

Advances in Catalysis
Volume 44

ADVANCES IN CATALYSIS

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Edited by

WERNER O. HAAG†

Lawrenceville, New Jersey

†Deceased

BRUCE C. GATES

University of California

Davis, California

HELMUT KNÖZINGER

University of Munich

Munich, Germany



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Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

- MASAKAZU ANPO, *Department of Applied Chemistry, College of Engineering, Osaka Prefecture University, Sakai, Osaka 599-8531, Japan* (119)
- CARROLL O. BENNETT, *Laboratoire de Réactivité de Surface, Université Pierre et Marie Curie, 75005 Paris Cedex, France* (329)
- MICHEL BOUDART, *Department of Chemical Engineering, Stanford University, Stanford, California 94305* (xxi)
- MICHEL CHE, *Laboratoire de Réactivité de Surface, UMR 7609-CNRS, Université Pierre et Marie Curie, 75005 Paris Cedex, France* (xxi, 119)
- JEAN GRIMBLot, *Laboratoire de Catalyse Hétérogène et Homogène, URA CNRS 402, Université des Sciences et Technologies de Lille, 59655 Villeneuve d'Ascq Cedex, France* (417)
- RYUICHIRO IWAMOTO, *Petroleum Refining Technology Center, Idemitsu Kosan Co. Ltd., Sodegaura, Chiba 299-0293, Japan* (417)
- PAUL MÉRIAUDEAU, *Institut de Recherches sur la Catalyse—CNRS, 69626 Villeurbanne Cedex, France* (505)
- CLAUDE NACCACHE, *Institut de Recherches sur la Catalyse—CNRS, 69626 Villeurbanne Cedex, France* (505)
- BERNARD E. NIEUWENHUY, *Leiden Institute of Chemistry, Gorlaeus Laboratories, Leiden University, Leiden 2300 RA, The Netherlands* (259)
- FRANK S. STONE, *Department of Chemistry, University of Bath, Bath BA2 7AY, England* (xvii)
- J. J. VAN DER KLINK, *Institut de Physique Expérimentale, Département de Physique, Ecole Polytechnique Fédérale de Lausanne, CH-1015 Lausanne, Switzerland* (1)
- PAUL B. WEISZ, *Foxdale Village, A-1, State College, Pennsylvania 16801* (xiii)

Preface

We note with sadness that this is the last volume of *Advances in Catalysis* edited by our colleague Werner Haag, who passed away last year. The catalysis community will miss him. His obituary appears in this volume.

This issue of the *Advances* reflects the expanding impact of experimental surface characterization on the understanding of catalysis. The catalysts emphasized here are representative of the complexity of today's technology; examples include catalysts for hydrocarbon re-forming, automobile exhaust conversion, and hydroprocessing to make clean-burning fossil fuels.

Nuclear magnetic resonance (NMR) spectroscopy continues to gain importance in catalyst characterization, and van der Klink contributes the first chapter on metal NMR to the *Advances*; the focus is on supported platinum catalysts, including those with adsorbed carbon monoxide or hydrogen. The method provides evidence of metal dispersions and distinguishes between hydrogen on the metal and hydrogen on the support.

Anpo and Che write about applications of photoluminescence techniques, which are powerful but only seldom used methods for the identification of surface sites and their local environments, particularly on oxide surfaces. The dynamics of energy and electron transfer processes are discussed in light of catalytic and photocatalytic phenomena.

Nieuwenhuys summarizes the understanding of supported metal catalysts for automobile exhaust abatement as it has developed from ultrahigh-vacuum surface science. The account is an impressive validation of the success of the surface science methods for elucidation of complex multicomponent catalysts.

The quantitative foundation of catalysis is kinetics, and lively recent developments in this field center around transient experiments, many quite elegant, as summarized in the chapter by Bennett.

Because of their widespread applications, hydroprocessing catalysts have been the subjects of chapters in two of the preceding three volumes of this series. Iwamoto and Grimblot add another chapter, focusing on the roles of phosphorus in these multicomponent catalysts.

Mériaudeau and Naccache conclude the volume with a concise description of skeletal isomerization of butenes catalyzed by medium-pore zeolites and molecular sieves. This isomerization is a relatively new industrial process, and it is remarkable how fast a good fundamental understanding of it has developed in a few years; the chapter is an account of catalysis by well-defined acidic groups in pores that exert a subtle control over catalyst performance, including selectivity. It is a story that was deeply appreciated by Werner Haag.

B. C. GATES
H. KNÖZINGER

Werner Otto Haag, 1926–1998

We have lost the presence of an exceptional scientist, but we have been enriched by the legacy of his contributions to basic catalytic science and to catalytic process technology. Werner Haag, born in Heilbronn, Germany, studied chemistry at the University of Tübingen and receiving his diploma (M.S. equivalent) in 1954. His doctoral work at Northwestern University with Professor Herman Pines provided him with an early introduction to heterogeneous catalysis (1958). He joined the research staff of the Mobil Oil Corporation in 1959, where he rose to the position of senior scientist in 1981 and laboratory advisor, the highest technical position. Upon his retirement in 1993, he remained active as a consultant. He became a research associate at the Fritz Haber Institute of the Max Planck Gesellschaft in Berlin, continuing his research activities as well as being a teacher to colleagues and students. He continued to be an active contributor to catalysis symposia and to interact with research colleagues internationally. Untiringly, he also found time to write two chapters for the *Handbook of Heterogeneous Catalysis* (G. Ertl, H. Knözinger, and J. Weitkamp, Eds., Wiley-VCH, Weinheim, 1997). He had been coeditor of *Advances in Catalysis* since 1994. His dedication went beyond that of the usual editorship. He often devoted time and effort to help authors expand and improve presentations by pointing to related issues and subjects.

Werner's contributions to catalysis were unique. They combined delving deeply into basic science with a keen awareness of technological relevance and utility. In addition, his ever readiness to share ideas, knowledge, and skills with others provided inspiration to research colleagues worldwide and patient guidance to new process development at Mobil. A proper recitation of his gifts to our science would fill a chapter of these *Advances*, but we must most certainly record the resolution he has provided to major and classical mysteries of heterogeneous catalysis. In addition, we must record his demonstration of new basic principles leading to the creation of new catalytic processes.

Two or three decades ago, no clear conceptual (mechanistic) or practical (experimental) bridge existed between homogeneous and heterogeneous catalysis. In some of his earliest work at Mobil, Werner demonstrated that hydroformylation, carbonylation, and other reactions catalyzed by transi-

tion metal complexes were accomplished equally by heterogeneous catalysis when these complexes were anchored to solid organic resins.

The seeds implanted by his early work with Herman Pines in acid catalysis grew into blossoming flowers: He developed an ever-growing and detailed map of the applicable carbonium and carbenium ion mechanisms in hydrocarbon conversion and their relationships to achievable product distributions. He provided the long-sought bridge between heterogeneous acid catalysis and the superacid chemistry of George Olah (recognized by the 1994 Nobel Prize in chemistry) when he, with his able associate Ralph Dessau, demonstrated the occurrence of direct protonation of paraffins to give pentacoordinated carbonium ions as a step initiating paraffin cracking.

The discovery that crystalline zeolites could be turned into active catalysts provided a plethora of challenges for research, basic and applied. Werner participated in both and brought findings in one activity to guide the other! The "active site," proposed by H. S. Taylor in 1925, had remained a prime mystery parameter in the science of heterogeneous catalysis. Could we identify or even count the active sites? Werner Haag was the center of generating and coordinating the research. By demonstrating the quantitative correlation of rate constants of hydrocarbon reactions with Al contents, Cs ion exchange capacity, as well as nuclear magnetic resonance quantification of tetrahedrally coordinated Al atoms in the silica structure of many ZSM-5 catalysts, he both identified and counted the active sites!

Another old "mystery" in heterogeneous catalysis, dating back to F. H. Constable (1925) and G.-M. Schwab (1929), was the "compensation effect" or "theta rule." The Arrhenius plots for similar reactants on the same catalyst or for the same reactant on similar catalysts would differ in slope across a common point of intersection. Approximately 70 years later, a First Workshop on the Compensation Effect was organized (DECHEMA, Berlin, 1997) to debate this enduring mystery. Werner Haag demonstrated that such an effect must necessarily result from the temperature dependence of reactant adsorption (and hence its site concentration) and that of the reaction rate of the adsorbed species, operating in opposite directions. A "second" workshop may never follow!

When published reports of the diffusivity of paraffins in ZSM-5 catalysts obtained from uptake rate measurements appeared grossly inconsistent with catalytic behavior, Werner participated in resolving the problem by determining diffusivities from catalytic behavior of catalysts of very different particle sizes. The analysis not only confirmed the many orders of magnitude higher true diffusivities but also allowed Werner to extend the technique to demonstrate that "shape selectivity" could occur due to lack of fit of a reactant (e.g., diffusion of a dimethyl paraffin) in the structure

or lack of fit of a reaction complex (transition state) that must be created on the active site (e.g., the methyl paraffin/propyl cation complex).

This and Werner's extensive investigations of reactions of aromatics led to a comprehensive view of the three ways by which molecular shapes and sizes can lead to unusual product selectivities: These are, for the competing species participating, differences in diffusion rates, equilibrium sorption constants, and relative sizes of the transition state (active site complex).

Werner Haag was both a scientist and a technologist. This is somewhat reflected by more than 70 U.S. patents that bear his name. A better illustration may be his essential contributions to the currently practiced paraxylene production processes. They provide 30% or more of worldwide production of this raw material for polyester. Probably a majority of readers are wearing clothing made from these molecules.

We will miss the constant enthusiasm for exploration and innovation, generosity, modesty, inspiration, cooperation, and friendship that Werner brought to so many of us. However, his many solid and lasting contributions will live on and grow in catalytic science and technology.

PAUL B. WEISZ

Charles Kemball, 1923–1998

Charles Kemball, who died on September 4, 1998, will be long remembered for his wide-ranging research on deuterium exchange reactions and for the insight he provided into the mechanisms of hydrocarbon reactions on metal and oxide catalysts. He was a leading figure in academic life in the United Kingdom for almost 40 years, highly respected, instantly recognizable, and widely sought for his skills in administration and management. He was one of the most distinguished British physical chemists of his generation.

Born in Edinburgh on March 27, 1923, the son of a dental surgeon, he was educated at Edinburgh Academy until 1940, when he attended Trinity College, Cambridge. He graduated with First Class Honors in both parts of the Cambridge Natural Sciences Tripos in 1943 and in the same year began research in the Department of Colloid Science of the university with Professor E. K. Rideal. At that time during the war, Rideal was carrying out work for the Ministry of Aircraft Production on adhesives and bonding to surfaces. Clean metal surfaces had been a concern of Rideal and others in Cambridge in the 1930s and Kemball was given the job of designing an apparatus to study the adsorption of hydrocarbons on a uniquely clean metal surface—that of freshly distilled liquid mercury. He did this by measuring the change in the surface tension of sessile drops. Because the adsorption of hydrocarbons on mercury was reversible, it was amenable to thermodynamic treatment, and Kemball used the entropy change to diagnose the degrees of freedom lost on adsorption. This work, which led to his Ph.D. in 1946, inculcated a respect for thermodynamic argument which was to surface frequently in his papers in the future.

Kemball kept an active interest in physical adsorption for several years, but a defining change came in 1946 with the award of a fellowship from the Commonwealth Fund of New York for research and travel in the United States. Influenced by Eric Rideal's long-standing friendship with Hugh S. Taylor, who had known Rideal since World War I when they worked together in London on the catalysis of carbon monoxide oxidation, Charles chose to spend his fellowship year with Professor Taylor at Princeton University. Here he was introduced to experimental work on catalysis and, significantly, to mass spectrometric analysis. He worked on the hydrogen-

lysis and decomposition of ethane, an investigation which stemmed from the ethane–deuterium exchange studies pioneered by H. S. Taylor and K. Morikawa at Princeton shortly after the discovery of deuterium in 1933. Kemball was greatly inspired by this experience. Returning to Cambridge, where he had been appointed a fellow of Trinity College, he used a grant from the Rockefeller Foundation to build a mass spectrometer and began a study of the exchange reaction of methane with deuterium catalyzed by evaporated nickel films. A feature of his technique was the continuous analysis of the reaction mixture by bleeding small amounts via a capillary leak directly to the adjacent mass spectrometer. This method of working was to become the mainstay of his research on deuterium exchange reactions for the rest of his career, albeit it was complemented eventually by other methods of isotope analysis.

Kemball's work on methane exchange, published in 1951, paved the way for further studies, notably with J. R. Anderson, on the exchange reactions of hydrocarbons and their derivatives on metal films. Much of this work has become classical. He introduced procedures for calculating the yields of deuterated molecules for comparison with experimental results, a methodology which has proved extremely useful in defining the mechanisms of the surface reactions of hydrocarbons.

In 1951 Kemball was appointed junior bursar at Trinity College, and recognition of his ability to combine administrative and research endeavor came with his appointment in 1954, when only 31 years old, to the chair of physical and inorganic chemistry in the Queen's University of Belfast. The university, at that time the only one in Northern Ireland, was constructing an impressive new building for chemistry, and Kemball soon found himself endowed with ample space for research and with able staff and students ready to join him in lines of work linked to his own interests. He remained at Queen's for 12 years, which was a very successful period in which he established the laboratory as a leading center of catalysis research, one which became internationally known and extensively visited by both academics and industrial researchers. F. G. Gault, R. B. Anderson, J. W. Hightower, and S. Siegel were among those who came from abroad for research visits.

In Belfast Charles met Kathleen (Kay) Lynd and they were married in 1956. From 1957 to 1960 he was dean of the science faculty and from 1962 to 1965 vice president of the university. He was honored both at home and abroad. The Chemical Society awarded him its Corday–Morgan Medal and later a Tilden lectureship. In 1962 he was awarded the Ipatieff Prize of the American Chemical Society. In 1965 he was elected a fellow of the Royal Society.

His research in Belfast remained centered on deuterium exchange reac-

tions, not only of hydrocarbons but also of derivatives such as ketones and mercaptans, but always with emphasis on the intermediates and how they were bonded to the surface. His mechanisms for reactions grew more sophisticated as the reactions studied became more complex. Together with J. J. Rooney, he enjoyed regular friendly sparring with R. L. Burwell, G. C. Bond, and others on the skillfully imagined (and still debated) roles played by π -bonded intermediates and by mechanisms of rollover and even, as he once suggested, rock and roll! Charles viewed the catalyst principally as an agent for providing adsorption sites able to give a particular type of bonding or a certain strength of bonding. He was content to leave others to debate what many viewed as equally great issues, such as the role of electronic, ionic, or crystallographic structure of the catalyst in activating or orientating chemisorbed molecules. Nevertheless, he investigated a wide range of metals as catalysts, the use of films being well suited to this, and established patterns of activity and selectivity differences between metals which remain very relevant for catalytic re-forming and the synthesis of fine chemicals.

In 1966 Kemball returned to Scotland to take up the chair of chemistry at the University of Edinburgh. His choice of catalysts became more versatile. With D. A. Whan he studied molybdenum obtained by carbonyl decomposition on alumina. Oxides and zeolites featured strongly among the solids whose catalytic properties he investigated, notably with assistance from H. F. Leach. Carbenium ion and carbanion mechanisms in deuterium exchange and isomerization became part of the repertoire, and there were often salutary reminders in his admirably clear papers of the interplay between thermodynamic and kinetic control in the catalytic reactions investigated.

His lucid and crisp style of writing had its counterpart in management. He was much in demand on this account and participated increasingly in chemistry on the national scene. He was president of the Royal Institute of Chemistry (1974–1976) and chairman of the publications board of the Chemical Society (1973–1981). He was a natural choice to act as chairman of the organizing committee for the 6th International Congress on Catalysis (ICC) held in London in 1976 and was subsequently president of the ICC Council, officiating at the congress in Tokyo in 1980. In Edinburgh he was dean of the science faculty from 1975 to 1978, a time of great financial trial for UK universities. His administrative skill and sense of fairness served the University of Edinburgh well.

A cardinal problem in the use of deuterium in catalytic reactions which remained to be addressed when Kemball moved to Edinburgh was that of locating the precise positions of the D atoms in the hydrocarbon or related products. By 1970 K. Hirota and his group in Japan had shown that the

rotational spectra of C_3 and C_4 deuterated hydrocarbons obtained by microwave spectroscopy provided a viable solution. Kemball searched for an opportunity to followup this discovery and, together with C. S. John, teamed up with J. K. Tyler in Glasgow to apply this method of analysis. However, it involved transport of samples in all weathers from Edinburgh to Glasgow and the method was limited to fairly small hydrocarbons. A much better prospect soon emerged, namely, the exploitation of nuclear magnetic resonance (NMR) spectroscopy for which there were good facilities in Edinburgh and expertise on hand from I. H. Sadler. The successful application of NMR spectroscopy to determine deuterium positions, coupled with gas-chromatographic and mass-spectrometric analysis, was Kemball's most notable contribution in the 1980s. It enabled previously proposed mechanisms to be checked and, when necessary, amended, and it opened the way to an extensive scenario for the future in the field of isotope-assisted kinetic analysis.

Kemball retired from the Chair of Chemistry in 1983, and from 1988 to 1991 he enjoyed the distinction of being president of the Royal Society of Edinburgh. He continued his research activity for another 10 years or so after 1983 as a university fellow. Toward the end of his career he had renewed his long-time interest in hydrogenolysis in a joint Edinburgh-Yale study with G. L. Haller of alkane decomposition on supported alloys. Charles always appreciated his links with the catalysis scene in America, and it was fitting that one of the last conferences he attended was the inaugural H. S. Taylor Conference in Nottingham in 1996. Those of us who were his contemporaries remember with affection his many contributions at conferences, some of which twinkled with mischief but all of which were stimulating. Not least among these conferences were the triennial Rideal conferences which he initiated in Belfast in 1961 (and which still continue). However, perhaps the meetings which gave him the greatest personal pleasure were the informal annual conferences which he held for his local colleagues and privileged guests at Firbush on the shore of Loch Tay, among the Scottish mountains with whose Munro summits he was intricately familiar, and walking on their slopes was his favorite outdoor recreation.

FRANK S. STONE

John Turkevich, 1907–1998

John died peacefully in Lawrenceville, New Jersey, on March 25, 1998. With him, the catalysis community lost one of its strongest and most fascinating personalities.

Born in Minneapolis in 1907, he was the eldest son of the Primate of the Russian Orthodox Church in the United States. He was educated first at Dartmouth (B.S. and M.S. degrees) and then at Princeton where he obtained a second M.S. degree in 1932. He defended his Ph.D. thesis in 1934, on the adsorption of hydrocarbons on oxide catalysts; this work was performed under the supervision of Sir Hugh Taylor. During the academic year 1935–1936, he did postdoctoral research at Cambridge University with Sir J. E. Lennard Jones and at Leipzig University with K. Bonhoeffer on quantum chemistry. He was appointed to the Princeton faculty in 1936, became full professor in 1952, and was named to the Eugene Higgins Chair in 1955. He was a very talented teacher and for many years taught a most popular freshman chemistry course. He retired from full-time teaching in 1975 but continued his research at Princeton for 20 years. Many of us will remember his enthusiastic talk on cancer chemotherapy at the International Congress on Catalysis in Baltimore in 1996. He delivered his last lecture at Princeton on October 9, 1997, at the age of 90, in his seventh decade of teaching and lecturing.

John Turkevich was a fascinating individual who made major contributions to several fields of human endeavor. With his wife Ludmilla Buketoff Turkevich, John initiated Russian courses at Princeton and edited a monthly "Guide to Russian Scientific Literature" from 1947 to 1952. He wrote several authoritative publications and articles in popular magazines on Russian science, particularly chemistry. He also lectured on government and science at the famous Woodrow Wilson School at Princeton.

He contributed to public service in an exceptional way, serving both his country and science. He was an expert in Soviet science and frequently advised the U.S. government and congressional committees on atomic energy and foreign affairs. He served on the Manhattan Project for the development of atomic energy, providing the first measurement and analysis of the infrared spectrum of uranium hexafluoride, a key step for its purification and isotopic enrichment. During World War II, with Hugh Taylor he devel-

oped a method for the production of heavy water. With G. Joris, Turkevich built an early isotope ratio mass spectrometer and was the first to apply the new technique to the study of isotope distributions in chemical reaction mechanisms. In 1941, following the Japanese blockade of shipment of natural rubber to the United States, he became head of a research team that developed a catalyst for preparation of synthetic rubber by dehydrogenation of butane to give butadiene. He taught extensively at various military institutions in the United States and in England. Following the war, he founded, with R. W. Dodson, the Chemistry Department at Brookhaven National Laboratory. He was an active advocate for the peaceful uses of atomic energy and participated as a U.S. delegate in two United Nations conferences on this key subject. He founded the office of scientific attaché in the U.S. Embassy in Moscow. In his house was a picture of him in discourse with Nikita Khrushchev that attracted much attention from his visitors. As chairman of the first U.S. delegation of University Professors to the Soviet Union, he initiated the first scientific exchanges and later served as mentor for five Soviet scientists and as the organizer of three U.S.-Soviet scientific conferences.

Professor Turkevich had a distinguished research career, starting in 1936 with the discovery in Sir Hugh Taylor's laboratory of the re-forming of linear heptane on chromium oxide. At that time, no pure hydrocarbons higher than C_3 were available. Having heard that pure *n*-heptane was obtained from pine trees growing on the shores of Lake Tahoe in California, Turkevich selected this hydrocarbon as the starting material. They discovered that linear heptane could produce not only toluene but also substantial amounts of hydrogen. During the war, toluene was important not only because high-octane fuels were badly needed but also because it was required in munitions works for production of trinitrotoluene. Furthermore, this dehydrocyclization process became the first bridge between aliphatic and aromatic chemistry. This discovery was followed by the synthesis and characterization of many other catalysts for controlling the rate and course of various chemical reactions. In the late 1940s and the 1950s, Turkevich pioneered the first and currently used method for preparation of platinum and gold microparticles called colloids, possessing the most uniform size and catalytic properties then known. He developed the first method for obtaining high-resolution images of the surfaces of catalysts by introducing a technique known as electron microscopy. He introduced methods for the determination of the number and chemical identity of the active species on catalytic surfaces. He had an insatiable curiosity which made him grasp the importance of any new discovery in a nearby discipline, be it chemistry, materials science, or physics. He thus was in the forefront in the use of organometallic compounds such as ferrocene or new crystalline solids such