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Dennis Dowden and the Development of Catalytic Science

Celebrating a twentieth century pioneer in the scientific understanding of catalysis

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In the twentieth century Dennis Albert Dowden, affectionately referred to as DAD by friends and colleagues, was an important figure in the development of an understanding of the structure of industrial heterogeneous catalysts, the species present and the processes taking place on them. He was born in Bristol, UK, and following education at the University of Bristol and a short period at Amherst College in the USA, in 1938 he joined Imperial Chemical Industries (ICI) at Billingham in the North East of England. He worked there on catalysis, catalyst manufacture and catalytic processes for the next thirty-seven years. His major contribution was to bring a wide range of sciences and a rational approach into what had been until then regarded as "black art", capable of only empirical analysis. His influence extended across ICI, which at that time operated many industrial catalytic processes, and academically he was influential worldwide and especially in the USA.

1. Dowden's Early Career and Domestic Life

1.1 Early Family Life

Dowden was born in Bristol, UK, on 15th August 1914, just a few days after the start of the First World War. His family was far from wealthy. His father, Charles Henry Dowden, worked at the Wills Tobacco Company, and the family situation was made very much more difficult when he, a pacifist, a committed socialist and a local political labour leader, spent two years in Dartmoor Prison as a conscientious objector. His mother, Ada, left alone with young Dennis, worked as a seamstress and somehow managed to support them both. At that time not "going to war" was seen as unpatriotic and very much looked down upon, and this made life even more difficult as they were shunned by shop keepers and many townsfolk. However, they survived and when his father returned home he eventually got a job in a warehouse through church contacts. Later, in 1920, the family was enlarged by the birth of a daughter, Joan. Dowden's parents thought that everything could be achieved through education and they encouraged their children to do well at school. When he was eleven or twelve Dowden was taken by his mother to the opening of the new University of Bristol (previously it was University College) by King George V. He said he looked up at the great tower and thought, "I will go there one day", and he did!

1.2 Academic Studies

Dowden excelled academically and he won a scholarship both to Merrywood Secondary School and subsequently to the University of Bristol where he studied Chemistry from 1932 to 1937 and his record card shows he had a "very satisfactory first year". In fact he later graduated with first class honours. Chemistry at Bristol was particularly strong in the area of interfacial chemistry, and as early as 1913 Professor James W. McBain postulated the existence of 'colloidal ions', now known as micelles, to explain the electrolytic conductivity of sodium palmitate solutions (1), while in the Physics Department, where Dowden studied for two years, there were eminent researchers like Nott, Jones, Lennard Jones, Gurney, Frolich, Heitler, the two Londons and Sucksmith.

In the Chemistry Department Professor William E. Garner worked on the gas solid interface developing adsorption calorimetry (2). During his time at the University of Bristol Dowden did postgraduate research (**Figure 1**) with Professor Garner on the heats of adsorption of gases on high surface area solids that at the time was a research frontier. Indeed, the now familiar BET method for estimating surface areas of catalysts was published (3) about the time Dowden left the University of Bristol. Although he had done good careful topical research, like many others at that time at the University of Bristol he did not submit a thesis for a PhD, something in later life he said he regretted. Notwithstanding this it was an exceptional achievement then for a child from his working class, anti-establishment background to go to university and do so well.

In the USA Professor Beebe at Amherst College had become involved with the measurement of heats of chemisorptions (4). He had spent several sabbatical years at Bristol where he developed a long-standing friendship with Professor Garner, so when he obtained research funds he perpetuated the connection through having visiting Bristol postdoctoral students, of whom Dowden was the first. Dowden went to Amherst College in 1937 and continued research on heats of adsorption of gases on chromia. He measured the heats of adsorption of argon, hydrogen, deuterium, carbon monoxide, nitrogen, and oxygen on reduced chromia by calorimetry at low temperatures. The results were interpreted in terms of an initial 'van der Waals adsorption' followed, in some situations, by a slow exothermic change leading to 'activated adsorption'. But his time in the USA was not all devoted to work, for Dowden found time to drive across the USA to California with a friend calling at some universities on the way and returning by Greyhound bus, at the height of the Great Depression! The research Dowden did at Amherst and Bristol resulted in two substantial publications, the first in the *Journal of the American Chemical Society* (5) and the second in the *Journal of the Chemical Society* (6). The latter paper was received on 29th March 1939 and the authors expressed their thanks for grants for the purchase of apparatus to ICI Ltd, and to the Colston Research Society. This Society was founded in Bristol in 1899 as the 'University College Colston Society', by Bristol citizens who wanted to assist the University College. From 1908 to 1948 it gave grants to specific research projects in various departments. Since 1948 the Society has supported symposia.

Fig. 1. Dennis Dowden when a postgraduate research student at The University of Bristol, UK, in 1935/36. His supervisor was Professor William E. Garner and his research involved measurement of the heats of adsorption of gases on chromic oxide, work he continued with Professor Beebe at Amherst College in the USA

1.3 Return to the UK and Start of Industrial Career

Dowden returned to the UK in 1938, probably in part because of the impending Second World War, and he joined the Billingham Division of ICI in the North East of England (**Figure 2**). ICI there at the time had a general policy for recruiting preferentially graduates with DPhils or PhDs from Oxford, Cambridge or Imperial College London. It is therefore quite remarkable that in the late 1930s ICI employed Dowden who came from the University of Bristol without a PhD. Professor Garner may have influenced the situation since he had contacts at ICI and their financial support was acknowledged in Dowden's paper (6). However, it is clear Dowden's exceptional abilities were recognised early in his career. At first at Billingham he was a Safety Officer in the Research Department, and a little later he moved to the catalyst manufacturing factory at Clitheroe in Lancashire, as a plant manager. Here catalyst for the production of high octane fuel for fighter planes and other catalysts were

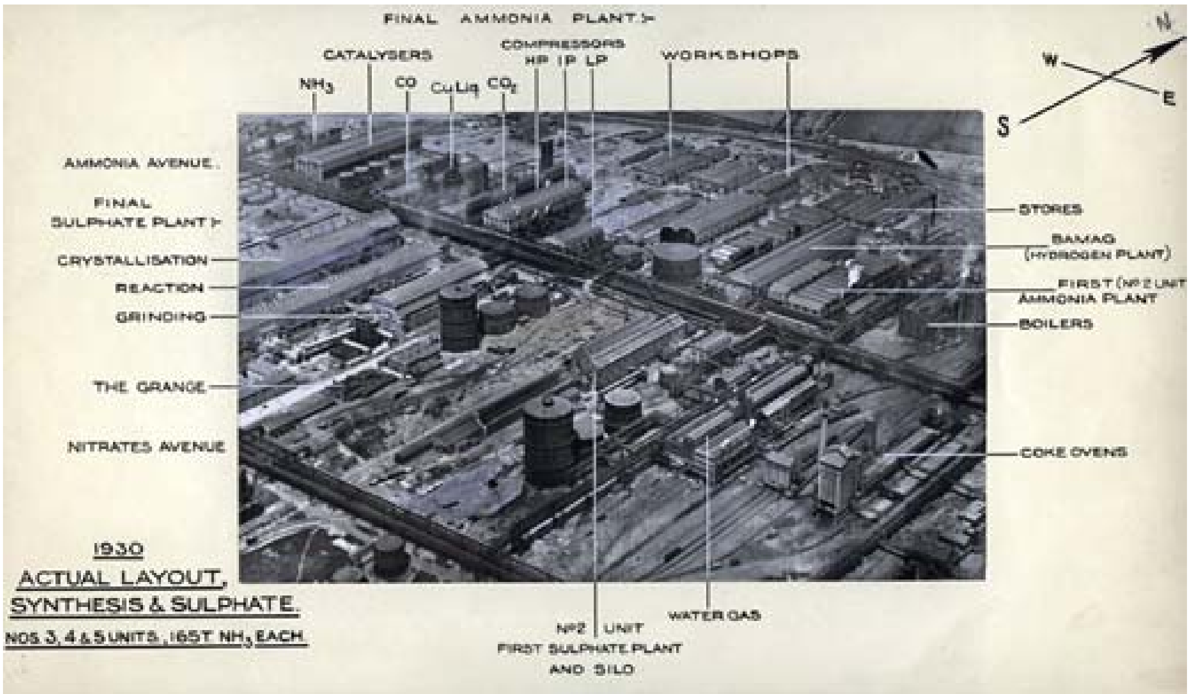


Fig. 2. An original image showing the layout and details of part of the Billingham Site in 1930. The site would have been somewhat enlarged by the time Dennis Dowden went to work there just before World War II

produced. During this time Dowden learnt about large-scale catalyst manufacture and the underlying inorganic chemistries involved before getting deeply involved in industrial catalyst research and development. He once said that the real impact of catalysis was not revealed to him until after he had joined ICI.

1.4 Research at Billingham and Domestic Life

Still during the war Dowden returned to do research at the main site at Billingham, where he worked on catalysts and catalytic processes for almost four decades. He was confronted with a broad spectrum of exploratory catalytic chemistry involving hydrogenation and oxidation as well as related pilot plant and full scale plant problems, and he said he did his first ‘plant training’ on coal liquefaction, though it is not clear if this was before or after going to the Clitheroe catalyst works. At Billingham Dowden got to know Iris Coxall who worked in a Drawing Office and they were married on 11th October 1947 at the Stockton Register Office. He was 33 and gave his profession as ‘Research Chemist at Chemical Factory’, she was 23 and a ‘shorthand typist’. Their fathers’ occupations were given as Warehouseman (Charles H. Dowden) and Boilersmith (Thomas Coxall), and the witnesses were Charles H. Dowden and Lavinia M. Coxall.

At first they lived in a company flat in Norton, a village only a short distance from Billingham, and later they bought a house in Eaglescliffe close to Yarm-on-Tees a few miles south of Billingham. They had two children, Diana born in 1952 and Simon born in 1956. In 1965 a property in Javea in Spain was purchased and this provided the family with many unforgettable happy summer holidays. Dowden liked to think of himself as something of a thespian, and for many years he had acting roles in Middlesbrough amateur dramatic society productions at The Little Theatre and he appeared in Norton Hall Club ‘Smoker’ productions. The company name Synthetic Ammonia and Nitrates Ltd at Billingham was the origin of the name of the Synthonia Club that provided a range of social amenities for workers that included bars and a large theatre area. Each year a Research Department Christmas musical revue took place there that mocked and made fun of the management, only occasionally was there a guest appearance by more senior people such as Dowden. Norton Hall Managers Club located some distance away in Norton Village was limited to senior staff while the Cross Roads Club at Hartburn Village was open to all ICI staff. Each year there was an evening entertainment known as the 'Smoker' at Norton Hall in which Dowden sometimes appeared. His liking for good wine and good food was legendary, and he especially enjoyed champagne that he would give as gifts to friends and colleagues. It is therefore not surprising that for many years Dowden was a member of the important Norton Hall Club Wine and Food Committee responsible for stocking the Club's extensive wine cellars.

2. Scientific and Technical Context

The Nobel Prize for Chemistry in the year Dowden was born was awarded for "the exact determinations of the atomic weights of a large number of the chemical elements". This award to Professor T. W. Richards of Harvard University was the first Nobel Prize in Chemistry awarded to an American. It was announced on 11th November 1915 and in many ways illustrates the stage to which chemistry had progressed (7). It was a very different world compared to that of today; now we have a fundamental understanding in many scientific and technical areas, whereas then many phenomena, such as catalysis, were known but far from understood. The life of Dowden ran parallel to the rapid development of the chemical sciences, the growth of industrial catalysis and in particular the gradual growth of the scientific understanding of catalysis in which he was so very much involved.

When Dowden was born catalysts were used commercially, in fact the origins of catalysis can be traced back to the researches of Humphry Davy at The Royal Institution in London who discovered the catalytic properties of platinum in 1817 (8). Several catalytic inventions followed and particularly notable was a patent for the oxidation of sulfur dioxide over platinum catalysts granted as early as 1831 for sulfuric acid manufacture (9, 10). (Like Dennis Dowden, Peregrine Phillips lived in Bristol. Phillips was a manufacturer of vinegar, and surprisingly little is known about him (see, for example, Cook (10)). However, the era of large scale industrial catalysis only really started with the operation of the first Haber-Bosch plant for ammonia synthesis at Oppau, Germany, in September 1913 that produced 7200 tons of ammonia annually (11).

The invention of many other catalytic processes followed, for example, in 1923 methanol from synthesis gas which was at the time derived from coal (12). Key to the successful development of the ammonia process was the catalysis work by a team led by A. Mittasch, who around 1910 obtained a more satisfactory ammonia synthesis catalyst than the original osmium Haber catalyst (13). This was obtained by an empirical scatter-gun approach involving the testing of some twenty thousand catalyst formulations (14). (Jennings' book has a foreword by Dennis Dowden in which he refers to "hydrogenolysis of atmospheric nitrogen" as an "epoch making advance".) This approach led to a widespread belief that this was the only way to obtain new or improved catalysts. Many workers did not believe a rational approach was possible and they described, often with some glee, the process of catalyst development as a 'black art'. While it now seems bizarre that this should have been so, the view persisted for a long time (15). The enormous improvement in understanding catalytic reactions and catalyst manufacture resulted in part from the general advance in experimental methods over the past century. Nevertheless our understanding was very much pushed forward by Dowden's rational scientific approach.

3. Contributions to Scientific Understanding

When Dowden began working at ICI he was surrounded by processes for the manufacture of industrial catalysts, their continual improvement and the many reactions they catalysed. His previous research at Amherst College (5) and the University of Bristol (6) on adsorption of gases on chromia was leading-edge and gave him insights into the nature of reacting adsorbed species on catalysts, and gradually he began to consider the ways in which these species might be bound to the catalyst surfaces. That is, the intimate bonding patterns involved during catalytic processes.

But this was to come later for starting a new job had many demands and there must have been little time to pursue such ideas. Indeed Dowden appears not to have published scientific papers for a decade after his university papers appeared. In fact he published surprisingly little during his career at ICI. In the 1950s he had been commissioned to write an introductory Methuen Monograph on catalysis but this was not completed. After retirement, in the 1970s he started work on turning his lecture series into a book on rational catalyst design but progress was difficult, and only a few chapters were completed when unknown to Dowden a book on this topic by D. L. Trimm appeared largely based on Dowden's lecture notes but with scant acknowledgement (16).

It is a great regret Dowden did not produce anywhere near as many scientific papers as might have been expected, and there seem to have been two broad reasons for this. First, as a highly sociable man he much preferred to talk about catalysis rather than sit down alone to write about it. Second, there was something of the perfectionist about him: he was never really satisfied with what he had written and he was a compulsive rewriter, going through many versions of every paper. Indeed those of us who read these drafts often felt the earlier versions were more satisfactory, before the various elaborations, qualifications and so on had been incorporated. It follows that it is not surprising that many of his papers were conference contributions, where time limits forced him to produce completed papers. Dowden enjoyed the intellectual stimulation and social aspects of participating in international catalysis conferences, and he attended all the important ones he could and made long lasting friendships with many eminent academics.

3.1 Fundamentals of Catalysis

Those working in industrial organisations often find it difficult to publish work in the scientific literature because in addition to finding the time required to prepare papers there are always commercial concerns that are raised. So it is not surprising that from the start and throughout his career in ICI most of Dowden's scientific publications dealt with general aspects of catalysis. His papers published over the period 1948–1950, were concerned with broad questions of relations between catalysis and the electronic structure of solids (17) and other theoretical aspects of catalysis (18), as well as contributions to an understanding of reactions on alloy catalysts (19) rather than a detailed study of a particular commercial catalyst. In particular Dowden wanted to relate catalyst performance, in terms of activity, selectivity and life, to electronic and physical structure properties, and it is characteristic that his first paper from ICI examined the relation between the performance of catalysts and their electronic structure. This was a different approach from most other workers, who were then more concerned with the mechanisms of the reactions taking place rather than why it took place on a certain solid. In contrast Dowden was following the early steps taken by Rideal and Taylor (20).

Dowden's other papers in the 1950s were concerned with the activity of nickel catalysts (21), and a long one with Professor Garner at the University of Bristol on the electrical conductivity of zinc oxide/chromia type catalysts for high pressure methanol synthesis, perhaps reflecting some of Dowden's original university research interests (22). Other papers during this time were concerned with properties of dehydration and dehydrogenation catalysts (23) and pioneering work on hydrogen-deuterium exchange on oxides rather than on metal catalysts (24), and a short review of work in this area was published (25). The role of chemisorption in catalysis was an ongoing theme with Dowden (26, 27). There was also a writing collaboration with George Bridger that resulted in a significant review on the scientific basis of catalyst testing that many researchers today would benefit from reading (28).

3.2 Academic Collaborations

At the time there was some opposition to trying to identify the places where the reactions took place on catalyst surfaces because many academics were happy to leave the description of the 'active site' as simply an asterisk on a straight line that only vaguely represented the catalyst surface (see for example (29)). Dowden wanted to go further and describe the surface and the molecular reaction mechanisms. He took a comparable approach to the reactions during catalyst manufacture. As a result he became concerned with these fundamental aspects while pursuing industrial research projects targeting very specific goals, and because of his acceptance by a wide circle of those in academia one of his roles in ICI was liaison with universities. As a result he brought many academics into ICI as consultants or 'visiting workers'. For example, in 1957 Professor Geoffrey Bond (University of Hull, UK) was a 'Summer Guest Worker' at ICI in Billingham working on the selective hydrogenation of acetylene to ethylene over palladium/silver catalyst that appears particularly topical when read today (30), and another 'Summer Worker' at about the same time was Professor B. M. W Trapnell (University of Liverpool, UK) who worked on hydrogen/deuterium exchange on oxides with Dr N. Mackenzie, a member of Dowden's team (24, 25).

3.3 Application of Crystal and Ligand Field Theory

One of Dowden's most significant papers, at the height of his career, was 'Crystal and Ligand Field Models of Solid Catalysts'. He delivered this at the Fourth International Congress on Catalysis, Moscow, Russia, in 1968. It was published in Russian in the Proceedings of the Congress and later in 1971 an English version appeared in *Catalysis Reviews* (31). His opening paragraph was: "Quantum chemistry is now some 40 years old, but the problem of calculating the rates of complex reactions, in a useful approximation, from fundamental atomic constants, remains intractable. Along with the rest of chemistry, heterogeneous catalysis has continued, in the main, to be descriptive and empirical although its study has mirrored changing attitudes in the cognate sciences, and there has been an uninterrupted search for unifying concepts." He continued: "Just as the simple band theory and its nomenclature ultimately failed to describe the properties of conductors so also it is an inadequate classification of catalysts and only a superficial interpretation of descriptive catalytic chemistry." He then considered the energy states of a number of perfect ionic lattices, and continued to attempt to deal with charged defects in solids (mostly oxides) with imperfect lattices, taking the chemisorptions of hydrogen, oxygen and water as examples. Progression from insulators to semiconductors brought him closer to useful catalysts: "… it was necessary to investigate the hydrogen-deuterium exchange reaction over some stable oxide of the first long period; the hoped-for twin peaked pattern was found and a consolidated theory outlined".

Dowden went on to show that a similar twin peaked pattern could be found in several hydrocarbon hydrogenation and dehydrogenation reactions. He then incorporated both crystal and ligand field effects in chemisorptions, and extended this approach to catalysis of some important reactions such as hydrogenation and dehydrogenation; polymerisation and depolymerisation; oxidation and deoxidation. He concluded that the qualitative aspects of the models he considered "…serve as guides in the investigation of chemisorption and catalysis. The potential power of these models for the prediction of catalyst activity and the design of catalysts has yet to be realised."

There were several other related publications around this time (32–35) and the immense advances in computational chemistry which have taken place now make much of this seem elementary, almost naïve, but at the time it clearly pointed the way forward.

3.4 Influence in ICI and Beyond

During Dowden's career at ICI his research group consisted of only a few people, in marked contrast to the large research groups prevalent today. Other groups at Billingham were directly working very successfully, on new processes, for example naphtha steam reforming and low pressure methanol synthesis (**Figure 3**). The remit of Dowden's group was to examine the fundamentals of existing processes and to look for new processes that could be used by ICI. In effect he was given the freedom to examine almost any aspect of catalysis that took his interest. The atmosphere within his group approached the academic and it was very different to later industrial research, tightly constrained to limited targets. The wide range is shown by examples of the subjects worked on by members of his group: methane/steam reforming over platinum group metals, the kinetics of the catalytic oxidation of sulfur dioxide, homogeneous catalytic hydrogenation of olefins and acetylene by cobalt and nickel complexes, nitrogen fixation over reduced molybdenum oxides, and the selective oxidation of methane to methanol and formaldehyde. Sometimes he went beyond catalysis into other process areas, for example, examining crystal agglomeration ('caking'), of importance in fertiliser manufacture. Not surprisingly, little of this work found its way directly into industrial practice but almost always there was an increase in the understanding of the underlying fundamental science.

Certainly of equal importance and possibly of greater influence was Dowden's readily available and penetrating advice to ICI research groups, not just those at Billingham but to many others across ICI. His advice always started from a detailed understanding of the process being considered and then incorporated his wide knowledge of the basic catalytic science. He was never an advocate of the empiricism of a Mittasch or a Ziegler. When Dowden retired he became more directly involved with research in universities and wrote several review papers, but he was still often at Billingham keeping up with the latest advances and offering advice on what should be done next. The

Fig. 3. Construction during early 1962 of the original naphtha steam reformers at Billingham that provided synthesis gas for the ICI Low Pressure Methanol Process. Both the naphtha steam reforming and methanol processes were commercially very successful with several hundred plants being licensed around the world

scientific papers published during this period are covered in the Retirement Section below.

4. Contributions to Technical Progress

While Dowden was well known in academic circles for his ideas about the structure of heterogeneous catalysts and the reactions taking place on their surfaces, his industrial work was of course more applied, and here his 'ICI work' is traced through published patents in which he is named as an inventor. There are as many of these patent families as publications in the open literature suggesting, understandably, that more time was devoted to the industrial work than to the more academic side. Here a representative number of Dowden's patents are discussed that provide insight into the kinds of industrial research he carried out.

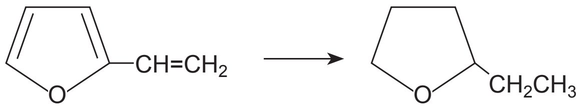
4.1 Research During the Second World War

Amongst his first patents was one on producing 1,5-pentanediol by hydrogenation of δ-hydroxyvaleric aldehyde (5-hydroxypentanaldehyde), Equation (i), using a nickel on Kieselguhr catalyst and the beneficial presence of water on the reaction, so presumably the reaction goes *via* the hydrated gem-diol.

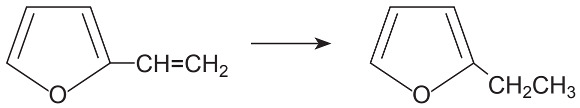
$$HOCH_2CH_2CH_2CH_2CHO + H_2 \rightarrow HOCH_2CH_2CH_2CH_2CH_2OH \quad (i)$$

This patent was filed during the war (23rd April 1943) (36) and might have been associated with possible explosive applications of 1,5-dinitratepentane, although there is no direct evidence for this. However it might be pertinent that Dowden's university supervisor, Professor Garner, was said by Dowden to be an explosives expert and to have worked with the Ministry of Supply.

A patent (37) filed on 11th June 1945, just after the end of the Second World War in Europe, must also have been based on work done during the war, and was concerned with the effect of ammonia (or amine) on the hydrogenation of vinylfuran catalysed by nickel on kieselguhr. In the absence of ammonia complete hydrogenation to ethyl tetrahydrofuran took place, whereas with added ammonia only the external double bond was hydrogenated to form ethylfuran in high yield, Equations (ii) and (iii).



(ii)

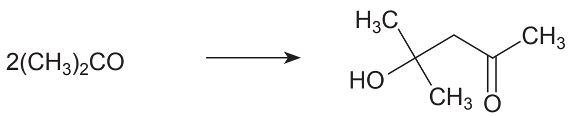


(iii)

Addition of amines produced a similar effect. Such selectivity effects was a theme Dowden often returned to.

4.2 Post-War Patents

A patent filed on 10th February 1949 concerned Raney-type catalysts made by alkali extraction of nickel/copper/aluminium alloys (38). This costly research must have taken a considerable amount of time and effort since it required specialised equipment for making alloys in addition to that for catalyst testing (the example given was hydrogenation of benzene to cyclohexane), and it was undertaken in the search for further ways of obtaining selective catalysed hydrogenations. This was followed by a patent (39) on the formation of diacetone alcohol (4-hydroxy-4-methyl-pentan-2-one) from the condensation of two molecules of acetone, Equation (iv), classically achieved using barium hydroxide, with a catalyst made by impregnating a lithium-stabilised alumina with molten calcium nitrate.



(iv)

An important feature was catalyst reactivation when necessary by calcinations at 750°C in air.

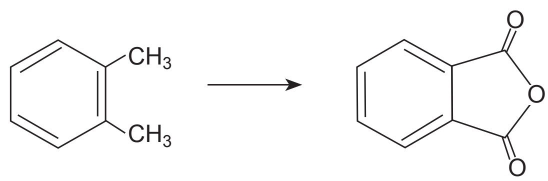
The next patent (40) disclosed an interesting method for producing a skeleton silica/alumina catalyst by heating a silica/alumina/alkaline earth glass to cause phase separation of the alkaline earth oxide followed by its dissolution in dilute hydrochloric acid. Applications mentioned for the catalyst so formed included hydrocarbon dealkylation and isomerisation as well as alcohol dehydration. An olefin hydration patent had been previously filed that claimed catalysts comprising a titania support with or without tungsten oxide and components such as antimony pentoxide and iron oxides (41).

4.3 Patents Concerning Key Processes

The ICI Billingham site was a major producer of nitrogen fertilisers, methanol and other commodity chemicals based on coal feedstock, and towards the end of the 1950s attention turned to the possibility of using straight-run naphtha that was increasingly available from European refineries as a more economic feedstock. Of the processes considered catalytic steam reforming was the most attractive, and while George Bridger was responsible for much of the catalysis work done in this area Dowden made a number of contributions especially in collaboration with Phin Davies on the use of platinum group metal catalysts with or without alkali (42), and addition of, for example, copper or silver to steam reforming catalyst (43). The effects of adding rhodium and other platinum group metals to alkalised and unalkalised nickel steam reforming catalysts was explored for operation at relatively low temperatures to produce methane rich gas for use as 'town gas' (44). With 'poison free' synthesis gas available from hydrocarbon steam reforming the use of downstream copper-based catalysts became possible and Dowden made contributions to copper-based low-temperature shift catalysts having a variety of compositions including standard copper/zinc oxide/alumina and those containing magnesia (45).

4.4 Selective Oxidation and Hydrogenation Reactions

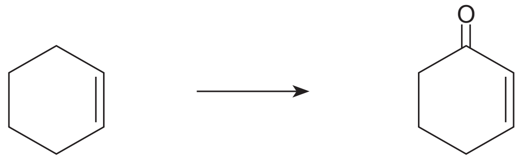
There was a period when Dowden's patents featured oxidation reactions and various metal vanadates were explored as oxidation catalysts for partial oxidation of short chain alkenes using catalysts prepared by fusing thallium, potassium or silver compounds with vanadium pentoxide, and by careful selection of reactant, catalyst and space velocity reaction conditions were obtained that gave encouraging conversions to oxygenated compounds, although the selectivity was not particularly high (46). Other oxidation processes that were worked on included the oxidation of aromatic compounds with the target of good selectivity and activity that included products such as phthalic anhydride from *ortho*-xylene, Equation (v), and naphthalene (47, 48).



(v)

The oxidation of *iso*-butene to various oxygenates was also explored (49).

The use of platinum group metal homogeneous catalysts was found to enable a number of useful low-temperature oxidations such as the selective oxidation of cyclo-hexene to 2-cyclo-hexenone, Equation (vi), (50).


(vi)

Other homogeneous catalysts, specifically cobalt cyano complexes, were also used in the selective hydrogenation of dienes, for example the formation of 1-butene from butadiene (51).

4.5 Carbon Formation in Steam Reforming

By the late 1950s it had been decided that the time of coal as a feedstock for synthesis gas production at Billingham was over, and much research had been done investigating the possibility of pressure steam reforming naphtha to provide relatively cheap synthesis gas. The main practical problem was preventing formation of carbon from the hydrocarbon feed, and two approaches were investigated. Dowden was involved in both. The first was through the use of platinum group metal catalysts that catalyse carbon formation much less than does nickel (42, 52, 53). In practice however it proved better commercially to use nickel steam reforming catalysts incorporating potassium to catalyse gasification of carbon with steam more quickly than it is formed, and Dowden examined the effect of additions of other metal components including about 5% copper (43).

4.6 Speculative Process Patents

In the decade before retirement Dowden worked on a wide variety of projects that included the selective oxidation of methane to methanol with some interesting results (54), the use of copper, cobalt and manganese catalyst formulations incorporated into self cleaning cooking oven surfaces (55), exploratory work on the formation of 2,2′-bipyridyl from pyridine (56), and the hydrogenation of adiponitrile to hexamethylenediamine catalysed by fused magnetite reduced with hydrogen containing a small amount of ammonia that enhanced the surface area of the active catalyst (57). Work on hydrocarbon reactions over stabilised zirconia formulations was initiated by a belief that doping zirconia would generate suitable acidic sites to catalyse hydrocarbon carbonium reactions facilitated by the presence of platinum (58, 59). It became understood that the actual active acidic component was sulfated zirconia and work in Billingham was halted mainly because of rapid progress elsewhere in zeolitic acid catalysis. However, much later the catalytic properties of sulfated zirconia were intensively studied (60).

5. Retirement and Beyond

In 1973 Dowden's wife Iris died after a long illness, leaving him alone just as his retirement was approaching and his children were leaving home for life abroad (daughter Diana) and university studies (son Simon). During this time Dowden's influential work was recognised by prestigious awards: The Chemical Society Industrial Medal in 1973 and a Frank G. Ciappeta National Lecturer of the American Catalysis Society in 1974. Later in 1996 Dowden was awarded the International Congress on Catalysis Diploma in recognition of a lifetime's service to the community of catalytic scientists.

Dowden was notably busy during retirement and he continued to be academically active (**Figure 4**). He was already a visiting professor at Imperial College London, UK, where he gave a series of lectures on catalyst design and he became a Research Fellow at Edinburgh University, UK, in 1975 where he shared accommodation with his son who was a student there. He was also a consultant and expert witness in patent litigation, he attended conferences whenever he could, wrote review articles and still he found time to visit ICI at Billingham often to keep abreast with the latest advances. He had been involved in a specialised debate with eminent scientists on the activation of hydrocarbons (61), and he became involved in research projects at Edinburgh University on hydrogen spillover (62) and ammonia synthesis (63, 64). The Head of Department there, Professor Charles Kemball, was chairman of the Publications Board of The Chemical Society and he actively solicited contributions to their publications (and especially ones he edited). As a result Dowden made several major contributions to the Chemical Society's *Specialist Periodical Report – Catalysis*, three early volumes of which he edited with Kemball (65–67). The chapters he wrote in *Catalysis* were on reactions of hydrocarbons on multimetallic catalysts (68) and spillover of chemisorbed species

Fig. 4. Dowden in 2005. He remained active for several years after retirement from ICI attending international conferences, lecturing and writing articles. He very much enjoyed his retirement with family and friends that was as long as his career in ICI, during this time he maintained contact with several former colleagues having regular lunch meetings with them

(69). He also prepared two long scholarly chapters on catalysis published in the Chemical Society's *Annual Reports on the Progress of Chemistry* (70, 71). Among his last academic publications was one based on a presentation given at an international conference on catalyst deactivation in the Algarve, Portugal during 18th–29th May 1981 (72). Rather fittingly his last publication listed in *Chemical Abstracts* is entitled 'The Catalysis of Synthesis Gas Production' reflecting his career at ICI Billingham and which appeared in the proceedings of the Priestly Conference held in London in 1983 (73).

6. Conclusions

With the death of Dowden on 16th June 2012 we lost one of the principal figures in catalysis, and especially in industrial catalysis, of the twentieth century. His work covered a wide area of academic and industrial catalysis and as a result he had a very broad knowledge in all of its aspects that in later life he was always very happy to share with others in constructive conversations. Invariably he showed an almost old-fashioned politeness, geniality and charm to everyone he met, and when he encountered spite or envy he was surprised and dismissed it with just a shrug. After he was retired he still regularly attended annual ICI meetings of academic workers, lectured at international conferences giving review lectures, and wrote many scholarly articles. At the Durham meeting to commemorate his life and work (74) it was notable that many people who had interacted with Dowden remarked on the help they received from him irrespective of whether they were students or senior people. His life ran parallel to the growth of catalysis and he contributed much to its development and fundamental understanding. He received various medals and awards in the USA and UK. His legacy is perhaps best illustrated by a comment given to one of the present authors by Professor Enrique Iglesia at the EUROPACAT IX international catalysis conference held at Salamanca in 2009: that his opening address to the conference was essentially Dowden's work brought up to date.

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11. References

1. E. K. Rideal,'James William McBain 1882–1953', *Obit. Not. Fell. R. Soc.,* 1953, **8**, (22), 529
2. C. E. H. Bawn, 'William Edward Garner 1889–1960', *Biogr. Mems Fell. R. Soc.,* 1961, **7**, 85
3. S. Brunauer, P. H. Emmett and E. Teller, *J. Am. Chem. Soc.*, 1938, **60**, (2), 309
4. R. A. Beebe, *Proc. Amer. Phil. Soc*., 1939, **81**, (1), 1
5. R. A. Beebe and D. A. Dowden, *J. Am. Chem. Soc.*, 1938, **60**, (12), 2912
6. D. A. Dowden and W. E. Garner, *J. Chem. Soc.*, 1939, 893
7. "Theodore W. Richards - Nobel Lecture: Atomic Weights", from Nobel Lectures, Chemistry 1901–1921, Elsevier Publishing Company, Amsterdam, The Netherlands, 1966
8. H. Davy, *Phil. Trans. R. Soc. Lond.*, 1817, **107**, 77
9. P. Phillips, 'Manufacture of Sulphuric Acid', *British Patent* 6096; 1831
10. E. Cook, *Nature*, 1926,**117**, 419
11. M. Appl, "Ammonia: Principles and Industrial Practice", Wiley-VCH, Weinheim, Germany, 1999
12. L. Lloyd, "Handbook of Industrial Catalysts", Fundamental and Applied Catalysis, Vol. 22, Springer, New York, USA, 2011
13. A. Mittasch and W. Frankenburg, *Adv. Catal*., 1950, **2**, 81
14. K. Tamaru, 'The History of the Development of Ammonia Synthesis', in "Catalytic Ammonia Synthesis: Fundamentals and Practice", ed. J. R. Jennings, Fundamental and Applied Catalysis, Vol. 20, Plenum Press, New York, USA, 1991, pp. 1–18
15. S. P. S. Andrew, *Chemtech*, 1979, **9**, (3), 180
16. D. L. Trimm, "Design of Industrial Catalysts", Elsevier, Amsterdam, The Netherlands, 1980
17. D. A. Dowden, *Research (London)*, 1948, **1**, 239
18. D. A. Dowden, *J. Chem. Soc*., 1950, 242
19. D. A. Dowden and P. W. Reynolds, *Discuss. Faraday Soc.*, 1950, **8**, 184
20. E. K. Rideal and H. S. Taylor, "Catalysis in Theory and Practice", Macmillan and Co Ltd, London, UK, 1919, p. 496
21. D. A. Dowden, *Ind. Eng. Chem.*, 1952, **44**, (5), 977
22. W. E. Garner, D. A. Dowden and J. F. Garcia de la Banda, *Anales de la Real Sociedad Española de Física y Química, Serie B: Química*, 1954, **50B**, 35
23. B. C. Alsop and D. A. Dowden, *J. Chim. Phys. PCB*,1954, **51**, 678
24. D. A. Dowden, N. Mackenzie and B. M. W. Trapnell, *Proc. R. Soc. Lond. A*, 1956, **237**, (1209), 245
25. D. A. Dowden, N. Mackenzie and B. M. W. Trapnell, *Adv. Catal*., 1957, **9**, 65
26. D. A. Dowden, 'Chemisorption and Valency', in "Chemisorption: Proceedings of a Symposium Held at the University College of North Staffordshire, Keele, Staffordshire, 16th–19th July, 1956", ed. W. E. Garner, Butterworths Scientific Publications, London, UK, 1957, pp. 3–16
27. D. A. Dowden, *Bull. Soc. Chim. Belges*, 1958, **67**, (7–8), 439
28. D. A. Dowden and G. W. Bridger, *Adv. Catal*., 1957, **9**, 669
29. C. Kemball, *Catal. Rev*.: *Sci. Eng.*, 1972, **5**, (1), 33
30. G. C. Bond, D. A. Dowden and N. Mackenzie, *Trans. Faraday Soc.*, 1958, **54**, 1537
31. D. A. Dowden, *Catal. Rev.: Sci. Eng.*, 1972, **5**, (1), 1
32. D. A. Dowden, C. R. Schnell and G. T. Walker, 'Design of complex catalysts', in "Proceedings of the Fourth International Congress on Catalysis", Moscow, Russia, 23rd–29th June, 1968, Volume 2, Akadémiai Kiadò, Budapest, Hungary, 1971, pp. 201–215
33. D. A. Dowden, 'Crystal and Ligand Field Models of Solid Catalysts', in "Proceedings of the Fourth International Congress on Catalysis", Moscow, Russia, 23rd–29th June, 1968, Volume 1, Akadémiai Kiadò, Budapest, Hungary, 1971, pp. 163–186
34. D. A. Dowden, C. R. Schnell and G. T. Walker, 'Creation of Complex Catalysts', in Osn. Predvideniya Katal. Deistviya, Tr. Mezhdunar. Kongr. Katal., ed. Ya. T. Eidus, Nauka, Moscow, Russia, 1970, Volume 2, pp. 198–210

35. D. A. Dowden, 'Electronic Structure and Ensembles in Chemisorption and Catalysis by Binary Alloys', in "Proceedings of the Fifth International Congress on Catalysis", Miami Beach, Florida, USA, 20th–26th August, 1972, ed. J. W. Hightower, North-Holland Publishing Company, Amsterdam, The Netherlands, Volume 1, pp. 621–634
36. J. G. M. Bremner, R. H. Stanley, A. W. C. Taylor and D. A. Dowden, ICI Ltd, 'Improvements in and Relating to the Production of 1,5-Pentanediol', *British Patent* 576,087; 1946
37. J. G. M. Bremner, F. Starkey and D. A. Dowden, ICI Ltd,'Catalytic Hydrogenation of Alkenyl Furans', *US Patent* 2,519,631; 1945
38. P. W. Reynolds, D. A. Dowden and J. A. Mackenzie, ICI Ltd, 'Preparation of Copper-Nickel-Aluminium Catalysts', *US Patent* 2,673,189; 1954
39. F. R. Charlton and D. A. Dowden, ICI Ltd, 'Aldal Condensation', *US Patent* 2,664,446; 1953
40. D. A. Dowden, L. V. Johnson and G. C. Vincent, ICI Ltd, 'Improvements in and Relating to the Production of Alumina/Silica Catalysts', *British Patent* 765, 468; 1953
41. D. A. Dowden, ICI Ltd, 'Improvements in and Relating to the Hydration of Olefines', *British Patent* 718,723; 1951
42. P. Davies and D. A. Dowden and C. Michaelstone, ICI Ltd, 'Improvements in and Relating to the Steam Reforming of Hydrocarbons', *British Patent* 1,029,235; 1961
43. D. A. Dowden and P. Davies, ICI Ltd, 'Improvements in or Relating to the Steam Reforming of Hydrocarbons and Catalysts therefor', *British Patent* 1,032,754; 1962
44. D. A. Dowden and P. Davies, ICI Ltd, 'Improvements to and Relating to Steam Reforming Processes', *British Patent* 1,032,752; 1962
45. P. Davies, A. J. Hall and D. A. Dowden, ICI Ltd, 'Catalysts of High Activity at Low Temperature', *British Patent* 1,131,631; 1965
46. D. A. Dowden and A. M. U. Caldwell, ICI Ltd, 'Improvements in and Relating to Oxidation Processes', *British Patent* 828,812; 1956
47. D. A. Dowden and A. M. U. Caldwell, ICI Ltd, 'Improvements in and Relating to Oxidation of Aromatic Hydrocarbons', *British Patent* 883, 314; 1957
48. D. A. Dowden and A. M. U. Caldwell, ICI Ltd, 'Improvements in and Relating to Catalysts', *British Patent* 883,315; 1957
49. D. A. Dowden and A. M. U. Caldwell, ICI Ltd, 'Oxidation Processes', *US Patent* 2,995,528; 1961
50. D. A. Dowden and M. S. Spencer, ICI Ltd, 'Improvements in and Relating to Oxidation of Hydrocarbons', *British Patent* 928,443; 1960
51. M. S. Spencer and D. A. Dowden, ICI Ltd, 'Selective Hydrogenation of Conjugated Diolefines to Monoolefines', *US Patent* 3,009,969; 1959
52. D. A. Dowden, ICI Ltd, 'Steam Reforming of Hydrocarbons', *US Patent* 3,222,132; 1961
53. D. A. Dowden and N. Harris, ICI Ltd, 'Steam Reforming Hydrocarbons', *British Patent* 1,211,847; 1967
54. D. A. Dowden and G. T. Walker, ICI Ltd, 'Oxygenated Hydrocarbons Production', *British Patent* 1,244,001; 1968
55. P. J. Denny and D. A. Dowden, ICI Ltd, 'Catalytic Composition', *US Patent* 3,718,498; 1971
56. R. F. Dalton, D. A. Dowden and G. H. Lang, ICI Ltd, 'Preparation of 2,2′-Bipyridyls', *British Patent* 1,377,213; 1971
57. T. G. Dewdney, D. A. Dowden. W. Morris and B. D. Hawkins, ICI Ltd, 'Catalysts and their Use in Hydrogenation', *British Patent* 1,486,890; 1973
58. D. A. Dowden, I. R. Shannon and M. S. Spencer, ICI Ltd, 'Treating Hydrocarbons', *British Patent* 1,391,453; 1971
59. D. A. Dowden, I. R. Shannon and M. S. Spencer, ICI Ltd, 'Treating Hydrocarbons', *British Patent* 1,405,097; 1971
60. X. Song and A. Sayari, *Catal. Rev.: Sci. Eng.*, 1996, **38**, (3), 329
61. G. W. Parshall, M. L. H. Green, F. Calderazzo, D. A. Dowden, F. G. Gault, J. Halpern, G. A. Hamilton, C. Kemball, S. J. Teichner and H. C. Volger, *Catal. Prog. Res., Proc. NATO Sci. Comm. Conf.,* Meeting Date 1972, 165–176, eds. F. Basolo, R. L. Burwell, Jr, Plenum Press, London, UK, 1973
62. D. A. Dowden, I. H. B. Haining, J. D. N. Irving and D. A. Whan, *J. Chem. Soc., Chem. Commun.*, 1977, (18), 631
63. D. W. Taylor, P. J. Smith, D. A. Dowden, C. Kemball and D. A. Whan, *Appl. Catal.*,1982, **3**, (2), 161
64. P. J. Smith, D. W. Taylor, D. A. Dowden, C. Kemball and D. Taylor, *Appl. Catal.,* 1982, **3**, (4), 303
65. "A Specialist Periodical Report: Catalysis", eds. C. Kemball and D. A. Dowden, The Chemical Society, London, UK, 1978, Vol. 2, 276 pp
66. "A Specialist Periodical Report: Catalysis", eds. C. Kemball and D. A. Dowden, The Chemical Society, London, UK, 1980, Vol.3, 285 pp

67. "A Specialist Periodical Report: Catalysis", eds. C. Kemball and D. A. Dowden, The Chemical Society, London, UK, 1981, Vol. 4, 253 pp

68. D. A. Dowden, 'The Reactions of Hydrocarbons on Multimetallic Catalysts', in "A Specialist Periodical Report: Catalysis", eds. C. Kemball and D. A. Dowden, The Chemical Society, London, UK, 1978, Vol. 2, pp. 1–27

69. C. Kemball and D. A. Dowden, 'The Spillover of Chemisorbed Species', in "A Specialist Periodical Report: Catalysis", eds. C. Kemball and D. A. Dowden, The Chemical Society, London, UK, 1980, Vol. 3, pp. 136–168

70. D. A. Dowden, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*,1979, **76**, 3

71. D. A. Dowden, *Annu. Rep. Prog. Chem., Sect. C: Phys. Chem.*,1982, **79**, 99

72. D. A. Dowden, 'The Catalytic Effects of Water and Halogens on the Alteration of Catalyst Surfaces', in "Proceedings of the NATO Advanced Study Institute on Progress in Catalyst Deactivation", ed. J. L. Figueiredo, Algarve, Portugal, 18th–29th May, 1981, NATO Science Series E, 1982, Vol. 54, p. 281

73. D. A. Dowden, 'The Catalysis of Synthesis Gas Production', in "Oxygen and the Conversion of Future Feedstocks", Proceedings of the Third BOC Priestley Conference, September, 1983, Royal Society of Chemistry, London, UK, 1984, Special Publication No. 48, pp. 31–61

74. M. V. Twigg, 'Dennis A Dowden - An Appreciation of a Life in Catalysis', Dennis Dowden Commemoration 'Catalysis – From Fundamentals to Application', Durham University, UK, 3rd–4th April, 2013

75. M. V. Twigg and M. S. Spencer, *Appl. Catal. A: Gen.*, 2014, **473**, 146

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Following Fellowships at the Universities of Toronto and Cambridge Martyn Twigg joined a polymer group at ICI's Corporate Laboratory in the North West of England, and after involvement in projects at Agricultural Division at Billingham moved there in 1977. He knew Dennis Dowden as a "Catalysis Sage" and discussions with him were important in understanding fundamental catalyst concepts. Martyn worked on catalysts and catalytic processes including synthesis gas production *via* naphtha and natural gas steam reforming, methanol and ammonia synthesis, and proprietary catalysts and processes for herbicide manufacture and environmental protection applications. He studied catalyst activation and built a much used off-site catalyst reduction unit. After managing an international polymerisation project he was head-hunted to work at Johnson Matthey as Technology Director in the autocatalyst area that he successfully led until being appointed Chief Scientist. This provided an opportunity for research diversity that included carbon nanotube manufacture and catalyst medical applications. He was associated with four Queen's Awards, and was awarded the Royal Society of Chemistry Applied Catalysis Prize. He has more than 200 papers, co-authored books on transition metal mediated organic syntheses and catalytic carbonylation. He produced the "Catalyst Handbook", co-edits the Fundamental and Applied Catalysis series with Michael Spencer, and has 150 published patent families on catalysts and catalytic processes. He opened the symposium 'Dennis Dowden Commemoration, Catalysis – From Fundamentals to Application' held at the University of Durham in 2013 with a lecture 'Dennis A Dowden – An Appreciation of a Life in Catalysis'. Martyn has on-going collaborations with universities and holds honorary academic positions, and runs an active consultancy and catalyst development business.

Michael Spencer graduated in Natural Sciences at Cambridge University and studied the kinetics of gas-phase chlorination reactions there with P. G. Ashmore gaining a PhD. In 1957 he moved to the Research Department of ICI Billingham Division, in the North East of England, initially working with Dennis Dowden and several patents resulted. He spent all his industrial career at ICI in research becoming an ICI Science Associate and until Dennis Dowden's death in 2012 he had a highly professional, hugely enjoyable and extremely rewarding relationship with him. He worked mostly on a wide variety of topics in catalysis and also on other industrial subjects relevant to ICI such as electrochemistry, nitrogen fixation in electric discharges and crystallisation processes. In catalysis he made major contributions to existing processes, such as methane/steam reforming and methanol synthesis, and also to the assessment of novel catalytic reactions for industrial use. In 1987 he was appointed Professor in the School of Chemistry, Cardiff University, Wales, where he has been involved in both teaching and research. Recent research work has included studies on the origins and the control of catalyst deactivation. He has over 150 publications, covering scientific papers, patents, book contributions and various articles of general interest. With Martyn Twigg he is co-editor of the book series Fundamental and Applied Catalysis, and currently he is working on a book about Welsh scientists.

