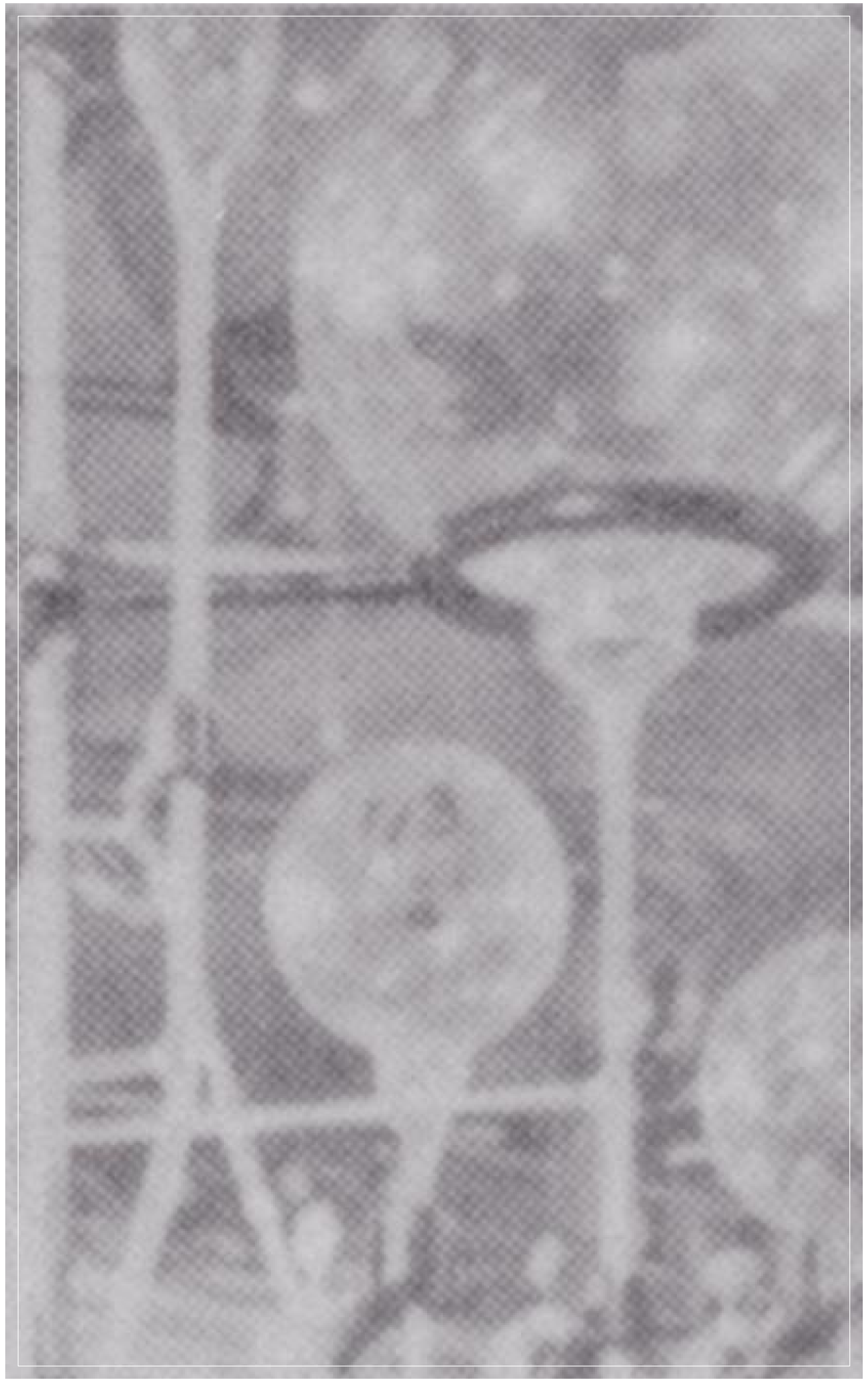


(1945 - 1965)

The impact of surface physics and the emergence of new experimental methods

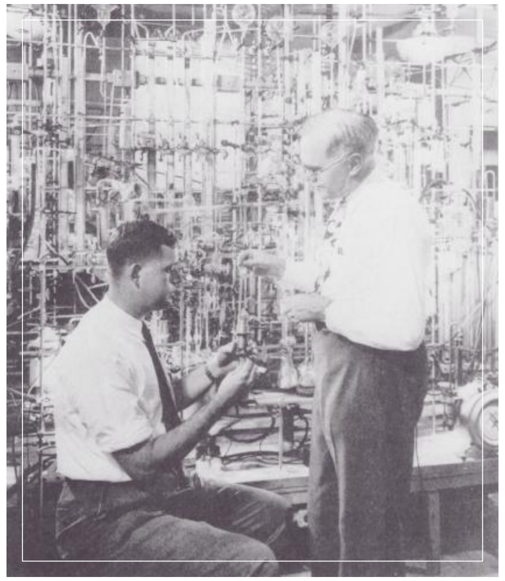
“What scientists are really after is the adventure of discovery itself”

Sir Cyril Hinshelwood

“Although catalysis is a very old art and a fairly old science, until the latter part of this century it has functioned as a part of various branches of chemistry, physics and engineering”. This was the view of Heinz Heinemann in 1983 who also indicated that “the first international meeting primarily devoted to catalytic research was held in Liverpool by the Faraday Society in 1950”. Regular research conferences on catalysis had, however, been held in the USA since 1943 and in 1949 a group of seven scientists Farkas, Ciapetta, Hansford, Heinemann, Kennedy, Krieger and Oblad started the Catalysis Club of Philadelphia and among the first speakers were Dennis Dowden, Paul Emmett and Otto Beeck.

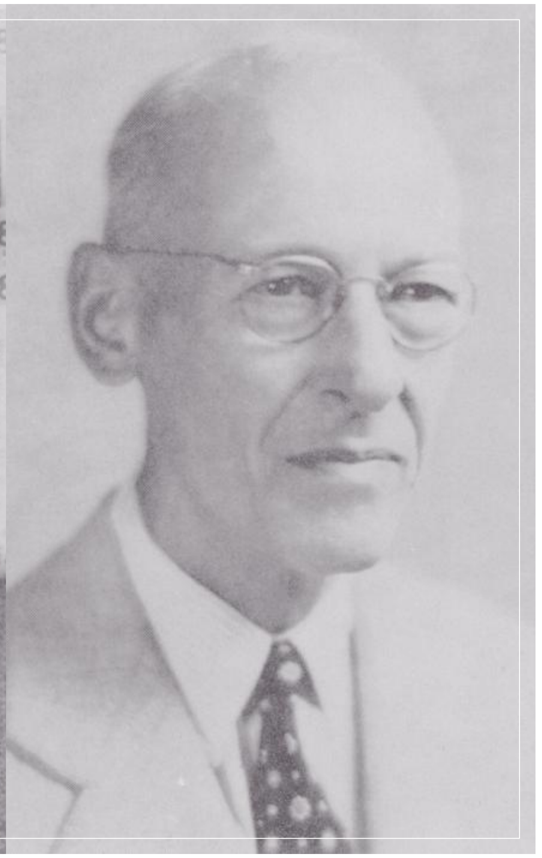
There was a need to obtain a more direct handle on surfaces species which led Mignolet, Tompkins and Pritchard using changes in work function to study both physical and chemisorption. But the biggest breakthrough came from the application of infrared spectroscopy to study the chemisorption of carbon monoxide at metal surfaces. It was mainly through developments by Eischens and his group at the Texaco Research Laboratories in the USA and Terenin in Russia that vibrational spectroscopy emerged in the 1950s as one of the most important experimental methods in surface catalysis. Low Energy Electron Diffraction as a means of studying the role of surface structure became a viable experimental method through the developments of Germer and Farnsworth, although the experiments of Davisson and Germer in 1927 which established the wave-nature of the electron had already shown its potential as a structural tool. In the United Kingdom Pitkethly’s group at the B.P. Laboratories at Sunbury on Thames and Mason in Sussex were some of the first to apply LEED to the study of surface catalysed reactions.

My introduction to surface catalysis was in 1952 when the problem I was asked to address by my Ph.D. supervisor, K.W. Sykes a student of Hinshelwood’s, was the role of sulphur in catalysing the formation of nickel carbonyl. Not surprisingly I was funded by the Mond Nickel Company later to become the International Nickel Company. Was the sulphur participating in an electronic mechanism or was the catalysis occurring via an intermediate compound?, two conflicting views of catalysis at that time. However, by the very nature of the problem I was “forced” to consider how to ensure that the nickel surface was well defined which brought me to consider the concept of atomically clean metal surfaces and their associated chemistry. In September



Paul Emmett & J.T. Kummer at the Mellon Institute

Otto Beeck



L.H. Germer

1952 a conference was held in Wisconsin the report of which was published in 1953 with the title of "Structure and Properties of Solid Surfaces" edited by Gomer and Smith. There were three articles that left a particular impression on me - the first was by Boudart 'Surface structure from the standpoint of chemisorption and catalysis', the second 'Physical and Chemical Adsorption of Gases on Iron Synthetic Ammonia Catalysts' by Emmett and the third 'Chemisorption on Solid Surfaces' by Wheeler (who was a co-author of Otto Beeck's paper published in 1940). In Wheeler's paper he emphasised the earlier work of J.K. Roberts in 1935 on metal filaments and the studies in the Physics Laboratories at Shell in Emeryville. In particular he drew attention to what were clear differences in chemical reactivity between practical catalysts and what he termed 'clean' metal surfaces. He highlighted the questions that needed to be addressed: the electronic structure of the metal surface; why was hydrogen dissociatively chemisorbed below liquid-air temperatures; is an adsorbed H-atom ionized or not?; the role of surface defects; the nature of slow adsorption on practical bulk catalysts; the need to address surface mobility of metal atoms themselves; rates of adsorption and desorption. In response to Wheeler's paper Becker, of Bell Telephone Laboratories, described 'a new technique by which one can determine the sticking probability of gases sticking on surface as a function of the coverage'. It was indeed the 'flash filament method', later exploited most elegantly by Ehrlich at the General Electric Laboratories in Schenectady, and which later became more widely known as 'temperature programmed desorption' (TPD).

The 1950s saw the rapid growth in surface physics stimulated by the development of the semiconductor industry. Otto Beeck, as early as 1945, had published in Reviews of Modern Physics his paper 'Catalysis - A Challenge to the Physicist' which concluded with the following:

'There seems to be no doubt that the basic problems of heterogeneous catalysis cannot be solved without the closest attention to the physics of the solid state, especially with regard to structure, energy and entropy of the surface'.

With the passage of over half-a-century how do we now view this advice?; Was is followed?; Was it dismissed?; Or was its significance not appreciated? There was an acute awareness of the need to develop ultra-high-vacuum techniques, the preparation of well defined surfaces and the need to be able to characterize them. The state of thinking at that time is well illustrated by the Conference on the Physics of Semiconductor Surfaces held at the University of Pennsylvania in 1956 the proceedings of which were published by the Oxford University Press in 1957 and edited by R.H. Kingston. A paper by Weisz points out the common ground between the physicist and the chemist in connection with the electron exchange process that occurs when molecules are adsorbed, while Hauffe and Schwab discuss the theoretical and experimental aspects of catalysis on semiconductor surfaces. Metal oxidation and the role of oxide overlayers is discussed by Cabrera - a co-author with Mott of the theory of oxidation paper published in 1948. Central to the Cabrera-Mott theory is the role of the field present at the metal-oxide interface lowering the barrier to metal diffusion resulting in oxide growth. The surface potential of chemisorbed oxygen is the source of the field and this stimulated work function studies of oxygen chemisorption and the growth of thin oxide films with questions raised as to the nature of thin oxide films and whether they simulated bulk oxides. This had significant relevance to the understanding of the reactivity of chemisorbed oxygen and oxides in heterogeneous catalysis and to probing further the reconstruction of metal surfaces in the presence of chemisorbed oxygen by studying the energy of electrons emitted in photoemission experiments. In his Inaugural Lecture at Imperial College, "Superficial Chemistry and Solid Imperfections" in 1960, F.C. Tompkins, Secretary and Editor of the Faraday Society, said:

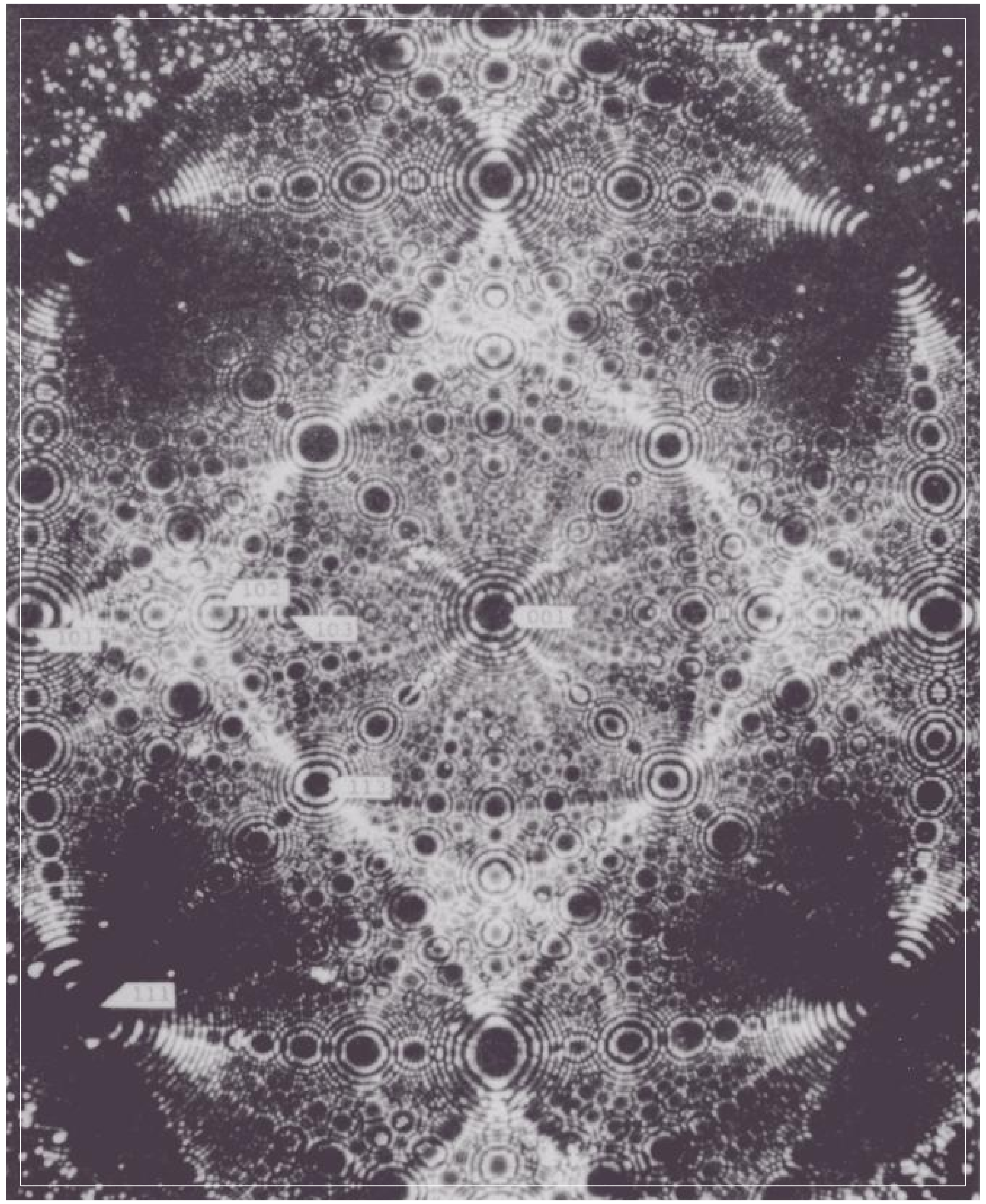
"Catalysis remains the fascinating meeting ground of little real knowledge and much valuable experience - it is a phenomenon, an art, but scarcely a science... it involves various disciplines of science and diverse scientific principle; this is its challenge and its fascination".

Although meant to stimulate discussion, views such as this did not always promote the subject in the United Kingdom but support from industry, and the Science Research Council through various initiatives, ensured that research in universities continued at a reasonable level. The Royal Society of Chemistry also set up in 1973 the Surface Reactivity and Catalysis (SURCAT) Group with Whan as its first Secretary and the author its Chairman and a new series: 'Surface and Defect Properties of Solids' published by the Royal Society of Chemistry with Thomas and the author as Editors provided a focus on the solid and its surface but with some attention also given to catalysis. Two symposia held in the mid 1960s which reflect the development of physics based techniques for understanding surface reactivity and catalysis are Discussions of the Faraday Society meeting "The role of the adsorbed state in heterogeneous catalysis", held at the University of Liverpool and the symposium on "The Structure of Surfaces" held in North Carolina. We see in the Faraday Meeting articles by Ehrlich, Holscher, Sachtler and Moss on field electron and field ion emission, Gomer on the role of potassium in controlling adsorption states on tungsten, Hayward and Tompkins on chemisorption sticking probabilities, Brennan on heats of adsorption, Eley and Norton on para-hydrogen conversion, Roberts on the significance of photoemission and work function studies in the nickel-oxygen system, Boreskov, Cimino, Teichner, Schuit, Wells, Kemball, Bond and Peri on aspects of heterogeneous catalysis, and Rabo on zeolites which have been modified by cation insertion. It was at this Discussion that I emphasised that the photoelectron escape depth was no more than about 10Å first published with Quinn in 1965 and which was the stimulus to pursue Siegbahn's work and develop photoelectron spectroscopy as an approach to study chemisorption and catalysis at metal surfaces. Schlier and Farnsworth described how they had applied low energy electron diffraction (LEED) to the study of clean germanium surfaces prepared by ion-bombardment. The need to "understand the properties of semiconductor surfaces through experimental work on clean and controllably contaminated surfaces" was the driving force for their work and as a consequence the development of ultra-high vacuum production and measurement. However, LEED in 1956 was experimentally tedious and time consuming, in that a large number of "diffraction points" had to be searched for measuring the current as a function of collector angle for a fixed electron beam current and energy, the process being repeated for other beam energies and other azimuths. It was nearly 10 years before the development of a direct visual display of the diffraction pattern became commercially available. This was largely due to the genius of Germer and MacRae at the Bell Telephone Laboratories who described in 1961 in The Robert Welch Foundation Bulletin a "New Low Energy Electron Diffraction Technique Having Possible Application to Catalysis". This article was based on a lecture Germer had given under the Robert A. Welch Foundation at the Texas Christian University, Fort Worth, Texas. Germer had of course been involved with the first experiments with Davisson in 1927 in establishing the wave nature of the electron. The possibility of determining the structure of adsorbates at metal surfaces attracted the attention of surface chemists (including crystallographers, Mason at Sussex) and industrial research laboratories, such as the B P Laboratories at Sunbury on Thames, where they invested in LEED systems with Edmunds, McCaroll and Pitkethly interpreting the complex patterns observed for sulphur chemisorbed at Ni(111) surfaces in terms of domain and coincidence lattice structures. The field of chemisorption and catalysis had been changed over-night! Surface structure was now an area where progress was possible using the scattering of low energy electrons. The approach had three main advantages: the penetrating power of "slow" electrons is very small so that the information they carry refers exclusively to the surface layer(s); their wavelength is of the same order of magnitude as the interatomic spacings so that diffraction provides surface structure information and thirdly the inelastically scattered electrons provide, through the Auger process, chemical analysis of the surface. At this stage new LEED patterns were assumed to reflect metal reconstruction, adsorbates being regarded as not effective scatteres of low energy electrons. This was not correct.

I could not help but perceive that there was slowly developing two cultural approaches to a fundamental understanding of heterogeneous catalysis. It was indeed central to my Ph.D. problem, should I study the kinetics of nickel carbonyl formation or should I be more concerned about the nature of the nickel surface? Plank of the Mobil Oil Co in 1982, reflecting on his long career in the oil industry, made his view very clear: "Industrial catalysis is the science of dirty surfaces". So what should be the fundamental approach to understanding heterogeneous catalysis?, it is a question that even today has no unequivocal answer but clearly it is an area of science that needs inputs from all possible sources: theory; new experimental developments; modelling; and real or applied catalysis.

It is quite remarkable when one reflects on how well heterogeneous catalysis had developed between the two world wars, when the ability to analyse the gaseous products was extremely tedious and there was no means available to determine the composition of the catalyst surface. It was very much the age of kinetics and the adsorption isotherm enabling one to relate surface coverage and gas pressure, with the Brunauer Emmett Teller theory playing an important part.

In 1948 the oil fields of Arabia had been discovered but their potential had not been realised - indeed at that time there was a fear of a worldwide oil shortage and one of Texaco's major projects was in the production of synthetic fuels by the Fischer-Tropsch reaction. The chemisorption of carbon monoxide at iron surfaces was the topic given to Eischens when he joined the Texas Company at Beacon (later to be known as Texaco) and in particular he was to explore the feasibility of using infrared spectroscopy. He was indeed fortunate in that it was in the chemistry of carbon monoxide that Texaco was interested - it had a high absorption coefficient in the infrared! - although ammonia was the first to be investigated. The question to be resolved was whether cracking catalysts' acidity was due to Lewis or Bronsted sites and with Mapes a paper was published (J. Phys. Chem. in 1954). The Perkin-Elmer Model 12 instrument was used and as success was achieved, it



Platinum image (He, 21 °K) after Z. Knor and E. W. Müller encouraged Eischens with Pliskin to investigate the CO-iron system. The idea of supporting metal particles on high surface over silica (cabosil), which was a good transmitter of infrared radiation, proved successful and CO absorption bands reported (J. Chem. Phys. 1954, 22, 1786) for chemisorption on copper, platinum, nickel and palladium. It was concluded that 'carbon monoxide is chemisorbed as a molecule and bonded to the metal through the carbon appears to be confirmed by the spectra'. The broadness of the bands in some cases (e.g. Ni and Pd) were suggested to indicate differences in bonding from that with platinum where the absorption band was very narrow.

A significant advance in catalytic research also took place at about this time with the development of the mass spectrometer for analysing the gas phase. One of the first studies was that of Kemball and Taylor who investigated the catalytic decomposition of ethane and ethane-hydrogen mixtures over a 15% nickel supported on kieselghur. While the mass-spectrometer (with gas chromatography) was to become over the next 20 years probably the most important experimental tool to be used in heterogeneous catalysis, and for Kemball's immense contribution through H_2-D_2 exchange studies, infrared spectroscopy was to be confined mainly to the study of carbon monoxide where its high extinction coefficient enabled it to be studied at the sub-monolayer level. Although the transmission method was the initial approach, using high surface area silica as a support, it was later replaced by the reflection-absorption technique, found to be in the 1970s so advantageous for investigating adsorption at single crystal surfaces.

Understanding bonding and charge-transfer process was realised to be fundamental to the understanding of chemisorption. Surface potential (change in work function) measurements were described by Mignolet in Liege and Tompkins in London while Selwood at Northwestern University described an apparatus for the simultaneous measurement of gas adsorption and the change in magnetization that occurs when hydrogen is chemisorbed on a nickel catalyst. Results were reported for the direction of electron transfer during adsoprtion by both approaches. This was in 1956 and reflected the thinking at the time, namely that it was essential to obtain, by whatever means, direct experimental information on the nature of the surface bond in chemisorption. In the same year a conference on 'Chemisorption' was held at the University of Keele where again there was emphasis on linking our understanding of the solid state and catalytic reactivity under the following five sub-headings: theory of chemisorption; chemisorption on insulators, metals, semiconductors and carbon. There were contributions from Dowden, Grimley, de Boer, Schuit, Eley, Trapnell, Bond, Suhrmann, Tompkins, Mignolet, Winter and Stone all of whom were, or would become, leaders in fundamental aspects of chemisorption and catalysis.

There is no doubt, however, that it was the emergence of infrared spectroscopy that was to make the greatest impact in the understanding of chemisorption and catalysis in the 1950s. In 1958 Sheppard wrote

"Infrared spectroscopy is unique among the spectroscopic methods of determining molecular structure in that it can be used to study compounds in all the state of matter - gas, liquid and solid - with comparable ease in each case. As a result it is the first of these methods to be used extensively to study the structure of molecules adsorbed on surfaces".

Sheppard discussed two areas of application: (a) physical adsorption on high area silica and (b) the chemisorption of carbon monoxide of carious metals supported on silica. The first successful infrared experiments on adsorbed molecules had been reported much earlier in 1949 by Yaroslavsky and Terenin and Kurbatov and Neumin in Russia where porous glass was a favoured adsorbent.

The first direct information on chemisorption, as mentioned earlier was in 1954 by Eischens, Francis and Pliskin. In the case of copper and platinum CO gave sharp bands at 2130 and 2070cm^{-1} respectively and assigned to chemisorbed molecules present in the linear state ((i) below)

whereas much broader and weaker bands at 1800cm^{-1} were attributed to bridged bonding (ii) by analogy with the spectra of gaseous metal carbonyls. At about the same time (1958) Sheppard with Yates and Little at Cambridge had embarked on studies of hydrocarbons chemisorbed on both metals and oxides.

In 1965 Eischens with Hammaker and Francis using dipole-dipole interaction arguments attempted to rationalise shifts in CO absorption bands with changes in surface coverage to surface heterogenity. The conclusions were not unambiguous and for this reason they studied intensity data from the co-adsorption of $C^{12}O$ and $C^{13}O$. This was developed further to explore which crystal faces were preferentially exposed on supported palladium catalysts.

`It was in the 1950s that Erwin Müller invented the field ion microscope and an image of the (III) plane of tungsten obtained with such a microscope is shown in the figure. Information concerning the behaviour of individual surface adatoms, particularly of their diffusional behaviour, was first obtained through the field ion microscope. Tungsten and rhodium have been most extensively studied with Ehrlich, initially at the General Electric Laboratories at Schenectady but then at the University of Illinois, and Bassett at Imperial College in London providing detailed information on the barriers to surface diffusion for different crystal planes. In 1982 Ehrlich wrote: "Systematic examination of different and more complicated systems will help delineate trends and should eventually establish a quantitative link between the properties of individual adatoms and those of monolayers". At that time the scanning tunnelling microscope had not been invented!

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