SUPPORTING INFORMATION

A Career in Catalysis: Enrique Iglesia

David G. Barton[1], Aditya Bhan[2], Prashant Deshlahra[3], Rajamani Gounder[4,*], David Hibbitts[5], Beata A. Kilos[1,*], Gina Noh[6], Justin M. Notestein[7], Michele L. Sarazen[8], Stuart L. Soled[9]

[1]*Core R&D, The Dow Chemical Company, Midland, MI 48674, United States*
[2]*Department of Chemical Engineering and Materials Science, University of Minnesota Twin Cities, Minneapolis, MN 55455, United States*
[3]*Department of Chemical and Biological Engineering, Tufts University, Medford, MA 02155, United States*
[4]*Charles D. Davidson School of Chemical Engineering, Purdue University, West Lafayette, IN 47907, United States*
[5]*Department of Chemical Engineering, University of Florida, Gainesville, FL 32611, United States*
[6]*Department of Chemical Engineering, The Pennsylvania State University, University Park, PA 16802, United States*
[7]*Chemical & Biological Engineering, Northwestern University, Evanston, IL 60208, United States*
[8]*Department of Chemical and Biological Engineering, Princeton University, Princeton, NJ 08544, United States*
[9]*ExxonMobil Engineering and Technology Company, Annandale, NJ 08801, United States*

*Corresponding authors: rgounder@purdue.edu; bakilos@dow.com

S1. Enrique Iglesia: Early History at Exxon's Research Laboratory
(A Personal Recollection by Stu Soled)

It was a cold day on Dec 26, 1979, when I walked into the Exxon research center in Linden NJ with a lot of hope and expectations, and a little bit of trepidation. I had spent 8 years at the chemistry department at Brown University first doing single crystal X-ray diffraction for my Ph.D. and then post-doctoral research working in the solid-state chemistry lab of Professor Aaron Wold, one of the early solid-state chemists in the US. In Professor Wold's lab, we worked on material synthesis with a focus on single crystal growth and electrical and magnetic measurements of sulfides, phosphides, thiophosphides, arsenides and antimonides- it was a time I really enjoyed and flourished as a researcher- the first time I felt that I had really made a good choice professionally. When I finally left Brown, my desire was to find a place to do solid state chemistry research where I could have a chance to make an impact in the real world. For that reason and also because the number of faculty positions in solid state chemistry in US universities at that time could be counted on one hand, I chose to pursue an industrial career. But what does a solid-state chemist do in industry? Several of my colleagues had gone to electronic/semiconductor companies like Texas Instruments and Motorola. A few went to chemical companies, like DuPont or 3M. And a few migrated into the petrochemical industry. I chose the latter path and my first job in mid-1977 was at a chemical company in Morristown, NJ, known at that time as Allied Chemical and which has morphed through multiple purchases and sales into a division of Honeywell. There they put me into a thermal analysis lab and told me to help interpret results on tests of inorganic samples coming from different parts of a very diverse company and create a research program by interacting with people in the rest of the research organization. Over the course of the next two and a half years I interacted with two researchers who were involved in catalysis, Curt Conner, who subsequently became a chemical engineering professor at the University of Massachusetts at

Amherst and John Armor who migrated to Air Products, where he had a long career. At Allied, I saw that my training as a solid-state chemist might be useful in catalytic materials research. Catalysis was a daunting area with multiple aspects of the discipline that I had had zero exposure to. Allied had a volatile environment with programs changing faster than the spots on a tree frog and I decided that it would probably be better if I could transition to a serious catalysis centric lab. So, at the end of 1979 I was able to get a job offer from the Exxon Lab in Linden, NJ and I joined them the last few days of that year.

With that odd background, Exxon did provide me with a challenging environment indeed. Here was a large group of catalysis professionals into which I was injected. When I joined, they also had two solid state chemistry groups (led by John Longo and Alan Jacobson) and I was asked which group I wanted to join. I said I wanted to be part of the catalysis group, not one of the solid-state chemistry groups since I figured that would be the only way to learn the trade. Little did I know I was essentially entering into yet another "postdoc"-like experience because I had so much to learn. But I had colleagues who were so smart, dedicated, and hard working. For me it was a perfect setting to try to learn something new. At times, it was daunting as I felt so ignorant on some of the topics and ideas that were discussed. Never having had a chemical engineering or even catalysis course in all my training, it did challenge me, and it took several years before I felt a little bit more comfortable. Nonetheless the first few years I was exposed to solid acids, working closely with Gary McVicker, and Fe-based Fischer Tropsch catalysts working with Rocco Fiato. There were constant seminars and lots of discussions about everything catalysis related. For me it was a challenging but perfect environment. And in 1984 the lab moved to Clinton, NJ into a brand-new large laboratory building.

I have a few early memories of my seeing Enrique when he first arrived toward the end of 1982. Gary had alerted me that there was this young kid from Stanford who was supposed to be special. He said it with a grain of sarcasm as Gary had been in the labs about 15 years at that point and was well versed in the process areas that were important to Exxon. Other than John Sinfelt, Gary was considered the senior statesman for the area. So, in the beginning although I had been introduced to Enrique I did not have many interactions with him as he was in a different group than I was. But then in 1983 a decision had been made that Exxon would start exploring synfuels made by Fischer-Tropsch (FT) chemistry. This was prompted by the fact that the company was flush in methane but that its liquids inventory seemed to be dwindling- thoughts of peak oil abounded. They had a very large onsite symposium in 1984 on all aspects of FT chemistry, with many renowned faculty coming to the facility, including Michel Boudart, Keith Hall, Kamil Klier and many others. Following that symposium many of us were recruited into projects in the area. This was the first time I really began to work with or more appropriately learn from Enrique. He always had a professorial streak and I guess I was an eager student. There was no better person to introduce me to the concepts of chemical engineering. Some of these stuck, some did not, but I thought we made a great team with me focusing on the catalyst discovery part of the work and Enrique on the kinetics and modeling. From the day the interactions began, I could see that Gary's initial remarks about this young scientist from Stanford being special were right on.

While I worked on some of the issues on how to best prepare a supported cobalt catalyst, Enrique focused on the effects of metal dispersion, alloying elements, supports, and reaction conditions on the chemical and transport features that determine rates and selectivities as well as the design criteria for optimal reactor types to maximize liquid yields. He co-authored some of the enabling patents and know-how for catalysts and bubble column reactors in what is denoted as

the ExxonMobil AGC-21 Gas-to-Liquid technology. He worked with Sebastian Reyes and Ross Madon to develop quantified models for product distribution and selectivity- particularly how readsorption of C_2 and C_3 olefins could explain the olefin/paraffin product ratio. In studying bimetallic systems, particularly those with Co-Ru and Co-Re, Enrique showed that Re gives samples with the same site activity but more sites, whereas Ru increases rate without change in dispersion, as a result of inhibited site poisoning. We investigated the use of $MgCr_2O_4$ spinel as a support that might provide epitaxial control over Co_3O_4. We investigated how Co eggshells on mm-sized particles would behave and developed simple ways of preparing rimmed eggshells. Enrique together with Sebastian Reyes, provided models of the eggshell formation as well as a detailed reaction transport modeling effort to help in the a priori design of large particle FT catalysts. He became interested in the unexplained the strong effects of water on Fischer-Tropsch rates and chain length and started to explore this topic- an area of interest which continued for many years in academia.

Enrique's early work in Fischer-Tropsch synthesis provided the enabling scholarship and discoveries for the AGC-21 gas conversion process developed by Exxon. His contributions spanned the design of Co and Fe catalysts and the development of accurate descriptions of the relevant chemistry and hydrodynamics. His later contributions elucidated the role of hydrogen and water assistance in kinetically-relevant CO activation; these advances, as many others in his career, arrived through the seamless application of kinetic, isotopic, spectroscopic, and theoretical tools. The quantification of metal crystallite size effects in supported cobalt and cobalt alloy catalysts and the development of reaction-transport models that for the first time explained the interrelationship between transport and selectivity, have provided a paradigm for the evolving generation of FT catalysts with improved activity, selectivity, and stability. Methods were

developed to separate primary and secondary reaction pathways during Fischer-Tropsch synthesis, to measure their rates and selectivities, and to model their role in determining selectivities. His work in this area has been well recognized with his receipt of the Natural Gas Conversion Award. With the renewed interest in producing clean and high performing diesel fuel and lubricants from renewable feedstocks and natural gas, his work provides a strong foundation from which many groups are trying to build. I know that in one company any researchers who begin studies on Fischer-Tropsch syntheses are required to read the suite of papers by Professor Iglesia in order to get started.

But Enrique did not limit himself to just Fischer-Tropsch chemistry. With Sebastian he helped advance the ideas of percolation theory in catalysis, he explained the mechanistic details of the C_6 aromatization reaction that occurs on Pt-KL zeolite, and how Pt was so special for this reaction compared to Ir and Rh. In other work with Sebastian, they developed Monte Carlo simulations of structural properties of packed beds. Enrique studied the role of bifunctional catalysis on tungsten carbides with surface oxygen, and he worked again with Sebastian on deriving reaction networks for oxidative coupling of methane. He started another one of his lifelong areas of understanding, particularly on solid acid catalysts with early studies providing mechanistic details of active site formation on sulfated and tungstated zirconias, an area he expanded shortly after transitioning to Berkeley.

I was one of many who profited from his brilliant intellect and mentorship. His influence on me was not only in introducing me to the fundamentals of catalysis and reaction engineering but providing a role model of someone who had a nonstop inquisitive interest in science and discovery. Some of his behavior got imbedded in my psyche. Maybe it partly explains how I have

spent parts of 6 decades (1970's, 80's, 90's, 2000's, 2010's and 2020's), working at Exxon or ExxonMobil in catalysis and particularly catalytic materials.

In 1986 the company experienced a major hiccup in the research organization. As happens often, the realities of business economics and strategy affects the pristine world of research and development. We were told in mid-1986, just two years after the move into the new Clinton, NJ site that 50% of the professional staff would be reduced in the following two months. As a young researcher this was a psychic explosion and a very painful process to live through. Most of the researchers were blitzed. Shortly after this Enrique was recognized by management as someone very special and that led to his assuming the role of group and then section head. Despite the huge cutbacks, he still had a group of over 20 principal investigators as well as couple of dozen technicians. Enrique became determined to prove that this group could make a huge impact on the company as well as the scientific community, and his efforts essentially led over the next few years to a recovery and rebirth of catalysis research at Exxon. I remember clearly how in the period before the 1991 North American Catalysis Society meeting in Lexington, KY our entire site was encouraged by Enrique to participate in the meeting. We had over 30 oral and poster presentations and even many technicians attended and presented their work. After the meeting there was a lot of buzz that Exxon was back.

Perhaps the most incredible part of Enrique's accomplishments while at Exxon, was that while he was the section head of a very large group, he kept two technicians working in his lab (Joe Baumgartner and Rich Ernst). No one else in this type of supervisory role has ever done this before. In 1993 when he had an overwhelming amount of section head responsibilities, he published four long articles in the Journal of Catalysis as well as four book chapters.

Of course, the management saw what a special talent they had, and they kept planning on bigger things for Enrique's future. In particular, Frank Sprow, who had been the vice president of Corporate Research and later became the corporations vice president for safety health and the environment, and who was also a Princeton graduate, was actively trying to convince Enrique that he should become a lab director in the development labs in Baton Rouge. It was clear that the path of being a scientific researcher at Exxon was drying up as he was just too talented for management to leave him alone. But that was not what Enrique wanted and despite some efforts by his coworkers to try to convince management to allow Enrique to manage a totally independent research group reporting only to the vice president, there was no path forward. He received an offer from the University of California at Berkeley and that became his life for the next 30 years. Frankly I am not sure the research organization at Exxon or ExxonMobil ever really recovered from that loss and I often wonder what the alternative timeline would have been like if he could have stayed in industrial research. Most of us who know him well realize that he was fated to be a professor, as his professional idol was Professor Michel Boudart. And in making this transition he could influence more lives than staying in industrial research and essentially populate the next generation of catalysis faculty members with some incredible academics. After becoming an academic he has consulted for several decades at several industrial companies, including ExxonMobil, so his wisdom and ideas have very much penetrated the industrial research world. In addition, his own research, sponsored by industrial partners, has had several discrete impacts on new processes used by industry. Consequently, his impact on practical catalysis has remained strong. For me, knowing and working with Enrique was a life changing interaction that I will always cherish.