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From the 1950s to the 1990s – my years as a scientist in an industrial laboratory

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I am deeply touched to be the honoree at this symposium, ‘Blending Research and Innovative Technology’, held as a part of the 1997 autumn meeting of the American Chemical Society. A lot of work goes into the organization of a symposium like this, and I especially want to thank Burt Davis, Gary McVicker and Jim Cusumano for the effort they have put into it. Also, I thank all of the speakers for their fine contributions to the symposium. Many of the speakers, and others attending the symposium, have been friends and colleagues of mine for a long time. It has been a great pleasure to see all the familiar faces.

About a year and a half ago, I retired from Exxon Research and Engineering Company after working there for 42 years. I spent the whole time doing catalysis research, and was fortunate to have worked in the era when support for science reached an all-time high. In closing this symposium, I will spend my time talking about those years and about a few things stemming from a scientific background and career that have been particularly important to me.

Before I became an Exxon employee, I obtained my Ph.D. at the University of Illinois under the direction of Harry Drickamer. My research at Illinois was concerned with diffusion through liquid–liquid interfaces. The objective was to determine if the interface itself, as distinct from the individual liquid phases, contributed a significant resistance to the transport process. Being introduced to research by Professor Drickamer was one of the best things that ever happened to me. I am delighted that he presented a talk at this symposium.

I left Illinois early in the fall of 1954 and went east to Linden, NJ to begin working at Exxon Research and Engineering, which was known then as the Standard Oil Development Company. My introduction to catalysis began on my first day at work, which was 18 October 1954. I remember the day very well.

At that time, catalysis was already fairly well entrenched in petroleum refining. This had come about largely through the introduction of catalytic cracking, in which silica-alumina catalysts were used to convert high molecular weight petroleum fractions to lower molecular weight hydrocarbons, thereby increasing the amounts of more valuable products such as gasoline that could be obtained from petroleum. Moreover, the gasoline obtained by catalytic cracking was of better quality than the gasoline produced by the older thermal cracking process.

Another catalytic process that was attracting a lot of interest at the time was catalytic reforming. The objective of the process was to convert alkanes and cycloalkanes in the virgin naphtha fractions of petroleum to aromatic hydrocarbons. The original process was developed jointly in the late 1930s by the Standard Oil Development Company, the M.W. Kellogg Company, and the Standard Oil Company of Indiana. Known in those early days as hydroforming, the process was utilized during World War II to produce toluene for explosives and for inclusion in aviation gasoline. The catalyst in these early applications was molybdenum oxide supported on alumina.

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After World War II, refiners became interested in exploiting the excellent anti-knock properties of aromatic hydrocarbons for gasoline for automobiles. Increases in the compression ratios projected for automobile engines in the years after World War II created a great demand for the aromatic hydrocarbons that could be produced by catalytic reforming.

In 1949, a major improvement in catalytic reforming was made by the Universal Oil Products Company when it started up a commercial reforming operation with a platinum catalyst. Val Haensel was a key figure in this development. The venture was a huge success, and generated much interest throughout the petroleum industry. In the meantime, various other companies were busy developing their own reforming processes based on platinum catalysts.

One such effort was underway at the Exxon Research and Engineering Company when I began working there in 1954. I became a part of this effort on my first day at work and remained part of it for the next 8 years. During this period, platinum catalysts became firmly entrenched in the reforming process. As a consequence of the excellent performance of these catalysts, the number of reforming units in petroleum refineries increased rapidly throughout the world. Eventually, catalytic reforming would be applied on a scale comparable to that of catalytic cracking.

I couldn't have picked a better time to begin working in catalysis. Throughout the chemical and petroleum industries, there was a strong interest in research and development. In a number of companies, at least a small part of the research effort was being devoted to fundamental issues underlying the technology of interest to the company.

As one example, I would cite some highly stimulating work by Mills, Heinemann, Milliken, and Oblad in the laboratories of the old Houdry Process Corporation. These scientists were interested in the mechanism of certain key reactions of alkanes and cycloalkanes on a reforming catalyst of the platinum on alumina type. They presented evidence that the reactions were multi-step processes in which certain steps occurred on metal sites and other steps occurred on acidic sites associated with the alumina support. They proposed that alkenes were intermediates in the reactions and were transported back and forth between the metal and acidic sites. The work provided a simple picture of the phenomenon of bifunctional catalysis in reforming.

The increased interest in fundamental research was also evident at Exxon Research and Engineering Company. The president of the company at the time was E.V. Murphree, who had been a key figure in the development of fluidized bed catalytic cracking. He was a strong advocate of fundamental approaches to the solution of technical problems. In the late-1950s, he made it very clear that he wanted to see more long-range fundamental research conducted in the company.

Two investigations undertaken in our laboratories in the area of catalytic reforming provided an indication of the favorable climate that was emerging for fundamental research at that time. In one of these investigations, a chemisorption method was developed by Larry Spenadel and Michel Boudart to determine how many of the platinum atoms in a reforming catalyst were present as surface atoms. When this work was carried out, Michel was teaching at Princeton and spending some time at our laboratories in the summers. The chemisorption data indicated that virtually all of the platinum atoms were surface atoms. This was an exciting result. If the platinum were present as clusters approximately spherical in shape, the result indicated that the clusters could not be larger than about 10 Å in diameter.

In the other investigation, the kinetics of various reactions of individual hydrocarbons over reforming catalysts were studied in considerable detail. I headed the group doing this work and found myself deeply immersed in the analysis of kinetic data. Other members of the group were Jim Rohrer, Howie Hurwitz, and Ron Shulman. The work improved our understanding of the reforming process enormously. It also provided guidance to an engineering group within the company in the development of a practical kinetic model describing the reforming of complex mixtures of hydrocarbons present in the petroleum fractions actually charged to reformers. A long time friend of mine, the late Walter Kmak, played a key role in developing this model and in applying it to reforming operations.

The kinetic studies provided me with a valuable foundation for the future work that I would do in catalysis. They were also important to me in another way. They catalyzed a career-long dialogue that I have had with my good friend Michel Boudart. Over the years, we have had innumerable discussions about a number of things that emanated from the reforming kinetic studies.

After working exclusively on platinum catalysts in the area of reforming for 8 years, 3 of which were spent on the kinetic studies, I extended my interests to other metal catalysts. One of the things that was of particular interest to me was the relation between the catalytic activity of a metal and its position in the periodic table. I was also interested in the way that such a relation is affected by the nature of the reaction. For example, is the relation for a hydrogenolysis reaction involving scission of carbon–carbon bonds different from that for a hydrogenation or dehydrogenation reaction where the formation or scission of a carbon-hydrogen bond is the issue of interest?

With the help of my colleagues Bill Taylor and Dave Yates, I began probing this question in the early 1960s. At that time, I also had another strong interest, namely, bimetallic catalysts. The two interests were not widely divergent ones. In my way of thinking, they fit together very well. Thus, in pairing one metal with another in a bimetallic catalyst, I wondered whether the effect on catalytic activity would depend on the reaction being catalyzed. In other words, would the catalytic selectivity of one metal be influenced by the presence of another metal?

It turned out that the activities of many transition metals, including the Group VIII metals and rhenium, for the hydrogenolysis of carbon-carbon bonds in hydrocarbons were strongly inhibited by the presence of a Group IB metal. At the same time, the activities for hydrogenation or dehydrogenation reactions, and for isomerization and dehydrocyclization reactions as well, were affected very little by comparison. Thus, the selectivities of the active host metals for the latter reactions were enhanced by the IB metal. A similar finding was made by Vladimir Ponec and Wolfgang Sachtler in the Netherlands.

In two papers on nickel-copper alloy catalysts appearing in the February issue of the Journal of Catalysis in 1972, the Exxon group of Sinfelt, Carter, and Yates and the Netherlands group of Ponec and Sachtler both suggested that a kind of geometric effect could be operative here, at least in part. We reasoned that hydrogenolysis reactions require multiple nickel atom sites and that the concentration of such sites would be particularly sensitive to dilution of the nickel by inert atoms of copper in the surface.

Another interest of mine regarding bimetallic catalysts was the possibility of preparing very small bimetallic entities in which virtually all of the atoms were present as surface atoms. I was interested in such entities for practical applications of bimetallic catalysts, since for a given amount of metal in a catalyst, the activity of the metal generally increases with increasing metal surface area.

When I began working on this question, I found that interesting bimetallic entities could frequently be prepared on common support materials, even when the total metal content of the catalyst was lower than 1% by weight. I decided to use the term bimetallic clusters rather than supported alloys in referring to such bimetallic entities. I did this because our early work showed that the bimetallic entities of interest for catalysis were not limited to combinations of metallic elements that formed alloys in the bulk. The ruthenium-copper system provides a good example. In this system, copper forms an adsorption layer on the surface of ruthenium, although the two metals are completely immiscible in the bulk. My colleagues Jim Cusumano, Yiu Lau Lam, and Bob Helms made significant contributions in elucidating the structure of ruthenium-copper catalysts in the days before we were able to apply EXAFS to the problem.

Our work on bimetallic cluster catalysts led to a platinum-iridium reforming catalyst, which found wide application in Exxon reforming units in the early 1970s. Two close colleagues of mine at Exxon, Al Barnett and Jim Carter, contributed very importantly to that development. Another close colleague, Shun Fung, made a vital contribution in developing an in-situ catalyst reactivation procedure that was practical in commercial units. Grayson Via and Bob Garten provided significant data for the characterization of platinum-iridium catalysts, and Gary McVicker helped define the catalytic properties through investigations of individual hydrocarbon reactions.

The bimetallic platinum-iridium reforming catalyst was several-fold more active than the monometallic platinum catalysts used prior to the 1970s. It also exhibited a significantly lower rate of activity decline in a reforming operation. Consequently, it could be operated for a much longer period of time before reactivation was necessary.

During the time that the platinum-iridium catalyst was under development at Exxon, the Chevron Corporation introduced a platinum-rhenium catalyst for reforming. This catalyst also exhibited major advantages over prior platinum catalysts and was widely applied in commercial reformers. A Chevron scientist named Harris Kluksdahl figured prominently in the early research leading to this important development.

While platinum-iridium and platinum-rhenium catalysts were finding application in commercial reformers, another development was underway in the Universal Oil Products Company. It involved a modification of the reforming process which made it possible to operate a reformer at a much lower pressure to obtain a substantial increase in the yield of the aromatics-rich product. The modification entailed changes in a reforming unit which made continuous regeneration of the catalyst feasible. This was necessary because of the much higher rate of catalyst deactivation experienced at the lower pressure. The modification was coupled with the application of yet another catalyst in reforming, a platinum-tin catalyst.

Over a period of time, the monometallic platinum catalysts used widely in reforming in the 1950s and 1960s were completely replaced by the new bimetallic catalysts. As a result, reforming operations were improved substantially.

By the early 1970s, the removal of lead from gasoline was a very pressing environmental issue. The economic feasibility of lead-free gasoline was enhanced greatly by the improvements in reforming due to bimetallic catalysts. The widespread use of unleaded gasoline in the US since the early 1970s has decreased lead emissions by 98%. Moreover, the availability of unleaded gasoline has been crucial for the use of catalysts in automobile exhaust systems to control the emission of carbon monoxide, unburned hydrocarbons and nitrogen oxides into the atmosphere. Since lead poisons exhaust gas catalysts, its removal from gasoline is necessary for successful exhaust gas purification. Thus, bimetallic reforming catalysts have played an important role in major environmental advances associated with two aspects of the control of emissions in automobile exhaust gases.

In addition to being concerned with the application of selected bimetallic catalysts in reforming in the 1970s, I continued to be interested in learning more about the structure and properties of bimetallic catalysts in general. Around 1973 or 1974, I had the good fortune to meet Farrel Lytle and learn about his pioneering work to use extended X-ray absorption fine structure (EXAFS) as a probe of various structural features of materials. At the time I knew absolutely nothing about EXAFS, but Farrel quickly made me aware of its great potential. Shortly after I met Farrel, I knew that I wanted to collaborate with him in using EXAFS to study catalysts, especially bimetallic cluster catalysts. So I discussed the matter with my friend Grayson Via, who was also very intrigued by EXAFS. Grayson thought that a collaboration with Farrel was a good idea. Soon afterwards, Farrel, Grayson and I were working together on the application of EXAFS to catalysts. About 6 years later, George Meitzner joined us in this collaboration.

Over a period spanning a little more than two decades, this collaboration has been a very rewarding experience. EXAFS proved to be a highly effective probe of the structural features of bimetallic clusters. Moreover, in addition to the structural information obtained from the EXAFS following X-ray absorption edges, useful information about electronic properties can be obtained from studies of features of the edges themselves. The work with Farrel, Grayson, and George convinced me that X-ray absorption spectroscopy is a very powerful probe for the study of metal catalysts.

In the late 1970s, I was given the opportunity to collaborate with Charlie Slichter and his students at the University of Illinois in nuclear magnetic resonance studies of dispersed metal catalysts. When I became involved in the collaboration, I knew very little about NMR, and did not have a clear perception of the kinds of information we might obtain from the work. However, I knew that my collaborators were among the very best in NMR, and I was enthusiastic about going ahead with it.

In proceeding with this collaboration, I supplied Charlie with a series of platinum on alumina catalysts with platinum dispersions varying by an order of magnitude. The average diameters of the platinum clusters or crystallites in the catalysts were roughly 15–200 Å. Charlie's students succeeded in detecting ^{195}Pt resonances and in differentiating a resonance associated with surface platinum atoms from the resonance associated with bulk platinum. When they found that the intensity of the resonance for surface platinum correlated with platinum dispersion as determined by hydrogen chemisorption, I was very impressed and convinced of the potential of NMR in fundamental studies of these catalysts. I decided at that point that I should learn a little more about NMR.

As the collaboration continued, the work was extended to include studies of adsorbed molecules. In these studies, Charlie's students were successful in obtaining much new information on the structures, reactivities, and mobilities of adsorbed species. For the surface species formed in the chemisorption of acetylene and ethylene on supported metal clusters, they obtained information on the kinetics of simple reaction steps such as the dissociation of a carbon–carbon bond or the formation of a carbon-hydrogen bond. Such information is of interest in interpreting the kinetics of more complex catalytic reactions of hydrocarbons on metals. Chris Klug, who currently teaches at Stanford, was one of the students doing these studies. He plans to continue work along these lines at Stanford, and I will be following it with great interest.

The collaboration has been a great experience for me. I have been fascinated by the many intriguing results that have been obtained in the work. Moreover, I have learned a great deal from Charlie and his students, and I have enjoyed the experience from the very beginning. What more can a person expect from a collaboration of this kind?

In the years immediately preceding my retirement, I managed to return to my long standing interest in the catalytic activity of a metal in relation to its position in the periodic table. The earlier work on hydrogenolysis of carbon–carbon bonds was extended to carbon–nitrogen and carbon–halogen bonds with the very able collaboration of George Meitzner, Bill Mykytka, and Shun Fung. While the broad pattern of variation of catalytic activity from one metal to another is similar for the hydrogenolysis of the different bonds, there are systematic differences regarding the position of maximum catalytic activity for a series of metals and the ranges of catalytic activities observed for the series. It seems to me that systematic studies of this type provide a useful framework for understanding chemical reactivity at metal surfaces in a very broad sense, in much the way that generations of chemists have traditionally organized their knowledge of chemical reactivity around the positions of elements in the periodic table.

In concluding these remarks, I return to the symposium theme of blending research and innovative technology to comment briefly on the value of science in the process. In common with many other fields of importance to industry, catalysis is one in which technology has generally been ahead of the science. However, efforts to understand the scientific issues underlying a catalytic process have frequently led to significant improvements in the process, and sometimes basic science efforts have led to new types of catalyst systems that have improved processes dramatically.

My experience in industry has convinced me of the value of fundamental science in support of the technology of interest to a company. I am grateful that I worked in a company which supported me in my efforts to follow my conviction in this respect. This support reinforced my interest in the science underlying my work, to the extent that I was thinking about it virtually all the time. As I have often said, science became my hobby as well as the basis for my everyday work.

This has been particularly important to me, since I have not pursued other interests to any great extent. Now that I am retired, it is even more important. I still think about science a lot, simply because I enjoy it. For me, the development of this hobby has been a valuable dividend of the kind of career I pursued. I am grateful for it.

Again I thank you all for being here. I enjoyed the symposium very much and have been delighted to see you all again.