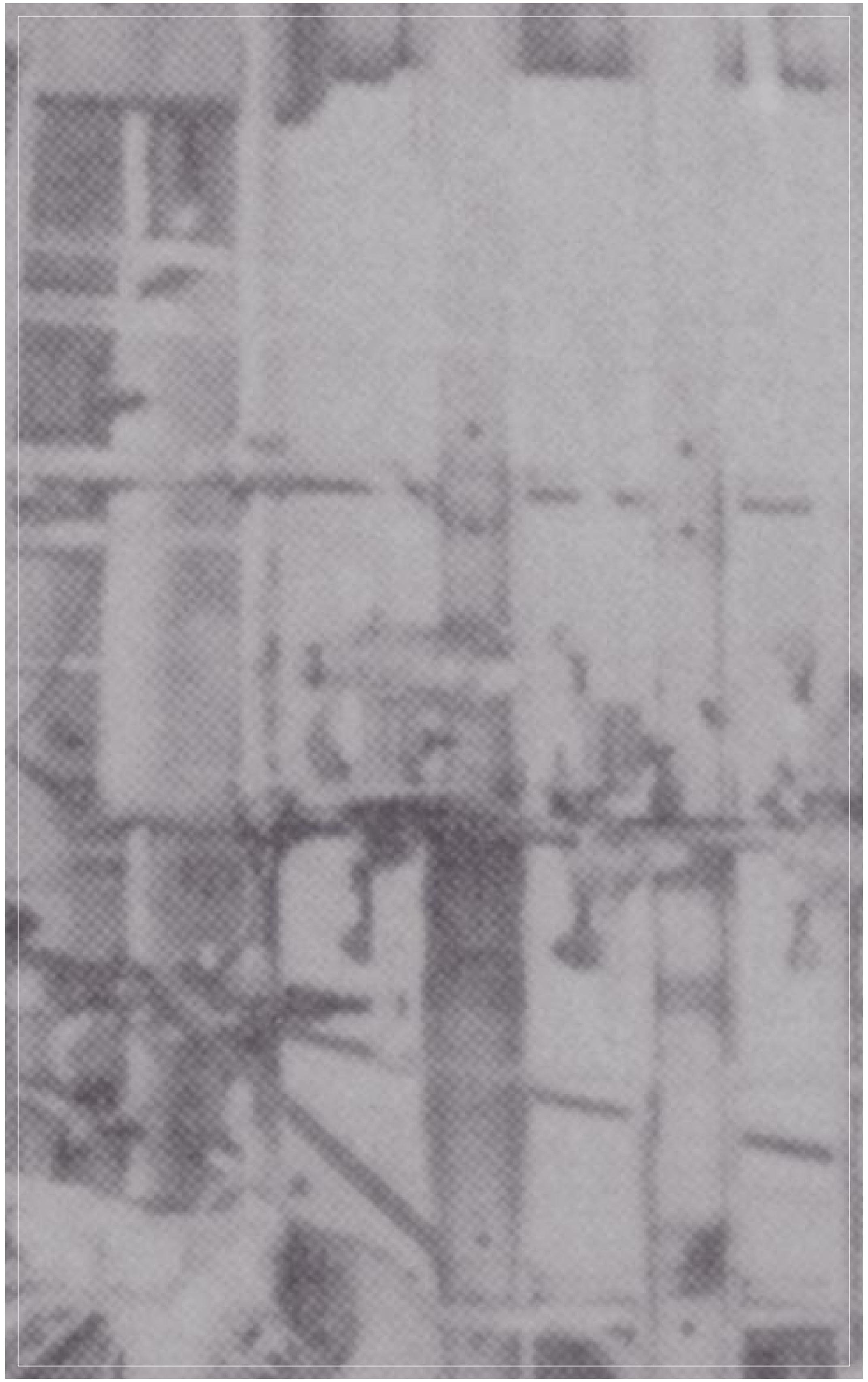


(1950 - 1980)

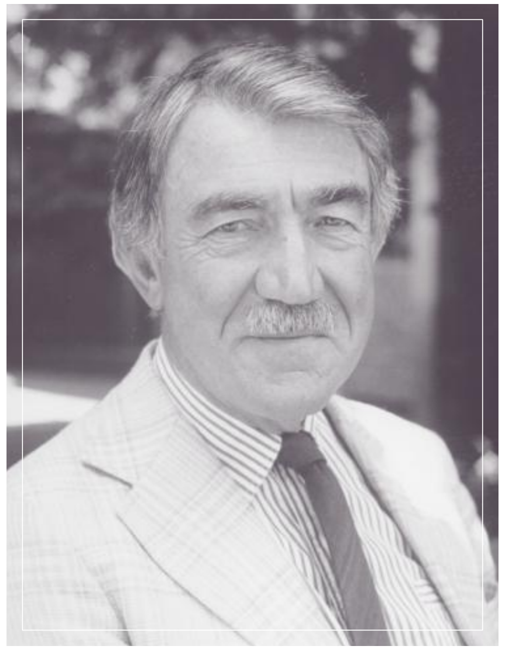
Mechanistic aspects of the heterogeneous catalysts: the classical approach

“Hypothesis is the General and Experiments are the Soldiers” Leonardo da Vinci

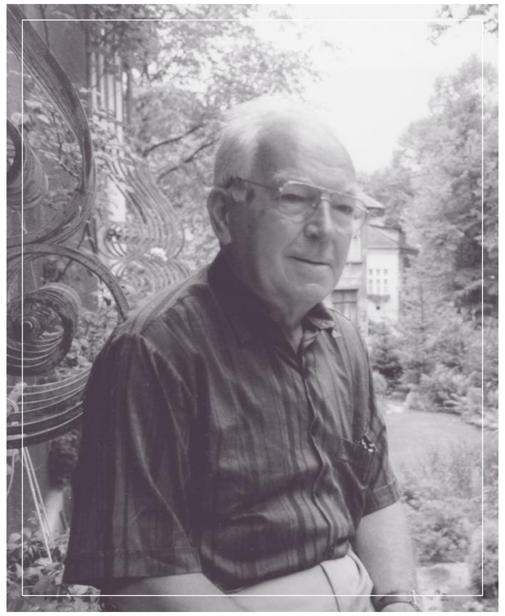
Strong “classical” heterogeneous catalysis groups were emerging in the USA (Boudart, Burwell, Emmett, Turkevich, Weisz), France (Imelik, Teichner), USSR (Boreskov, Kazansky, Balandin, Volkenstein), Netherlands (Schuit, Sachtler, van Reijen, Ponec), Poland (Haber) and the UK (Bond, Dowden, Eley, Kemball, Stone, Thompson, Webb and Wells). In the main there was an emphasis on ascertaining reaction mechanisms from monitoring the gas phase through for example exchange and kinetic studies, with less attention given to the surface although catalyst preparation and knowledge of solid state chemistry, particularly the role of defects in oxide surfaces and the electronic theory of catalysis, were recurring themes. Two spectroscopic techniques that were most significant in supporting the classical approach was infrared (widely used) and electron spin resonance (Che, Tench, Kazansky, Pink and Rooney). During the last decade of this period surface sensitive spectroscopies (X-ray photoelectron, Auger and Reflection Absorption Infrared) had become established but in the main were confined to the surface science schools (Pritchard, Chesters, King, Yates, Somorjai, Solymosi and Roberts) who were giving more attention to reactions and chemisorption (mainly CO!) at single crystal metal surfaces.

A hypothesis contains a speculation or an assumption that goes beyond the known facts - when it is accepted as having a wide and comprehensive scope it becomes a theory and this is usually achieved through further experiments.

Both physical adsorption and chemisorption studies had been accepted by 1950 as important approaches to the study of catalysts. Two distinct uses for physical adsorption had been developed - one was concerned with the measurement of the surface areas of finely divided catalysts, the other with the determination of the pore-size of catalytic materials. The former made use of the BET theory while the latter was mainly due to the work of Wheeler who showed that by taking into account the formation of both multilayers of adsorbed gas and the capillary condensation of adsorbate in the small capillaries one could calculate the size distribution of capillaries in catalysts. Wheeler went on to develop a theory for interpreting the behaviour of catalysts towards various reactants. In particular he showed that pore-distribution can influence the apparent reaction order of a catalytic reaction, its temperature coefficient, the specificity of the reaction and the behaviour of the catalyst after it had been exposed



Michel Boudart



Jerzy Haber

to various poisons. In summary he demonstrated how the method of catalyst preparation resulting in a particular pore-distribution would optimise the catalytic activity for a particular reaction.

Chemisorption in the early 1950s was being used in two ways. First to measure the fraction of a catalyst surface which consists of the catalytically active component compared to that which acted merely as a support or as a promoter. And second to how chemisorbed species actually participate in catalytic reactions. In 1951 Zabor and Emmett estimated by volumetric means that less than 0.1% of the surface of a silica-alumina catalyst was covered by chemisorbed hydrocarbons during cracking reactions. Soon afterwards the use of radioactive techniques indicated that the hydrocarbons such as isobutane chemisorb but only to about 0.01% of the total surface area.

Nitrogen chemisorption and particularly its relevance to ammonia synthesis was receiving considerable attention with Horiuti who was at the Research Institute for Catalysis at Hokkaido in 1955 introducing the concept of “stoichiometric number” applied to the individual steps in a catalytic reaction. Horiuti concluded that the rate determining step in ammonia synthesis over an iron catalyst could not be the chemisorption of nitrogen. There was considerable disagreement with Scholten and Zwietering in the Netherlands showing that at 250°C and above the ratio of ammonia synthesis and nitrogen chemisorption were identical. The mechanism of ammonia synthesis has provided over the last 40 years a stimulus for both extensive experimental work using surface science techniques and single crystal surfaces, and also theoretical, including modelling, approaches to establish which of the various steps involved is the rate-determining one.

We have discussed elsewhere the awareness that had emerged in 1930s and 1940s and probably clarified in the early 1950s for the need for fundamental studies of chemisorption and catalysis using clean surfaces. The evaporated film approach of Otto Beeck became fashionable and in 1953 Trapnell published an account of his studies of the chemisorption of a whole range of gases (N_2, H_2, CO, C_2H_4, C_2H_2, O_2) at some twenty different metal surfaces, all prepared by the evaporation method. Trapnell reported an order for the affinities of the gases in chemisorption and concluded that “with few exceptions a high activity is associated with transition metals or metals having the characteristic partly filled d-band of the transition metals”. The affinity of the metals for oxygen was largest. Chemisorption (except for oxygen) was believed to employ the metal d-band and by comparison p bands were considered to be inert in chemisorption. Trapnell emphasised the significance of d-band structure in the catalytic reactions of the gases he had studied and went further to rule out the significance of d-character in catalytic oxidation but suggested its relevance to the hydrogenation of ethylene, H_2-D_2 exchange, ammonia synthesis and Fischer-Tropsch catalysis. Trapnell believed that his experimental data were a vindication of the d-band theory which Dowden had proposed in 1950, and where there had already been some experimental support from the papers of Couper and Eley, Dowden and Reynolds and Beeck.

Charles Kemball in the Alps with George Haber (back to camera) and the author

While Trapnell at Oxford was studying chemisorption on metal films Kemball at Cambridge had initiated a far reaching programme of research on fundamental studies of catalytic reactions also using evaporated metal films. Kemball’s aim was to pursue work that he had been involved with Taylor at Princeton where he had become familiar with the advantages of using deuterium exchange studies to study the chemisorbed state. The latter had been pioneered at Princeton by Taylor and Morikawa soon after deuterium had become available in the 1930s. Kemball’s work on methane exchange using mass-spectrometry in 1951 showed that at nickel surfaces CD_4 was formed directly and was the main product in the initial stage of the reaction. It was the availability of the mass-spectrometer which provided a continuous analysis of the reaction mixture by bleeding small amounts via a capillary tube to the separately pumped mass-spectrometer that characterised Kemball’s studies over the next 30 years. In 1952 he studied the ammonia-deuterium exchange reaction over a range of metals (platinum, rhodium, palladium, nickel, tungsten, iron, copper and silver) with the view of exploring whether the kinetics (activation energies and frequency factors) showed any dependence on electronic or geometrical properties of the catalysts. Kemball with J.R. Anderson extended the studies on exchange reactions to various hydrocarbons and in particular developed a methodology for calculating the yields of deuterated molecules for comparisons with experimental data.

In 1959 Kemball reviewed the contributions of deuterium exchange studies had made to the understanding of the surface chemistry and catalytic reactions of hydrocarbons drawing attention to the method that had been adopted for analysing the data and the contributions made by the ‘Princeton Group’ - Bond, Parravano, Turkevich and Morikawa. There was also considerable interest in exchange reactions at Northwestern University where Burwell was also studying hydrocarbons: n-heptane, 3,3-dimethylhexane and 2,2,3-trimethylbutane over nickel supported on kieselguhr.

Kemball gave details of the methodology of analysing the reaction products, the kinetics observed and the occurrence of both simple and multiple exchange reactions. The latter is considered to be an exchange reaction in which more than one deuterium enters the hydrocarbon molecule on each interaction of the molecule with the catalyst surface. Kemball discussed possible mechanisms for exchange and in the case of “simple exchange reactions” he considered three possibilities:

(a) the hydrocarbon is not chemisorbed except during the actual exchange which takes place with a chemisorbed deuterium atom

$$\begin{array}{cccc} C_nH_{2m} & D & H & C_nH_{2m-1}D \\ \vdots & \vdots & \vdots & \vdots \\ S & S & S & S \end{array}$$

(b) the mechanism may be dissociative and involve adsorbed radicals of the type C_nH_{2m+1}

or

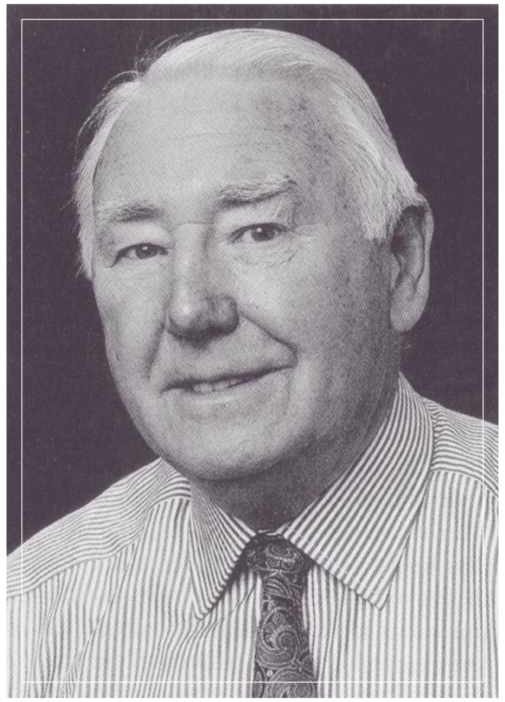
(c) the mechanism may be associative and involve adsorbed species of the type C_2H_{2m+1} which might be radicals or possibly ions.

He was unable to distinguish whether, for example, where the dissociative mechanism operates it was possible to distinguish between a Langmuir-Hinshelwood mechanism where all the species are chemisorbed or alternatively an Eley-Rideal mechanism where one of the reactants is gaseous or physically adsorbed. In the case of multiple exchange reactions the arguments for delineating a mechanism become more complicated and even less convincing.

Studies of exchange at oxide surfaces were comparatively rare at this time but Burwell and Littlewood reported data for chromium oxide gel activity in deuterium exchange with n-hexane. At high temperature it was suggested the production of highly deuterated species might occur through dehydrogenation to hexene followed by deuterium addition. This was also the time when there was scope for considerable debate on mechanism with J.R. Anderson (who later moved back to Australia) questioning some of Burwell's views on the exchange reactions and racemization of optically active 3-methylhexane.

Kemball in summarising the important conclusions from exchange studies emphasised how the activity of metals in the cleavage of C-H bonds could be related to the ease of the exchange reaction. But at the same time drew attention to the lack of attention that had been given to "the nature of the surface during exchange reactions", this was an aspect of surface catalysis he chose not to pursue. Kemball also pointed out that in more complex catalytic reactions radicals may participate and that *"a species covering only one-thousandth part of a surface may play an important part in a reaction, provided that it is formed readily and is also reactive"*.

There was much friendly debate between Kemball, Bond and Burwell in the early 1960s particularly on whether or not π-bonded intermediate were involved in exchange, Gault - initially in Belfast and later in Caen - and Rooney's imputs here were also significant. But Kemball was not too interested in unravelling the atomic nature of the active site, or whether the electronic theory was applicable and what might be the significance of surface structure. Nevertheless he did establish patterns of activity and selectivity which distinguished one metal from another with kinetic and thermodynamic arguments playing an important part in his approach. In a review in 1964 Bond suggested that hydrogen-deuterium exchange and para-hydrogen conversion "appear to have lost some of their former attraction as catalytic probes" - this view may well have reflected the growing awareness of the lack of attention that had been given to the precise nature of the surface site active in bonding the reacting species, an asterisk being used for its designation! We were also beginning to see serious attention being given to the study of catalytic reactions at evaporated film surfaces which had been prepared under ultra-high-vacuum conditions (10^{-9} torr). It is perhaps not surprising that one of the first papers drawing attention to the inadequacies of conventional vacuum techniques, where the background pressure was sometimes no better than 10^{-5} torr, was from the General Electric Laboratories, at Schenectady (the 'home' of Irving Langmuir), R.W. Roberts reporting in a paper in Nature in 1961 on the decomposition of n-propane and n-butane at clean rhodium film surfaces. In the following year he showed that ethane underwent catalytic cracking to yield gaseous methane and an adsorbed hydrocarbon residue at rhodium at 0°C and the need for ultra-high-vacuum techniques emphasised. Prior to Roberts' studies of rhodium Robertson and Fabian at King's College, London had reported the dehydrogenation of ethane at low pressures (10^{-7} torr) at a hot platinum filament with a detailed kinetic analysis providing estimates of the probability of an ethyl radical being formed per collision.



Frank S. Stone

Kinetic studies through determining the sticking probabilities of molecules (mainly CO and N_2) at metal surfaces (mainly tungsten) were also fashionable in the 1960s. Two different approaches were favoured: the flash filament method used by Ehrlich, Redhead and Degras (later known as the temperature programmed desorption method) for studying chemisorption at metal filaments or single crystals and the flow method, first used by Oda, Wagener and Bloomer and subsequently by Hayward, King, Tompkins and Roberts for studying chemisorption at evaporated metal films of high surface area. The significance of precursor states in chemisorption kinetics was established providing further experimental evidence for both the Lennard-Jones model for chemisorption and also support for Kisliuk's analysis of adsorption. The significance of kinetic studies is discussed fully in the books, 'Chemistry of the Metal-Gas Interface' (1978), also available as a Russian translation (1981), and 'Introduction to Surface Physical Chemistry' (1991), with emphasis given to the proper design of experiments and interpreta-

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Kenzi Tamaru

tion of experimental data obtained from high area, porous, metal films. A noteworthy development during this period was the molecular beam approach used by King and Wells.

Dowden continued to develop his ideas on the relationship between chemisorption and the electronic configuration of the solid and whether it is an metal, semiconductor or insulator. He emphasised at the Chemisorption Symposium held at Keele in 1956 how "the electronic configuration controls all the degrees of interaction with sorbates, from the accommodation coefficient through physical adsorption and the several chemisorptions to final solution or occlusion". Attention was turning very much to the nature of the solid state at this time with electron transfer between the solid and adsorbate playing the crucial role. Work function measurements (Mignolet and Tompkins) supported this as a significant aspect of chemisorption. Lattice defects and dislocations were suggested to be the possible "active centres" first suggested by Taylor in 1925. A different idea had been proposed by Volkenstein in 1949 namely that the "active centres" were created on an otherwise homogeneous surface by the act of adsorption and was the inspiration for Taylor (H.A. not H.S.) and Thon explaining the somewhat ubiquitous validity of the Elovitch equation for describing the kinetics of chemisorption. Michel Boudart who had been a colleague of H.S. Taylor at Princeton was, and still is, a devotee of the kinetic approach for unravelling reaction mechanisms in heterogeneous catalysis. In his Plenary Lecture at the 6th International Congress in 1976 he addressed questions relating to selectivity, structural sensitive reactions, the role of ensembles first emphasised by Dowden and the Balandin sextet theory. However, my first recollection of Boudart was through his paper in 1952 on the "induction effect" in catalysis to describe the role of alkali metals in the activation of nitrogen at an iron surface; it was an intriguing concept to a young post-graduate student!

The other area receiving particular attention during the 1950s and early 1960s was the fundamental understanding of the mechanism of catalytic cracking over silica-alumina catalysts. The 1950 Faraday Discussion illustrates the thinking at that time with papers by Steiner (Manchester), Tamele (Emeryville), Milliken, Mills and Oblad (Houdry Laboratories) and May, Saunders, Kropa and Dixon (American Cyanamid Co). It was, however, the General Discussion reported on these papers that is most revealing (a characteristic feature which still persists today with Faraday Discussion Meetings!). Of particular interest to me were the comments of A.G. Evans, then at Manchester, but my predecessor at Cardiff. Evans suggested that when 1,1-diphenylethylene was adsorbed on a clay surface a carbonium ion, ϕ_2C^+-CH_3, was formed by proton transfer from the clay to the olefine. The conclusion was based on ultraviolet absorption spectra for carbonium ions known to form for $\phi_2C{=}CH_2$ in sulphuric acid. Webb much later (in 1959) referred to Evans' observation for the interpretation of the electronic spectrum he had observed using infrared spectroscopy for the study of olefines chemisorbed at silica-alumina catalysts. The presence of radical ions of this type were further established by the electron spin resonance studies of Pink, Flockart and Rooney in Belfast in the early 1960s, reviewed by Flockart in 1973.

The electron-acceptor properties of catalytic aluminas were studied and comparisons made with what had been observed by ESR with silica-alumina catalysts. With alumina the oxidizing site was considered to involve molecular oxygen where aromatic hydrocarbons are readily oxidized to the corresponding cation-radical and subsequently oxygenated products. In contrast with silica-aluminas the cation radical is stable for long periods. The application of ESR has played a very significant role in unravelling the molecular details of catalytic reactions, particularly at oxide surfaces with the pioneering work of Tench and Che of magnesium oxide surfaces providing evidence for individual paramagnetic chemisorbed oxygen states in the early 1970s. Other adsorbents were also investigated including rare-earth exchanged Y-zeolites where evidence for anthracene cation radicals were obtained by Naccache and Ben Taarit in Lyons.

The Mars-van Krevelen mechanism proposed in 1954 has dominated the interpretation of hydrocarbon oxidation catalysis. The essential feature of the mechanism is that the hydrocarbon is oxidized and the oxide reduced followed by re-oxidation of the oxide by the gaseous oxygen to generate the reactive oxygen species. The species directly responsible for the catalytic oxidation is generally assumed to be the O^{2-}-ion of the oxide surface and Sachtler and de Boer in 1965 postulated that the tendency of an oxide to donate its oxygen should determine whether it is a selective oxidation catalyst. If the reduction of the oxide is easy then oxygen can be easily 'donated' to a molecule from the gas phase and the catalyst would be expected to be active and non-selective. On the other hand for "a difficult to reduce oxide" (metal-oxygen bond strong) it would be anticipated to be a catalyst of low activity. Although there was support for this general approach to oxidation catalysis it is somewhat surprising that so much emphasis was given to the active oxygen being the O^{2-} species of the oxide lattice since one might have expected a stepwise series of electron transfers generating a range of oxygen states:

$$O_2 + e \rightarrow O_2^-$$
$$O_2^- + e \rightarrow O_2^{2-}$$
$$O_2^- \rightarrow 2O^-$$
$$O^- + e \rightarrow O^{2-}$$

Early ESR studies by Kazansky of TiO_2 suggested the presence of O^- species but according to Che and Tench in 1982 they were not confirmed by using ^{17}O enriched O_2. At MgO surfaces, using N_2O, the presence of O^- species are well established but with ZnO the O^- species are located close to but not on the surface. The peroxo-type O_2^- species has been observed by Katzer et al (1979) at Pt/Al_2O_3 catalysts, while Cordischi et al in Rome reported O_2^- species at an MgO surface. Similar conclusions were reached by Zecchina and Stone (1975) who had also emphasised the concept of co-ordinately unsaturated oxygen sites and their role in chemical reactivity. The surface coverage of these sites was exceptionally small (less than 0.005). Boudart and Derouane had earlier (1972) also established the presence of paramagnetic species at "vacuum treated" MgO and which they had assigned to a "triangular array" of O^- ions at (111) micro-planes. That O^--type species exhibited special reactivity, particularly in selective oxidation and dehydrogenation of alkanes at MgO was thoroughly studied by Lunsford in the mid 1970s and particularly in the late 1980s when methane coupling reactions became a fashionable area of activity. In 1992, Oyama and Hightower, reacting to the petrochemical industries' interest in enhancing the yield of high value products, organised a Symposium on Selective Oxidation where modern techniques as well as more traditional approaches were described. At least a third of the papers dealt with the use of vanadium in one of its several oxidation states!

We will return to the significance of such transients as $O^{\delta-}$ and $O_2^{\delta-}$ when we consider the dynamics of dioxygen chemisorption at atomically clean surfaces and how through applying surface sensitive spectroscopies and with the use of carefully chosen probe molecules, proof of their transient existence was established during the formation of the chemisorbed overlayer in the mid 1980s by the Cardiff group.

Spill-over was a popular concept that emerged in the 1970s, particularly when hydrogen was involved. For cases like the reduction of MoO_3 by hydrogen dissociated at the platinum promoted oxide the mechanism is clear but what is less clear are the details of the hydrogen migration. Burwell was at the 11th International Congress on Catalysis (1996) somewhat critical of authors who involved spillover but did not establish its catalytic relevance. He goes on to say:
"It is difficult now-a-days to be conversant with all previous catalytic literature, but the level of ignorance appears to have increased substantially (and mea culpa)."

During the period 1960-1980 considerable influence on reaction mechanisms in heterogeneous catalysis came from homogeneous organometallic chemistry and Rooney in particular at Belfast was a strong proponent of the strong links that existed. Nevertheless it was always difficult to establish unequivocally the mechanistic details of a heterogeneously catalysed reaction. In 1976 Thomson and Webb at Glasgow stated:

“Olefin hydrogenation on metal catalysts is the subject of a vast literature, yet it lacks a basic unifying theory. There is controversy over mechanism and kinetics and the underlying properties of metals which account for their behaviour as catalysts”.

They proposed a general unifying mechanism for the hydrogenation of olefins and suggested that it should be interpreted as hydrogen transfer between an adsorbed hydrocarbon species $M\text{-}C_2H_x$ and the adsorbed olefin and not as hydrogen addition directly to the olefin. The suggestion made the metal of secondary importance and hydrogenation is seen as an extension of self-hydrogenation.

Haber and his colleagues in Kracow have given much attention to the mechanistic pathways involved in the selective oxidation of hydrocarbons drawing attention to the work Cotton and Lewis and Johnson and the significance of small metal clusters and metal cluster compounds containing metal-metal bonds. Theoretical calculations by Haber and Witko have provided an understanding of the point of attack preferred by an oxygen atom interacting with a hydrocarbon molecule - whether it is an electrophilic or nucleophilic attack - and the relevance of the charge distribution within the hydrocarbon molecule. Haber in 1989 emphasised the fundamental difference between discussing the reactivity of intermediates in surface catalysis and those participating in homogeneous catalysis as isolated transition metal complexes. In the latter we are dealing with a fixed number of electrons whereas for a complex present at a solid surface we can control the electron density on the molecular orbitals (e.g. by doping the solid) and therefore control its reactivity along specific reaction pathways. An early example is the control of CO dissociation at an iron surface by preadsorbing sulphur which decreases the extent of back bonding of electrons into the antibonding orbitals of the chemisorbed CO and therefore inhibiting cleavage of the carbon-oxygen bond (Kishi and Roberts 1975).

Much emphasis was given to Dowden’s electronic theory which stimulated much of the thinking for understanding catalysis at semiconductor and metal surfaces. Band theory played a dominant role with chemisorption and catalysis being rationalised in terms of whether the solid was n-type, p-type or an insulator. Stone summarised the position in 1956 at the Keele Symposium reviewing progress over the previous decade. Hauffe also was a strong advocate of the band theory approach while others had also drawn attention to the connection between catalytic activity or electron concentration (Schwab in 1943), and that there was according to Suhrmann and Sachtler a synchronous coupling between electron-spending to an electron-accepting species as a fundamental pre-requisite for a process to take place, whether it is a purely chemical reaction, a catalytic process or adsorption. Suhrmann and Sachtler had relied very much on monitoring changes in the conductivity of thin metal films and also work function changes during the chemisorption of gases, over a wide temperature range (90K-295K) for their conclusions.

In 1962 Balandin at the Zelinskii Institute of Organic Chemistry reviewed the development of his multiplet theory, first proposed in 1929, and in which he interpreted catalytic activity in terms of the geometric arrangement of atoms at the catalyst surface. This indeed was the forerunners of the “geometric factor” in catalysis elegantly demonstrated, for example, by Beeck with his studies of catalytic hydrogenation over differently oriented metal films in 1940. It was, however, studies of the hydrogenation of benzene and dehydrogenation of cyclohexane that Balandin explained in terms of the molecules being adsorbed in a “flat” state on specifically arranged metal sites with particular interatomic distances. He correlated catalytic activity with special arrangements of atoms in metal surfaces but exceptions were found and Balandin’s theory declined in its predictive ability. An excellent account of the status of geometric and electronic factors in 1967 is to be found in the book ‘Introduction to the principles of heterogeneous catalysis’ by Thomas and Thomas.

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