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ScienceDirect
Catalysis Today 123 (2007) 2–5
CATALYSIS TODAY
www.elsevier.com/locate/cattod

M. Albert Vannice Festschrift

On behalf of the colleagues, postdoctoral and visiting scholars, and graduate students that have had the opportunity to work with Professor M. Albert Vannice throughout his distinguished career, we are honored to dedicate this special issue of Catalysis Today to mark his retirement.

Dr. Vannice has authored or co-authored over 230 papers, been granted 9 patents, and written 13 books or book sections. To date, his papers have been cited over 6000 times according to the Institute for Scientific Information (ISI) Web of Science. His final publication entitled ''An Analysis of the Mars Van-Krevelen Mechanism'' will be printed in this special issue. The paper continues on the core subject of Dr. Vannice's research throughout his entire career, heterogeneous catalytic kinetics. Other areas of emphasis during his career were catalyst preparation and characterization, metal-support interactions and hydrogen spillover, carbon materials in catalysis, applications of diffuse reflectance infrared spectroscopy (DRIFTS) in adsorption and catalytic studies, environmental catalysis, bimetallic catalyst characterization, and heterogeneous reaction kinetics in the liquid phase.

0920-5861/$ – see front matter
doi:10.1016/j.cattod.2007.04.006

Biographical summary

Merlin Albert Vannice was born on January 11, 1943 in Broken Bow, Nebraska. His early life on a small ranch near Halsey, Nebraska, of which he was 1% of the population, was an excellent source of material for the stories that are a hallmark of the sense of humor that all around him have enjoyed. His Nebraska days also fostered his love of cars and Cornhusker football.

After attending a high school of 19 students, he left for Michigan for his final year of high school and then to Michigan State University (MSU) in 1960, where he received an MSU fellowship and graduated with a B.S. in chemical engineering in 1964. While at MSU, he was a member of the MSU Honors College, the national engineering honors society, Tau Beta Pi, the national collegiate honors societies, Phi Kappa Phi and Phi Eta Sigma, and Phi Lambda Tau. His studies continued in chemical engineering as he moved to northern California to join the group of Professor Michel Boudart at Stanford University. At Stanford, Professor Boudart introduced him to the kinetics of heterogeneous catalytic reaction kinetics. His master's thesis work included compiling reaction and adsorption data and analyzing them for thermodynamic consistency. His analysis of the literature with Boudart and Mears led to a very important publication, M. Boudart, D.E. Mears and M.A. Vannice, Kinetics of Heterogeneous Catalytic Reactions, Ind. Chem. Belge 32 (1967) 281, which provided two firm rules and two guidelines to determine whether reported equilibrium constants for nondissociative adsorption have physical meaning and can therefore support a proposed rate model. Early in his own independent academic career, Vannice further extended these rules and guidelines to dissociative adsorption (M. A. Vannice et al., J. Catal. 56 (1979) 358). After receiving his M.S. in chemical engineering in 1966, he spent a year with Dow Chemical Company in Midland, MI on special assignment. He returned to Stanford to complete his doctorate with Professor Boudart in 1970. His PhD thesis was entitled ''The Adsorption and Activation of Hydrogen on Platinum.'' Papers resulting from his thesis have been cited often and represent some of the first quantitative work on hydrogen adsorption on platinum. During his PhD at Stanford, he spent 5 months at the Universite de Louvain in Belgium as a visiting student working with Jose Fripiat. After graduating, he joined the Sun Oil Company outside of Philadelphia, PA as an industrial postdoctoral fellow for a period of 1 year. It was here that Dr. Vannice met his future wife, Bette Ann, to whom he has been happily married for 36 years. He joined Exxon Research and Engineering Company in Linden, NJ in 1971 as a research engineer, becoming a senior research engineer in 1975. While at Exxon, he devoted much of his research to the kinetics of CO/H_2 catalytic chemistry on supported metals and the influence of metal-support effects on CO/H_2 chemistry. In 1976, Dr. Vannice and Bette Ann moved to central Pennsylvania, where he joined the Chemical Engineering Department at The Pennsylvania State University. While at Penn State, he continued to pursue research in heterogeneous catalysis with emphasis on catalyst synthesis, methods for catalyst characterization, and the kinetic modeling of catalytic reactions. During his tenure at Penn State, he taught over 30 courses, supervised 26 students to a master's degree and 32 students to doctorates, and hosted 27 postdoctoral associates and visiting scientists. A number of his students and postdoctoral associates hold important positions in both academia and the chemical industry abroad as well as in the United States. Dr. Vannice officially retired from the Department of Chemical Engineering at the Pennsylvania State University on December 31, 2005.

His love of cars hasn't waned over those 26 years and at the moment his collection includes 16 cars, down a bit from the peak at 21. He continues to travel the roads to car shows where he has won numerous awards. Much to his departing graduate students chagrin, these prized collectables were not offerings upon completion of their thesis, but his invaluable knowledge, guidance, and catalytic perspective always were.

Honors and awards

Numerous researchers have used Professor Vannice's studies involving the role of metal-support interactions, as well as his advanced experimental techniques to examine and develop catalytic systems for a variety of commercial processes. The importance of Professor Vannice's research has been recognized nationally and internationally by his peers. He has received numerous awards including the New York Catalysis Society Award in 1985, the American Institute of Chemical Engineers Professional Progress Award in 1986, the Catalysis Society P.H. Emmett Award in 1987, and the Pittsburgh-Cleveland Catalysis Society Award in 1988. He was an invited speaker at four Gordon Conferences, the Emmett Lecturer at the University of Utah in 1984, and the Schuit Lecturer at the University of Delaware in 1989. In 1992, he won an outstanding presentation award at the national AIChE Fall Meeting and in 1993, he was chosen by the Chilean Chemical Society as the American Chemical Society visiting professor. Dr. Vannice spent sabbaticals at the Centre de la Recherche Scientifique (CNRS) in Orleans, France (1982–1983), the KFA in Jülich, Germany (1990) on a Humboldt Senior Scientist Award, the University of Münich in Münich, Germany (1997) via a Fulbright Sr. Award and a Humboldt Revisitation Award and the University of Alicante in Alicante, Spain (2004), where he wrote his textbook entitled, *Kinetics of Catalytic Reactions*, which was published by Springer in 2005.

Internally at Penn State, Dr. Vannice has been recognized for the quality of his research. He was promoted to full professor in 1980. He has been acknowledged with the College of Engineering Research Award in 1982, the title of Distinguished Alumni Professor in 1986, as well as receiving the College of Engineering Premier Research Award in the same year. He earned the titles of Distinguished Professor of Engineering in 1991, the Merrell R. Fenske Professorship in Chemical Engineering in 1996, and was appointed the William H. Joyce Chair in Chemical Engineering in 2002.

Dr. Vannice served the greater catalysis community in various capacities. He has been involved with the North American Catalysis Society (NACS) at both the local and

national level. He was secretary of the Catalysis Society of New York from 1973 to 1974 and director from 1974 to 1975. He was involved with the Pittsburgh-Cleveland Catalysis Society, serving as its director from 1987 to 2001. Nationally, he served the NACS in various roles as a member of the board of directors (1987–2005), vice president (1993–1997) and society president from 1997 to 2001. He served as the general chairman of the 13th North American Meeting of the Catalysis Society in Pittsburgh, PA in 1993. He also served on the NACS committee on Visibility of Catalysis in the USA (1991–2001) and as chairman of the NACS committee on Uses of the Educational Trust (1991–2001). He was also involved with the international catalysis community as a member of the organizing committee and chairman of the finance committee for the 11th International Congress on Catalysis held in Baltimore in 1996. He was a member of the American Institute of Chemical Engineers (AIChE) sub-committee on catalysis and a member of the awards committee (1992–1997). Dr. Vannice served as the chairman-elect (1978–1979) and the chairman (1979–1980) of the central PA section of the American Chemical Society (ACS). He was co-chairman of the Coal Conversion Catalysis Symposium at the Materials Research Society (MRS) 1979 meeting and chairman of the Characterization of Catalysts session at the 1991 fall meeting. He was involved in the Gordon Conference on Catalysis early in his career. He was an invited speaker in 1975, 1980 and 1987 and chairman of the same conference in 1982. Dr. Vannice also participated in the Gordon Conference on Fuel Science as an invited speaker in 1977.

He was a member of the editorial advisory board for *Adsorption Science and Technology* (1982–1995), on the editorial board of the *Journal of Catalysis* from 1987 to 1994 and again from 2001 to 2006, and served as Associate Editor from 1994 to 2001.

Summary of research contributions

Professor Vannice has been a leader in the field of catalysis for over three decades, first in an industrial research laboratory, then at Penn State. He has been among the vanguard of catalysis researchers who have tried to develop new catalysts based on fundamental concepts and a better understanding of the complex interactions of molecules with active metal surfaces. The heterogeneous catalysts used to enhance the rate and control the selectivity of these chemical reactions typically consist of small metal particles dispersed on a high surface area oxide support. Measuring the number of surface metal atoms in these catalysts allows specific activities in the form of turnover frequencies (molecules per second per surface atom) to be calculated. Dr. Vannice took this approach at Exxon in his seminal study of CO hydrogenation over Group VIII metals to produce fuels and chemicals from natural gas or coal. That work resulted in the first quantification of specific activities for this reaction, which allowed the performance of each metal to be accurately evaluated. The need for this investigation was perceived prior to the oil embargo in 1973, and the initial results were published while this energy shortage was having its full impact on the major industrial nations. Many world-wide research efforts were initiated in this area during this period; consequently, Dr. Vannice's papers became the standard of comparison for subsequent work and they attracted widespread attention. One in particular, ''The Catalytic Synthesis of Hydrocarbons from H_2/CO Mixtures over the Group VIII Metals. Part I. The Specific Activities and Product Distributions of Supported Metals'' (J. Catal. 37 (1975) 449), was recognized as a Citation Classic in 1986.

The leadership role in this area of catalytic chemistry that Professor Vannice assumed with these initial studies, which were carefully conducted to provide very accurate kinetic data, was carried on after he moved to Penn State in 1976. The manner in which these investigations were conducted provided fundamental information that resulted in an important additional benefit—it allowed him to show that interactions between the metal and the support surface can significantly influence the catalytic behavior in this reaction. For the first time, it was clearly demonstrated that turnover frequencies for CO hydrogenation could be enhanced by factors of 10–100 and product selectivities could be altered, thus providing improved catalyst systems. This discovery led to nine patents related to CO/H_2 catalytic chemistry, and Exxon now has a commercial process using technology originating from this work. Professor Vannice's discovery of the influence of strong metal-support interactions (SMSI) in this reaction not only spurred a multitude of studies of this phenomenon around the world, but it also gained him recognition in the form of a number of awards. Vannice demonstrated that SMSI effects are not limited to CO hydrogenation; they are also responsible for altered activity and selectivity during the hydrogenation of ketones and aldehydes. His work demonstrated that the reactivity of the carbonyl is enhanced at the interface between reducible oxide and metal crystallite. During the reforming of CH_4 by CO_2, Vannice proposed that the SMSI effect on M/TiO_2 (where M = Pt, Ni, Rh) led to catalysts with enhanced stability because of decreased M ensemble sizes which resist carbon deposition. Increased activity by three orders of magnitude was observed over a high temperature reduced Pt/TiO_2 catalyst compared with a Pt/SiO_2 during the liquid-phase hydrogenation of citral.

Shortly after his arrival at Penn State, Dr. Vannice began a program on the use of carbon as a catalyst support. In collaboration with Professor P.L. Walker of the Fuel Sciences Department at Penn State, various aspects of the synthesis of carbon-supported catalysts and their characterization were examined. They concentrated mainly on carbon-supported Fe catalysts—utilizing a number of carbon allotropes in the work. Dr. Vannice and his group verified that clean carbon is a robust support and has many advantages over metal oxides typically used to support small metal crystallites, and they continued to study carbon supports concentrating on their surface chemistry and its impact on metal dispersion. A number of his studies have shown the influence of oxygen functionalities on metal dispersion and the importance of metal precursor choice. Dr. Vannice demonstrated that the method of catalyst pretreatment significantly influenced the cleanliness of Pd dispersed on carbon supports—carbon atoms could be present on the nanoparticle surface or interstitially in the bulk of Pd. In

collaboration with his Penn State/Northeastern University colleague, Dr. R.T.K. Baker (currently of Catalytic Materials, LLC), Dr. Vannice's group examined the utility of various forms of carbon (turbostratic amorphous carbon, graphite fibers, and diamond) as supports for Cu-based catalysts.

Dr. Vannice has also developed a number of surface characterization tools, based on chemical adsorption, to determine the composition of supported bimetallic catalysts. Exploiting differences in the strength and affinity of adsorption of a particular adsorbate on bimetallic catalysts, his group has demonstrated that the surface composition of bimetallic catalysts can be determined and correlated with catalytic activity. Such measurements are essential because surface compositions of bimetallic materials often differ from the bulk compositions. Particular examples of bimetallic catalysts studied in Professor Vannice's laboratory include Pd–Cu, Pt–Cu, and Pt–Fe.

Development of analytical techniques for *in-situ* study of heterogeneous catalysts under adsorption and reaction conditions is another focal point of Dr. Vannice's work. Most notable is the application of diffuse reflectance IR spectroscopy to study carbon and oxide supported catalysts. Carbon supported catalysts are not amenable to characterization by transmission infrared spectroscopy due to absorption of infrared radiation by the carbon support, but Vannice and coworkers demonstrated that DRIFTS could interrogate the carbon surface during preparation and under reaction conditions. His initial work in this area demonstrated that the decomposition of mono- and bimetallic carbonyl clusters to form nanoparticles on the carbon surface could be followed by DRIFTS. A number of his publications have identified reaction and surface intermediates on metal crystallites supported on carbon and oxides under reaction conditions. In collaboration with his colleague, Dr. Arden Walters (currently of Advanced Energy Research), they built a microwave Hall effect apparatus to study the mobility and absolute concentration of charge carriers in powdered carbon and metal oxide materials. This technique was used to determine the influence of adsorbates on the electrical properties of catalyst particles and has been used to distinguish between adsorption sites for CO_2 and O_2 on ZnO powder.

He has devoted a significant portion of his career studying catalysis important to the environment—specially NO_x conversion with lanthanum- and manganese-based catalysts. His group studied the selective catalytic reduction of NO by various reductants, such as methane, carbon monoxide, hydrogen and methanol on unsupported and supported La oxides. This effort has led to several publications that have identified relevant temperature ranges for each reductant, as well as reaction mechanisms and surface intermediates. Additionally, the lanthanum oxide catalysts have been probed with various promoters and dopants, which identified that strontium increases the activity by promoting lattice-oxygen vacancies at the catalyst surface. This identification of catalytically active sites has been a cornerstone of much of his research. Towards the end of his career, Dr. Vannice began a research program in liquid-phase heterogeneous catalysis with a special interest in rigorously measuring reaction rates free of mass and heat transfer effects. His publications in this area have shown that correcting for transport artifacts and ensuring measured kinetic parameters are free of such artifacts are critical for proposing and testing reaction mechanisms for liquid-phase reactions.

Integrated into all of Dr. Vannice's research is the rigorous measurement of reaction rates under conditions free of heat and mass transfer, and the normalization of reaction rates based on the concentration of the catalytically relevant surface sites. Kinetic modeling has been accomplished by measuring the reaction rate as a function of appropriate process parameters such as temperature, reactant, and product partial pressures in order to postulate a plausible mechanism based on a series of elementary reaction steps which in total constitute a catalytic cycle. After assumptions are made regarding the dominant surface species and uniformity of the surface, rate expressions, typically of a Langmuir–Hinshelwood type, were derived and checked against the data. Finally, following the guidelines set forth in his Master's research, kinetic and thermodynamic consistency of the constants determined from modeling was then evaluated. By combining these kinetic studies with work on catalyst synthesis and detailed surface characterization, Professor Vannice has demonstrated for us all the complexity and beauty of working catalytic surfaces.

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