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A Career in Catalysis: James A. Dumesic

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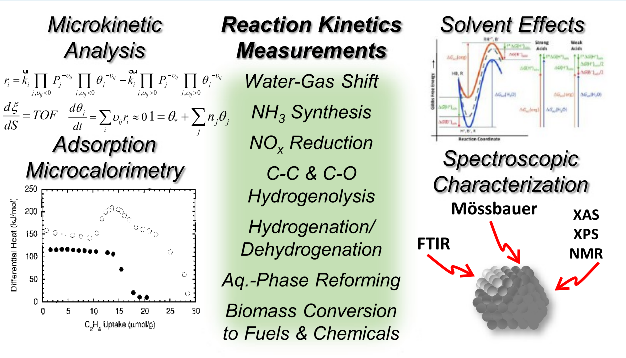

ABSTRACT: After 43 years as a professor in the Chemical and Biological Engineering Department at the University of Wisconsin-Madison, James A. Dumesic retired in 2019. Jim is one of the most influential researchers in the field of heterogeneous catalysis. In this Account, we discuss the scientific discoveries that he made and the intellectual processes that he followed during his illustrious career to steer the field of heterogeneous catalysis into new frontiers. He began his career by fundamentally probing the nature of active sites on heterogeneous catalysts using in situ Mössbauer spectroscopy, electron microscopy, FTIR, and kinetic analysis. This tool kit was used to elucidate the "strong metal support interaction" (SMSI) effect. He developed new microcalorimetric tools to measure the energetics of adsorbates on catalyst surfaces. Jim pioneered microkinetic analysis as a tool to describe heterogeneous reaction kinetics incorporating the essential surface chemistry into kinetic analysis, thereby providing a novel strategy for kinetic assisted catalyst design. Density functional theory (DFT) was combined with FTIR and microcalorimetry to elucidate catalytic surface reactions which were then incorporated into microkinetic models. In the early 2000s, Jim developed the aqueous-phase catalytic processing of biomass-derived oxygenates into fuels and chemicals. This led to the development of new processes to make diesel fuel, jet fuel, gasoline, aromatics, and oxygenated chemicals from renewable resources, several of these technologies are in the process of being commercialized. Jim tailored nanostructured catalytic materials by atomic layer deposition and controlled surface reactions to withstand harsh aqueous-phase biomass processing conditions. He used careful selection and tuning of the solvent composition to achieve substantial control over the activity and selectivity of various biomass upgrading reactions and developed a theory to explain these solvent effects. Underlying these discoveries was a thought process that used fundamental surface chemistry to explain the relationship between the structure, properties, and performance of the catalytic system. Leveraging this thought process across many different reaction classes helped to establish both new tools for catalysis research and to develop new processes for the sustainable production of fuels and chemicals.

KEYWORDS: *heterogeneous catalysis, kinetic analysis, microcalorimetry, biomass conversion, solvent effects*

1. INTRODUCTION

James A. Dumesic graduated with a B.S. degree in Chemical Engineering from University of Wisconsin-Madison (UW) and then completed his M.S. and Ph.D. degrees from Stanford University under the direction of Professor Michel Boudart. Jim then spent 43 years as a professor at UW in the Chemical and Biological Engineering Department before retiring in 2019. There are several quantitative metrics that can be used to discuss the impact of his career. He received numerous awards and became a member of the National Academy of Engineering, National Academy of Science and National Academy of Inventors. Jim has published more than 500 papers with more than 70 000 citations, graduated 71 Ph.D. students, and mentored 15 postdoctoral scholars. As shown in his academic tree (Figure 1) 21 of his Ph.D. students have chosen the academic path becoming professors. Jim Dumesic and his academic protégé have mentored over 267 Ph.D. students and postdoctoral scholars. The objective of this paper is not to discuss the accolades that Jim received through his career. Instead, our objective is to discuss the scientific discoveries and the intellectual process that Jim leveraged to become one of the most influential scientists in the field of heterogeneous catalysis.

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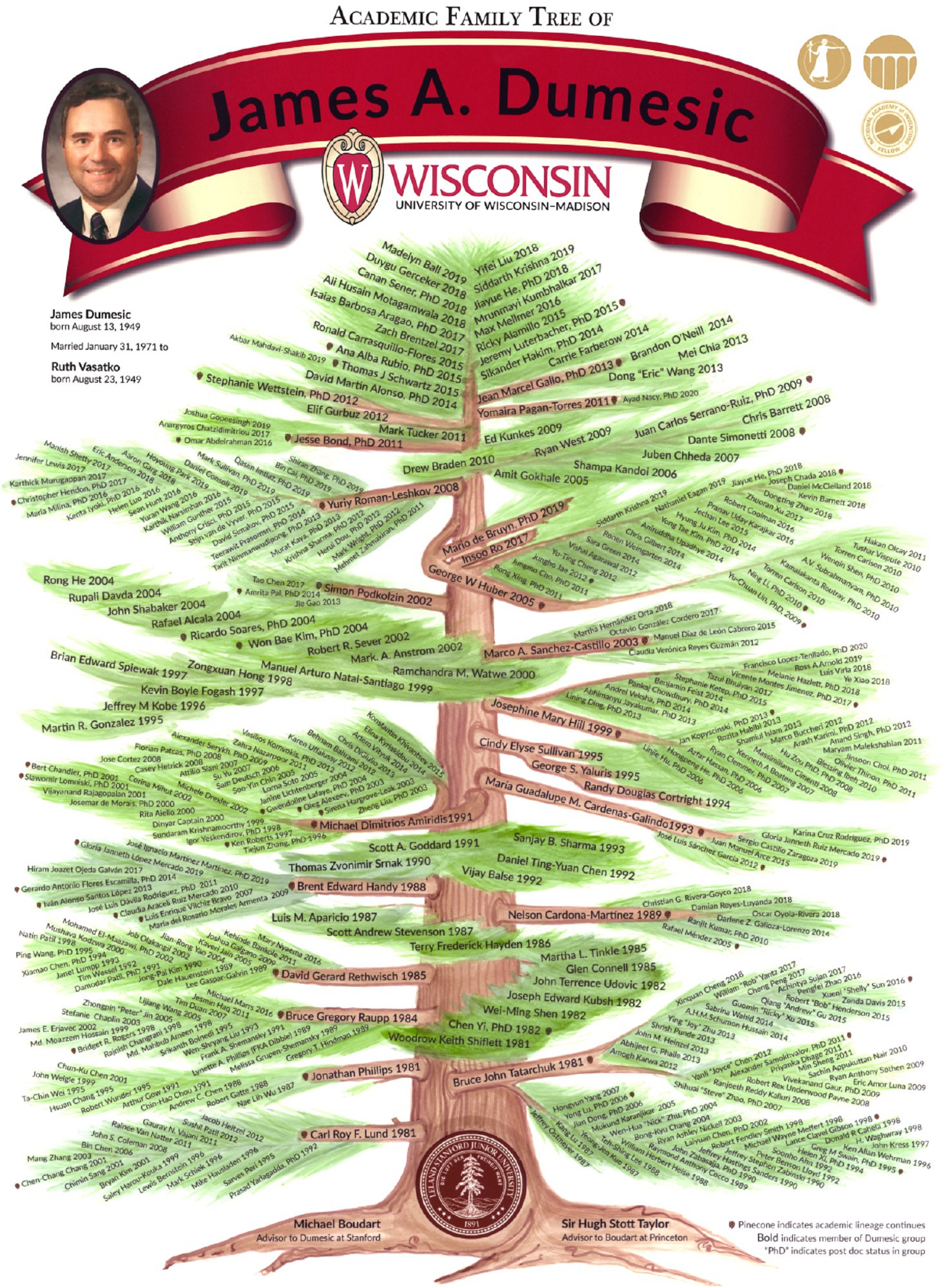

Figure 1. Academic Tree of James A. Dumesic showing his graduate students, postdoctoral scholars, and their students as of September 2019 (Credit: Gretchen Erdmann Hermans).

Creativity, vision, intelligence, drive, and perseverance are among the qualities that set Jim apart. The glue that held these skills together was focus. Indeed, a relentless focus on the technical understanding and solution of vexing and truly impactful problems that confronted the catalysis community. In this overview of Jim's career, we highlight the broad spectrum of catalytic systems he impacted and advanced, while also showing the recurring principles, approaches, and problem solving strategies that he used throughout his career to address challenging research questions. For example, the investigation of each catalytic system was always designed to elicit a fundamental understanding of the relationship between active site structure and catalytic function. At the same time, experiments were conceived and designed with a keen

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awareness that site, surface, and support geometries were dynamic and dependent upon chemical environment and catalyst history. An additional aspect of this awareness was an intensive following of the technical literature and the confident ability of Jim's cogent mind to adeptly conduct his research in an interdisciplinary manner that leveraged the platform of his efforts against the body of knowledge within the community··· from first-principles to process level impacts. These efforts also spanned a broad spectrum of investigations and seminal contributions that included state-of-the-art the experimental and computational tools. While model-supported catalytic systems were often investigated, working catalysts (i.e., ones that could be loaded into a packed bed or similar reactor) were almost always included among the catalyst systems examined. Measurements of catalytic activity and selectivity were combined with a wide range of complementary bulk and surface characterization tools. As Jim's laboratory repertoire and body of impactful contributions increased, so did his capacity to evolve his vision and contributions from those of a foremost problem solver into those ultimately of a gifted solution provider. Few careers have crossed so many interdisciplinary borders, so effectively, and with so much recognized impact on the field of heterogeneous catalysis.

2. THE EARLY YEARS

Jim Dumesic's study of ammonia synthesis,[1−9] primarily during his doctoral studies with Professor Michel Boudart and his early collaborations with Dr. Henrik Topsøe at Stanford provide the earliest examples of some of these principles and approaches. In general, at that time, surface science techniques using single crystals cut to expose surfaces with specific Miller indices were emerging as a means for examining relationships between surface structure and catalytic activity. Studies involving supported catalysts similarly revealed structure sensitivity when the turnover frequency (TOF) varied with supported particle size. By combining such structure sensitivity experiments with chemisorption, Mössbauer spectroscopy, and magnetization measurements, Jim and co-workers were able to not only demonstrate structure sensitivity but also to show that on working ammonia synthesis catalysts, surface iron atoms with seven nearest neighbors were more active for ammonia synthesis than other site geometries.[5] They found that the surface of small Fe particles underwent dynamic reconstruction in the presence of hydrogen−nitrogen mixtures to form such sites and elucidated the dynamic changes in alumina that was added as a textural promoter.[1]

The first equipment built in the Dumesic laboratories at UW consisted of reactors, chemisorption racks, and Mössbauer spectrometers suitable for in situ catalyst investigations. Important add-ons included incorporating electron backscatter spectrometers and detectors for incorporation into typical ultrahigh-vacuum (UHV) catalyst and surface characterization systems. While Mössbauer spectroscopy can only be used to study a few elements, Jim took advantage of the facts that (a) unlike many analytical spectroscopies, it could be used to characterize working catalysts at ambient and higher gas pressures; and (b) two of the elements that can be studied using Mössbauer spectroscopy, Fe and Sn, are also components of several important catalysts. He was a vocal proponent of the use of Mössbauer spectroscopy in catalysis research[10−16] and more generally for the use of techniques that facilitated characterization in environments as close as possible to reaction conditions or in tandem with the burgeoning growth in complementary UHV surface science techniques and methodologies.

The first catalyst systems studied in the Dumesic laboratories at UW were magnetite (Fe_3O_4) catalysts for the high-temperature water−gas shift reaction,[17,18] supported Ru, Re and Pt catalysts for ammonia synthesis,[19−21] and supported metallic Fe catalysts.[22−26] Each of these initial project areas provided a foundation from which new initiatives evolved. Indeed, as one examines the evolution of research projects over the course of Jim's career, the cross-fertilization between projects stands out. Results, methodologies, and interpretations from one project informed other projects and/or motivated new projects even when they appeared to be unrelated.

The water−gas shift can occur by two distinct mechanisms: one where surface catalyst sites are alternately oxidized and reduced or one that involves the formation of surface formates, carbonates, and carboxylates that do not include oxygen from the catalyst. The active site geometry and the electronic structure of magnetite-based water−gas shift catalysts were manipulated by varying the support and substituting other cations for Fe in working catalysts and by fabrication of model catalysts with planar geometries for comparison. Catalyst pretreatment was used to change the oxidation state of the catalyst surface and to cause support and cation migration. The catalytic activities of the resulting collection of catalysts were compared and interpreted with insights gained by complementary characterization using chemisorption, gravimetric reduction/oxidation measurements, Mössbauer spectroscopy, magnetization, isotopic exchange, Fourier transform infrared spectroscopy (FTIR), and electron spectroscopies.[17,18,27−49]

Using unsupported chromia-promoted magnetite catalysts, the rates of oxygen removal by CO and H_2 and the rates of oxygen replenishment by CO_2 and H_2O from the catalysts were measured as a function of the degree of reduction of the catalyst surface.[31] The rate of oxygen removal in CO/CO_2 became equal to that in H_2/H_2O and also equal to the rate of the water−gas shift, at the same degree of catalyst reduction, showing that the oxidation/reduction mechanism was favored over the unsupported chromia-promoted catalyst and simultaneously identifying the oxidation state of the active catalyst surface. Isotopic exchange studies indicated that a surface carbonate was an intermediate in the interconversion of CO and CO_2.[41] When magnetite was supported on oxides including SiO_2, Al_2O_3, TiO_2, and MgO, it was found that, depending upon the magnetite loading, surface structures involving both the FeO_x and the support oxide were formed. As a consequence of the formation of these mixed metal oxides, the mechanism changed to one where the water−gas shift reaction occurred via associative mechanisms between adsorbed species that do not involve oxygen from the catalyst oxide.[42,45,46] Similarly, when bulk mixed oxides were prepared, the mechanism again was associative and did not involve alternating oxidation and reduction of the catalyst surface.[43,44]

The interaction of nitrogen oxides with FeO_x surfaces was first investigated as a means of titrating the surface of supported magnetite catalysts.[17,27] The characterization of the resulting adsorbed surface species revealed that they were similar to those observed in cation-exchanged zeolites and during NOx abatement.[33,50] In such zeolites, the location and coordination of the active sites, that is, the exchanged cations, is dynamic depending upon the environment. The characterization capabilities in the Dumesic group, particularly

Mössbauer spectroscopy, were well-suited to study these systems,[50−61] leading to productive collaborations with Keith Hall's group at the University of Wisconsin−Milwaukee and Wolfgang Sachtler group at Northwestern.

In Fe−Y zeolite catalysts, a combination of IR and Mössbauer spectroscopies revealed the migration of cations during oxidation and reduction, with slow diffusion of cations in the oxidized form of the zeolite from inaccessible locations to locations in the supercages where nitrosyl species formed. Increasing the Si/Al ratio increased the number of such sites and was accompanied by an increase in the rate of catalytic N_2O decomposition. The active sites were identified as those that formed mononitrosyls when exposed to NO. Similar sites were identified in Fe-mordenite and Fe-ZSM-5 zeolites.[50−53,56,58] The activity for N_2O decomposition was further improved when Y zeolite was exchanged with iron and a second polyvalent cation that resulted in a larger fraction of iron in the accessible, active sites.[54]

Ammonia synthesis over Ru, Re, and Pt[19−21] was another of the initial reactions of interest in the Dumesic laboratories. Specifically, this reaction was used to probe changes in active site performance as a function of catalyst support or alloying partner for bimetallic systems. The use of bimetallic catalyst to affect the catalytic cycle became a recurring theme in the Dumesic group and often one of the catalyst components was iron or tin, allowing additional characterization using Mössbauer spectroscopy.[62−68]

3. STRONG METAL SUPPORT INTERACTION (SMSI)

As Professor Dumesic's laboratory was being established, the first studies in water gas shift and ammonia synthesis were just underway when an interesting account was published by Sam Tauster and co-workers in 1978.[69] This paper, describing a phenomenon that became known across the catalysis community as strong metal support interactions (SMSI), caught the attention of Jim and his group. At its onset, SMSI was an unexplained anomaly that occurred after titania-supported metal catalysts were exposed to high-temperature reduction. Following such pretreatments, subsequent hydrogen and carbon monoxide chemisorption uptakes were both suppressed, and the observed catalytic activities and selectivities for a number of reactions were markedly altered. Interestingly both these effects could be reversed following catalyst calcination and lower temperature (ca. 200 °C) rereduction.

The first SMSI related papers emerging from the Dumesic group[23−26] investigated model Fe/TiO_2 supported and powder-based catalysts using a variety of electron microscopic and spectroscopic techniques. Iron was the obvious choice for these efforts because of its suitability for investigation by Mössbauer spectroscopy (which was pursued at liquid helium temperatures) and in situ UHV investigations (in both the traditional transmission geometry as well as in the backscatter conversion electron mode). The first microreactor study using Fe/TiO_2 appeared a year later[70] using ammonia synthesis as the probe reaction.

Bimetallic catalysts with supported Ni and Fe were prepared, characterized, and used as methanation catalysts.[63,71,72] The method of preparation and the support were shown to affect the nature of the active sites formed. When titania was used as the support, the extent of alloy formation was greater, the methanation kinetics changed, the catalytic activity increased, and the selectivity for higher hydrocarbons increased. The SMSI effect in this system was shown to be due to migration of TiO_x species onto the surface of the metallic particles leading to decreased carbon deposition and thereby increasing the fraction of active carbon. Dumesic's lab was one of the first groups to clearly show the fundamental reasons for the SMSI effect.[23−26,62,71−84] TiO_x species in particular were shown to migrate onto the surface of supported catalyst particles wherein they were responsible for altering the chemisorption of key species such as H_2 and CO (or reaction intermediates) via a combination of both electronic and ensemble effects.

Later, bimetallic Pt/Sn catalysts were studied as isobutane dehydrogenation catalysts where the addition of Sn was shown to increase the selectivity for isobutylene.[68] Mössbauer spectroscopy showed that an alloy formed, reducing the number of sites that strongly bind H or CO. These sites featured smaller surface Pt ensembles. Alloys also were shown to form when L zeolite was used as the support, again resulting in high activity and selectivity and reduced deactivation.[64] Adding excess potassium was found to further decrease the size of surface Pt ensembles which reduced isomerization and hydrogenolysis. When ceria was present, Mössbauer spectroscopy revealed that the reduction of Sn was inhibited, the reduction of Ce(IV) was enhanced, and the Pt surface area was again decreased due to PtSn alloy formation possibly together with the presence of Pt-SnO_x moieties.[67]

Other projects initiated during the initial setup of the Dumesic laboratories focused upon the effect of preparation methodology upon the geometric and electronic structure of small, supported iron particles.[22,70,85−89] The initial studies utilized iron pentacarbonyl as the catalyst precursor and high-surface-area oriented graphite as the support. A combination of Mössbauer spectroscopy, computer simulation and TEM showed that the Fe took the form of thin rafts located at edges and steps on the graphite support.

A central theme that emerged from the early years in the Dumesic lab and the investigation of SMSI in particular[23−26,70−72,74−84,86,90] was the splendid opportunity and platform for cross-fertilization between apparently unrelated projects in the lab. Support migration during catalyst pretreatment was observed not only on titania but also in the water−gas shift project on other supports. Much of the early efforts and overarching findings on SMSI were subsequently summarized in an ACS symposium series book edited by Baker, Tauster, and Dumesic.[91]

4. MICROCALORIMETRY

During the evolution of Jim's career, he developed new microcalorimetry techniques and continuously added a growing number of complementary and supplementary experimental and theoretical techniques to balance the method's limitations and exploit its strengths. Jim wrote four authoritative adsorption microcalorimetry reviews. The first review presents a survey of theoretical and applied aspects of microcalorimetry to heterogeneous catalysis up to 1992.[92] The next two reviews focus on applications for the characterization of solid acidity and basicity from 1986 to 2005.[93,94] The fourth reviews adsorption microcalorimetric studies of unsupported metals and metal-based catalysts performed up to 1997.[95]

The Dumesic group made substantial innovations that contributed to the development of adsorption microcalorimetry for the effective characterization of solid catalysts. During the early years, they developed innovative calorimeter cells and adsorption microcalorimetry systems to overcome some of the limitations of those commercially available. The first calorimeter cells developed by the Dumesic group had considerably lower leak rates than commercial ones and high baseline stability, while the computer-controlled microcalorimetric system decreased the effect of the air admitted to the system through small leaks.[96] With that system, the Dumesic group studied the acidity, using basic molecules adsorption, and the basicity, with CO_2 adsorption, of metal oxides without structured pores[96−102] and microporous catalytic materials.[99,103−106] From those studies, Jim developed Sanderson electronegativity scales to describe and predict the strength of Lewis acid sites on metal oxides.[97,100,101,107] Additionally, he found good correlations between acid strength and the proton affinity of various basic molecules.[98,108,109] Jim used some of these semiempirical correlations combined with microkinetic simulations in his first attempt to guide the design of new catalytic materials.[110] Jim's early acidity studies inspired an industrial collaboration with Ross Madon on acid catalysis using zeolites that lasted over a decade.[103,111−122]

The Dumesic group expanded the use of different experimental approaches to provide information about possible relationships between acid strength and catalytic properties. The combination of microcalorimetric, IR spectroscopic, and kinetic studies provided valuable information to demonstrate the importance of both strong and weak adsorption sites for methylamine synthesis and related reactions over acid catalysts.[105,106,108,109] Jim used the same experimental approach to describe the reaction kinetics for isobutane[113−115] and 2-methylhexane[117,119] cracking on USY-zeolite-based catalysts. Using adsorption microcalorimetry, infrared spectroscopy, and microkinetic analysis he developed a model capable of effectively describing the activity and selectivity of isobutane cracking on calcined Y-zeolite compared with a calcined and steamed Y-zeolite.[103,114,115] The key for the success of the model was the use of the enthalpy of a carbenium ion transition state relative to the enthalpy of stabilization of a surface proton in the zeolite framework (ΔH_+) as a parameter. That parameter is related to the Brønsted acid strength of the catalyst. Using the same parameter, Dumesic developed another microkinetic model that effectively describes the trends in activity and selectivity for 2-methylhexane cracking.[117,119] The model predicted that the value of ΔH_+ increased, the catalyst activity per Brønsted acid site decreased, and the strength of the acid sites decreased with increased steaming severity of a Y-based FCC catalysts.[119] An important outcome of these studies was to get an accurate quantification of the number and strength of Brønsted acid sites as a function of the catalyst pretreatment. These results were later used in the development of more comprehensive microkinetic models for isobutane cracking.

Another Dumesic group innovation was the design and construction of a low-cost microcalorimeter suitable for measuring heats of adsorption and reaction on solid surfaces.[123] The flow cells designed and built for that calorimeter provided the capability of performing reaction kinetics measurements for samples that subsequently were used in microcalorimetric studies without exposure to the atmosphere or for selective poisoning followed by reaction kinetic measurements.[123]

Jim used this last approach to study the selective poisoning of sulfated zirconia with ammonia to demonstrate that Brønsted acid sites of intermediate strength are active for *n*-butane isomerization and deactivate slower than the strongest acid sites at 423 K.[124,125] Coupling adsorption microcalorimetry of ammonia, water, *n*-butane, and isobutane with FTIR demonstrated the promotional effect of controlled amounts of water on sulfated zirconia samples dehydrated at 773 K.[126] The presence of the proper degree of hydroxylation prevented irreversible sulfur reduction.[127] These studies of the acidity of sulfated zirconia, coupled to a series of papers where the Dumesic group studied the reaction kinetic behavior of sulfated-zirconia catalysts for butane isomerization, led to another review that included microcalorimetric characterization of surface acidity of sulfated-zirconia catalysts.[128]

The Dumesic group also used conventional microcalorimetry techniques to study supported Pt,[68,129−133] Pt−Sn,[64,68,132,133] Pd,[129,133] Ir,[129] Co,[129] and Cu[134] catalysts and unsupported Ni powder, Ni−B, and Ni−P[135] catalysts. Combining adsorption microcalorimetry of CO or H_2 with ^{13}C NMR spectroscopy and reaction kinetic studies showed that hexane cyclization, aromatization, and isomerization reactions over Pt in L-zeolite and on SiO_2 are similar and that differences in activity and selectivity are primarily caused by differences in catalyst deactivation.[130,131]

Using a combination of kinetic, microcalorimetric, and Mössbauer spectroscopic studies, it was shown that the addition of Sn to supported Pt inhibited the formation of highly dehydrogenated surface species that enhanced the selectivity for isobutane dehydrogenation to isobutylene.[68] Addition of K, Rb, or Cs to supported Pt/Sn increased the dehydrogenation activity and selectivity and improved the resistance of the catalyst to deactivation.[132] The addition of alkali species substantially increased the hydrogen adsorption capacity and decreased the adsorption capacity for carbon monoxide.[136] The alkali species promote supported Pt/Sn catalysts for isobutane dehydrogenation by decreasing the size of surface platinum ensembles, thereby inhibiting isomerization, hydrogenolysis, and coking reactions that proceed through the formation of highly dehydrogenated surface species over large ensembles of surface platinum atoms.[64,136,137] Applying microkinetic analysis with the previously studies suggested that the higher reaction rates observed over Pt/Sn/K-L zeolite may be the result of the zeolite pore structure and/or the presence of potassium promoting the hydrogenation and dehydrogenation reactions by stabilization of activated complexes for elementary steps involving hydrocarbon species.[64,137] Microcalorimetric measurements combined with density functional theory (DFT) calculations showed that the addition of tin to platinum results in the inhibition of the dissociative adsorption of ethene, isobutene, and isobutane.[133,137]

Low surface area unsupported metal powders, and metal-based catalysts may be easily contaminated by oxygenates. To solve that difficulty, Jim developed special calorimeter cells that allow high surface cleanliness of metallic samples during the time of a complete adsorption microcalorimetry study.[95,136,138,139] After meticulous treatment, the samples are sealed in Pyrex capsules and placed in the stainless-steel cells that have been allowed to attain thermal equilibrium with the microcalorimeter. The cells employ a bellows-sealed linear-motion drive to break the sealed Pyrex capsule containing the sample. The addition of submonolayer amounts of metallic potassium or cesium to reduced nickel powder[138,139] and rubidium or cesium to reduced platinum powder[136] generated sites with weaker strength that significantly increased the adsorption capacity of CO. The novel microcalorimetric

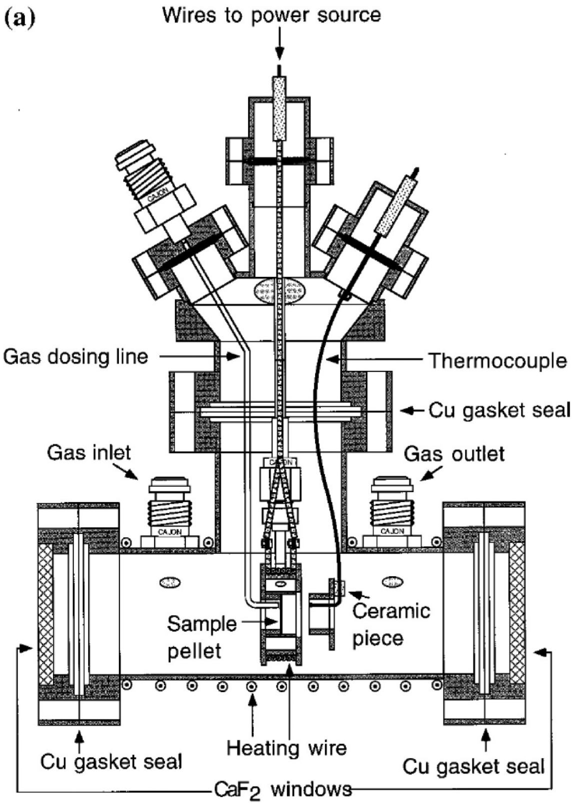

Figure 2. Schematic diagram of the IR cell for measurements at temperatures from 150 to 673 K: (a) front view; (b) side view. Notes: (1) There is a cooling water line around the windows. (2) The heating wire outside of the chamber is used to heat samples up to 773 K for reduction and purging. (3) The heating wire inside of the chamber is used to maintain constant low temperatures. Reproduced with permission from ref 141. Copyright 1999 American Chemical Society.

method was effective for measuring the strengths of adsorbate−surface interactions for temperatures between 173 and 473 K, not only on clean metal surfaces but also on metal surfaces that have been exposed to reaction conditions.[140]

5. DFT, FTIR, AND MICROCALORIMETRY

While microcalorimetry was indeed a powerful technique, further information about the adsorption sites required complementary experimental techniques such as FTIR. Another Dumesic group innovation was the design and construction of an infrared spectroscopy cell for collection of in situ FTIR spectra at temperatures from 153 to 673 K (Figure 2).[141] The Dumesic group used the microcalorimetric and spectroscopic results over a wide range of temperatures (173 to 573 K) to calibrate the DFT methods by comparing results for observable stable surface intermediates. They then applied the calibrated theoretical methods to estimate structures and energetics for reactive species that cannot be readily observed[142] as well as for transitions states involved in C−C bond cleavage of various C_2H_x adsorbates.[142] The theoretical calculations provided a strategy for estimating values for energetic parameters that are necessary to conduct kinetic analyses of reaction pathways.[143] The analysis of reaction kinetics data collected over a wide range of conditions provided a feasibility test of the proposed reaction scheme.

Jim was one of the early adapters of using density functional theory (DFT) to understand the energetics of adsorbates on surfaces. As he indicated in a 2001 review paper:

> *"The recent advances in quantum chemical techniques, combined with improved computer performance, make it possible to conduct quantum chemical calculations to represent more realistic models of active sites and more complex reaction schemes. Since these experimental and theoretical investigations are conducted under different conditions and on a variety of related materials, it is useful to conduct analyses of appropriate reaction schemes to consolidate the results. An important consequence of conducting reaction kinetics analysis in conjunction with results from quantum chemical calculations and experimental studies is that quantitative knowledge about the catalytic process is built at the molecular level into the kinetic model. This process of extracting fundamental knowledge provides a molecular-level basis for comparisons between catalyst systems and provides unifying principles for the design of new catalyst systems".*[9]

Jim's first publication containing DFT was published in 1997[144] and involved the study of isobutene adsorption on silica. Isobutene was of great interest at the time as a precursor/intermediate in the production of oxygenated molecules (e.g., methyl *t*-butyl ether, MtBE) used as additives to improve the performance of unleaded gasoline. While it was known that the reactivity of light alkenes over solid acids was positively correlated with the acid strength of the catalyst, the details of the adsorption and reaction steps were not well understood. Microcalorimetry provided the strength of adsorption between isobutene and silica (56 to 27 kJ/mol as the coverage increased to 540 mmol/g), and FTIR indicated that the majority of the isobutene was reversibly bonded to the silica surface through π-bonding, with some alkoxy species. The DFT calculations elucidated that the localization of positive charge in the corresponding transition states was not favored for the adsorbed isobutene to convert to the more reactive alkoxy species on the weakly acidic silica. Thus, although favored thermodynamically, the alkoxy species were kinetically limited from forming (activation energies over 170 kJ/mol).

Using a combination of microcalorimetry, FTIR and DFT, the Dumesic group described the kinetics of ethane hydrogenolysis on Pt.[143] They combined the innovative microcalorimetric techniques to study the adsorption of H_2,[140,141,143,145] CO,[141,146,147] C_2H_4,[140,141,143] and C_2H_2[140] with infrared spectroscopic measurements for adsorption of ethylene,[141] DFT to study the interaction of CO[146,147] and of C_1 and C_2 hydrocarbons species[141−143] with Pt, and results of reaction kinetic studies[143] to develop a quantitative description of the catalytic chemistry for ethane hydrogenolysis over platinum that was consistent with the results from the experimental and theoretical investigations. Figure 3 shows an example of the adsorption microcalorimetry results for ethylene adsorption.

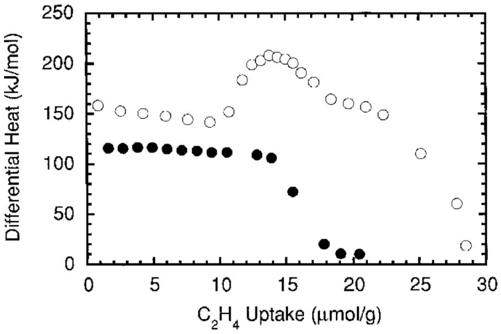

Figure 3. Differential heats of ethylene adsorption on platinum powder at 303 K (○) and 173 K (●). Figure reproduced with permission from ref 143. Copyright 1999 Elsevier.

The Dumesic group also studied the adsorption of ethylene between 173 and 300 K on Pt/SiO_2,[141] Au/SiO_2,[148] Pd/SiO_2,[149] Ru/SiO_2,[150] Cu/SiO_2,[150] $Pt/Sn/SiO_2$,[141] $Pt/Au/SiO_2$,[148] $Pd/Sn/SiO_2$,[149] $Ru/Sn/SiO_2$,[150] and $Ru/Cu/SiO_2$[150] catalysts using a combination of adsorption microcalorimetry, FTIR, and DFT. The addition of Sn to Pt[141] and to Pd[149] on SiO_2 weakens the bonding with the surface of ethylidyne species more than di-σ-bonded or π-bonded ethylene species. Addition of Au withdraws electrons from Pt and leads to a more attractive interaction between Pt and ethylidyne species and suppresses the formation of ethylidyne species only by exerting a geometric effect.[148] However, Sn was located preferentially at the surface of Ru, and addition of Sn to Ru appeared to weaken the adsorption of molecularly bonded ethylene species more than ethylidyne species.[150] The addition of Cu to Ru led to a decoration of the Ru surface by Cu that gave lower heats of CO and C_2H_4 adsorption primarily as a result of those adsorbates binding on both Cu and Ru.[150] For a Pt−Zn/X-zeolite catalyst, the effects of adding Zn to Pt were qualitatively similar to the effects of adding Sn to Pt observed above.[151]

Following similar methodologies used in previous studies, the Dumesic group developed a microkinetic model that described the high activity and selectivity of the Pt−Zn/X-zeolite catalyst for the dehydrogenation of isobutane to isobutylene.[151] Addition of Sn to Pt catalysts inhibited the cleavage of the C−C bond in ethanol and acetic acid, such that Pt−Sn-based catalysts were active for dehydrogenation of ethanol to acetaldehyde and selective for the conversion of acetic acid to ethanol, acetaldehyde, and ethyl acetate.[66] The suppression of C−C bond cleavage in ethanol and acetic acid upon addition of Sn to Pt was confirmed by microcalorimetric and infrared spectroscopic measurements at 300 K of the interactions of ethanol and acetic acid with Pt and Pt−Sn on a silica support that had been silylated to remove silanol groups.[66] Adsorption microcalorimetry of CO at room temperature combined with X-ray photoelectron spectroscopy and ^{119}Sn Mössbauer spectroscopy helped explain that adding Sn (in a Pt/Sn 1:1 atomic ratio) and/or CeO_2 to Pt/Al_2O_3 catalysts improved the selectivity to crotyl alcohol during crotonaldehyde hydrogenation.[67] Continuing the work on oxygenates, the Dumesic group combined microcalorimetric, infrared spectroscopic, and reaction kinetics measurements with DFT calculations to investigate the selective reduction of acetic acid, methyl acetate, and ethyl acetate over silica-supported copper catalysts.[152] They studied the adsorption of methanol and ethanol on silica;[153] the adsorption of acetaldehyde, methyl acetate, and ethyl acetate on silica;[154] and methyl acetate, ethyl acetate, acetaldehyde, methanol, and ethanol on silica-supported copper.[152] The experimental and theoretical results led them to conclude that the rate of reduction of *n*-alkyl acetates is determined by the dissociative adsorption of these molecules and by the surface hydrogenation of surface acyl species.[152] These were the first papers the Dumesic group wrote on catalytic conversion of oxygenates which led to his future work on catalytic conversion of biomass-derived oxygenated.

6. MICROKINETIC ANALYSIS

At the end of 1980s, Jim proposed microkinetic analysis (MKA) as a tool to describe heterogeneous reaction kinetics by incorporating the essential surface chemistry involved in the catalytic reaction.[155] The need to optimize catalytic processes of commercial relevance had motivated a growing interest in understanding the relationship between the catalyst active site and the surface chemistry. This work was also inspired by more comprehensive kinetic models that were being used to describe combustion reactions, discussions with Professor Dale Rudd at UW, and computational methods to solve differential equations by Warren Stewart at UW. Jim's motivation was to provide a methodical framework to consolidate essential information about a catalytic process with the goal of providing fundamental knowledge to guide further research and development.[156] Over time, MKA has proven to be a remarkable tool to reconcile experimental and theoretical data for diverse reaction systems elucidating key features of catalytic performance based on molecular-level descriptors. Importantly, the discoveries of MKA are now a reliable framework to guide the improvement and design of new catalysts and catalytic process.[157−163]

Jim's microkinetic approach was the result of a visionary intuition to integrate, interpret and generalize experimental and theoretical results available for catalytic reactions. Many authors inspired Jim but, certainly, the primary influence came from Prof. Michel Boudart and Dr. Haldor Topsøe. His lasting and successful academic relation with Prof. Boudart may be seen in different stages of evolution of MKA.[156,164,165] Jim was

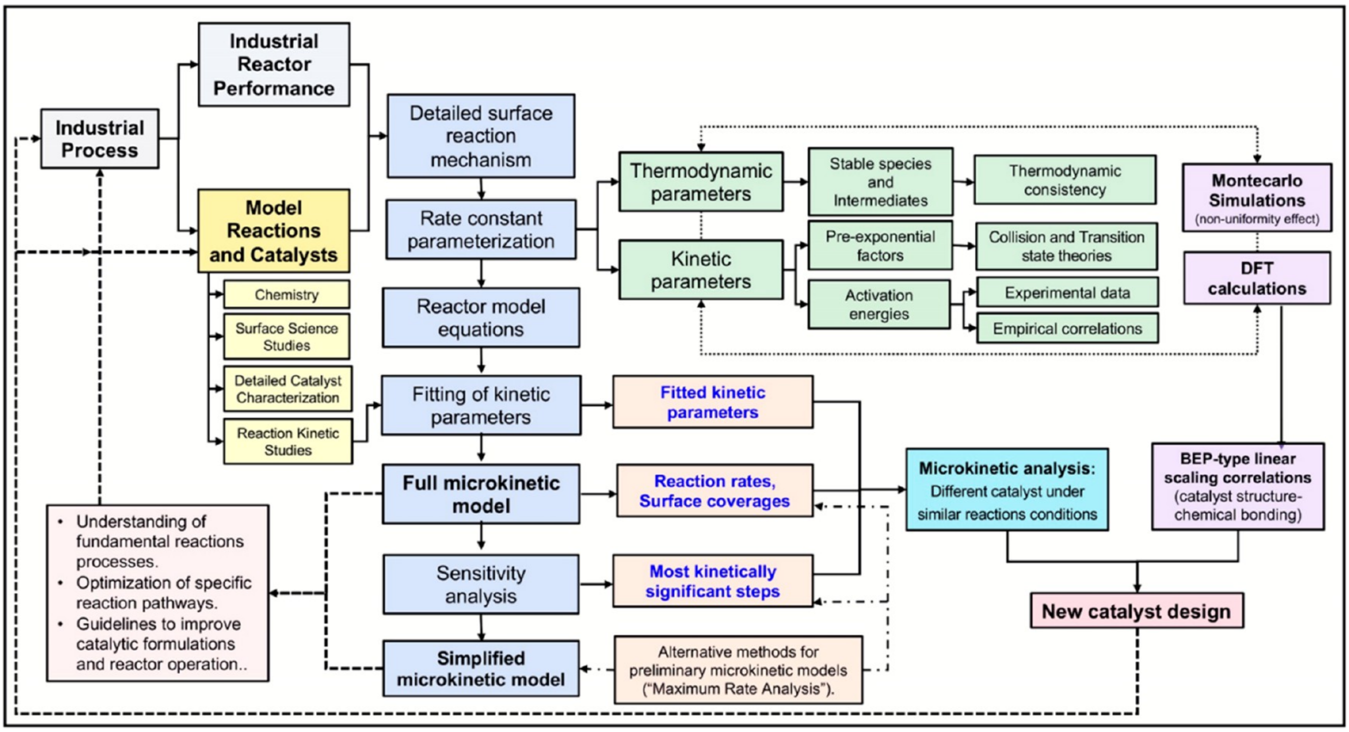

Figure 4. Simplified schematic representation of the microkinetic analysis approach. ("BEP-types" stands for Brønsted−Evans−Polanyi-type.).

always inspired by Dr. Topsøe's vision for synergies between industrial and academic catalysis research. Technical contributions and encouraging influence from Dale Rudd were also significant.[110,155] Jim had the leadership to integrate catalysis, surface science, theoretical quantum chemical calculations, and numerical methods. Jim was always open to critical discussions and willing to incorporate concepts and tools set by other researchers, in an atmosphere in which respect and interest in solving challenges at the frontier created innovative results. Jim had close collaborations with industry, which undoubtedly contributed to identify what elements of MKA could be relaxed so that the model had practical contributions without losing the rigor and strength of its fundamental structure. Jim always had the distinctive ability to interpret how the crucial findings from MKA had practical and beneficial consequences for the industry.

A simplified schematic representation of the microkinetic approach is shown in Figure 4, and a detailed description of MKA concepts and tools is reported elsewhere[9,156,162,165] The starting point in the construction of a MKA is identification of the elementary steps with appropriate stoichiometric numbers, including stable and intermediate species. All steps are considered reversible, and there is no need to assume, a priori, the kinetic significance of elementary steps or the most abundant surface intermediates. Given the importance of maintaining thermodynamic consistency, Jim outlined a general strategy to parametrize the kinetic model.[9,165] Pre-exponential factors in rate constants are usually calculated from collision theory or transition state theory. Activation energies are estimated from experimental data, but when reliable data are not available, they are estimated from theoretical calculations or by using empirical correlations based on chemical similarities between elemental surface reactions.[162,166−172] With the remarkable development of computational chemistry, Jim actively promoted the use of DFT to determine the structure, stability, and reactivity of adsorbed species and also Monte Carlo (MC) simulations to study nonuniformity effects on the catalyst surface.[66,141,142,144−146,150−152,154,173−185] More recently, a multiscale approach models the essential surface chemistry combining DFT calculations and MC simulations to get further insight about kinetically significant steps.[186−191] However, MKA was developed before these computational tools were available, and Jim suggested that the interest to learn deeper details of surface chemistry by using more sophisticated theoretical methods must be balanced by the practical need to solve complex challenges faced by society.

A masterpiece of Jim's creative work was to show that De Donder relations are very useful for deriving general principles about reaction schemes.[164,165] Jim demonstrated that De Donder relations provide a simple method of determining the number of kinetic parameters required to calculate overall reaction rates, and they offer a rigorous approach for assessing whether a reaction scheme contains a rate-determining step. Jim showed that kinetic parameters identified by De Donder analyses are controlled by quasi-equilibria between reactants and products of the overall reaction with the transition states of the elementary steps. In addition, Jim demonstrated that De Donder relations make it possible to calculate the maximum rate at which a given transition state may contribute to the overall reaction rate, providing a starting point for conducting sensitivity analyses of kinetic parameters. Jim realized that there are cases for which De Donder relations do not distinguish the relative importance of each step and he suggested the use of Campbell's degree of rate control ($X_{RC,i}$)[192,193] as a measure of the sensitivity of the overall reaction rate to the kinetic parameters for each step. Jim demonstrated that De Donder relations and the degree of rate control are complementary tools for analyzing reaction schemes.[9,164,165]

MKA has shown that net reaction rates are controlled by the properties of the transition states of kinetically significant steps as well as by the properties of abundant surface intermediates.[121,122,194] On the basis of these premises, Jim realized the relevance of adsorbate−surface interactions to achieve optimal catalyst performance. If the surface coverage is low, a more active catalyst can be prepared by increasing the strength with which the rate-controlling transition states are bonded to the surface. Typically, as the nature of the catalyst surface is changed to bind transition states more strongly, it is expected that the surface will also interact more strongly with reaction intermediates, which will become abundant on the catalyst surface, thereby decreasing the fraction of free sites and eventually leading to lower reaction rates. In fact, Jim suggested that Sabatier's principle can be restated to read: "A good catalyst is a material that interacts strongly with the rate-controlling transition states but that does not interact too strongly with the reactants, products, or intermediates of the reaction".[165] Thus, the catalytic reaction rate is maximized at an optimum interaction strength of the reactants with the catalyst. The challenge then becomes determining what energy should be considered as the descriptor for binding the reactive species. For many catalytic reactions, a linear relationship exists between the activation energy (E_a) and the stability of intermediates on the catalyst surface given by the dissociative chemisorption energy (ΔE). These relationships (i.e., $E_a = \alpha \Delta E + \beta$) are considered Brønsted−Evans−Polanyi-type (BEP-type) relationships, and extensive work has been under way, mostly using metal surfaces, to establish a number on these relations based on simple descriptors by using DFT calculations.[167,171,195]

Jim's research work in MKA has been published in more than 130 papers. Two features have been instrumental for the success of his microkinetic approach: (1) his persistent interest to progressively incorporate new experimental and theoretical tools and (2) his close collaboration with industry to be aware of the industrial challenges and to test the applicability of MKA fundamental findings. The insights that Jim acquired in the analysis of model catalytic reactions were key to visualize new horizons in his research. Jim incorporated the concepts and tools needed to extend the usefulness of MKA to several different catalytic systems. Jim's scientific production related to MKA accounts for about 20% of his prolific scientific career. However, the impact of Jim's MKA should rather be measured in terms of other achievements. Jim created and disseminated the application of a unique tool to conduct fundamental studies in heterogeneous reaction systems and to guide the development of optimized and new catalysts and catalytic processes.

Jim and his collaborators initially applied MKA to study ammonia synthesis,[196,197] ethane hydrogenolysis,[129] oxidative coupling of methane,[198] methane dimerization,[199] methane partial oxidation,[200] ethylene hydrogenation,[201,202] SCR of NO,[203] and isobutane dehydrogenation.[204] These early investigations were mostly directed to reconcile reaction kinetic data collected at lab and industrial conditions, with results from surface science and catalysts' characterization. From a fundamental basis, a number of MKAs were generalized and then used to describe catalytic reactions with similar chemistries. The ability to transfer quantitative information among diverse reaction catalyst systems proved to be of critical importance for catalytic reaction synthesis. Jim emphasized that microkinetic models (MKM) should be constructed with an appropriate level of complexity to reconcile all macroscopic observations but using a limited number of kinetic parameters with physical significance. Sensitivity analysis provided a formal approach to determine kinetically significant steps, which can be used to build simplified MKM describing experimental trends with precision similar to the full MKM. Jim's research group showed that significant changes in catalytic activity and selectivity over metal and metal oxides catalysts were related to changes in the strength of adsorption of reactive species. These trends were initially explained in terms of established semiempirical relations, but most importantly, the latter became the basis to the search for BEP-type linear scaling correlations to link catalyst structure and chemical bonding relations.[162,166−172] Jim provided a rational strategy to optimize catalytic reaction rates. By comparing different catalysts under the same reaction conditions and measuring the reactant-adsorption energies and catalytic rates, it is possible to determine whether the reaction rate increases or decreases with the adsorption energy of the reactants. In this scenario, the trends in measured or calculated adsorption energies as a function of the catalytic material, makes it possible to select surfaces that might improve catalytic performance. These concepts have evolved and are now extensively used to simulate the extent to which catalytic activity could be enhanced by increasing strength of an adsorbate−surface bond and also to speed up the design of new catalysts.[160,195,205−207]

One of the industrial reactions that attracted Jim's interest was understanding the role of the addition of rare earth (RE) cations in the Y zeolite-based catalysts widely used in FCC. Jim worked on this project with his graduate students and Dr. Rostam J. Madon from Engelhard Corporation, another Boudart graduate whom Jim met in graduate school. Jim's approach in this research reflects his vision of using model molecules to analyze complex chemistries, to progressively incorporate new concepts and tools for deeper understanding of reaction systems and, then, to rationalize how fundamental results explain macroscopic observations. Jim selected isobutane conversion as model reaction. Jim developed a low-temperature experimental technique that significantly reduces, if not eliminates, the role of monomolecular initiation processes while studying catalytic cracking. This technique allowed them to focus on the study of bimolecular hydride transfer and oligomerization/β-scission reactions. Based on experimental and theoretical work conducted in his research laboratories,[111−116,118,119,126−128,173,208−211] the Dumesic group constructed a 370-step MKM for isobutane conversion over USY-based catalysts applicable over an extended temperature range, 523−773 K.[120] This MKM included 2 steps for monomolecular initiation of isobutane to produce hydrogen or methane and the corresponding alkoxy species, 106 steps for oligomerization/β-scission, 78 steps for isomerization, 88 hydride transfer steps which form paraffins, and 93 steps for desorption of adsorbed alkoxy species to form olefins. Olefin adsorption/desorption steps were assumed to be reversible, with adsorption steps initiating reactions and desorption steps terminating surface reactions. Parameterization of the MKM took into consideration several well-established correlations and DFT calculations carried out for similar catalytic reactions, and as a result, only 12 kinetically significant parameters were required to reconcile kinetic data of isobutane conversion over the USY-C catalyst. A sensitivity analysis was conducted using Campbell's degree of rate control ($X_{RC;i}$), finding that a limited

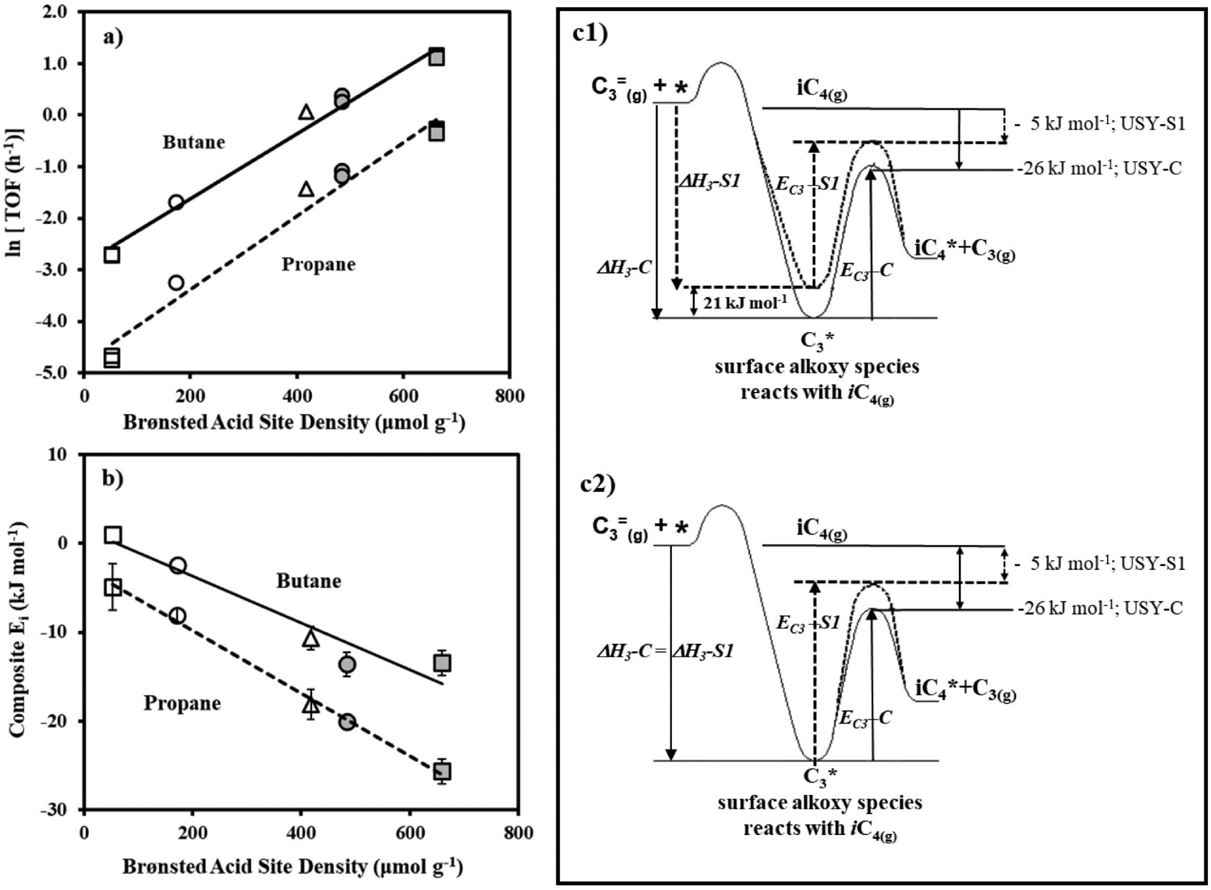

Figure 5. Representative results of microkinetic analysis of isobutane conversion over calcined and steamed USY zeolite (USY-C, USYS1, USY-S2) and Rare-Earth USY zeolite (REUSY-C, RE-USY-S1) catalysts, for experiments carried out at 573 K, with 80% isobutane and 400 ppm of isobutylene in the feed. First column: Linear fit of (a) the logarithmic values of experimental TOFs (ln TOF), and (b) composite activation barriers for hydride transfer steps (E_i) to produce propane and *n*-butane versus Brønsted acid site density. Error bars determined from 95% confidence interval. Second column: (c1) and (c2) Potential energy diagrams for the formation of propane from propylene (Solid line: pathway for USY-C; dotted line: pathway for USY-S1). Symbols: ■USY-C; ●REUSY-C; △USY-S2; ○REUSY-S1; □USY-S1 (Figure 5 was adapted from Figures 3, 6, and 7 with permission from ref 122. Copyright 2005 American Chemical Society.

number of elementary steps had $X_{\mathrm{RCi}} > 0.1$, which were used to develop a 48-step simplified reaction scheme that resembled the trends in reaction rates given by the full MKM. More importantly, sensitivity analysis clearly shows the effect of reaction conditions on $X_{\mathrm{RC,I}}$ for each family of reactions, thus determining the set of conditions that facilitate the study of a given reaction family with the least influence of the others reactions.[120]

MKM of isobutane conversion was then used as a tool to understand the critical role of RE in USY-zeolites catalysts. RE cations determine Brønsted acid sites density and the zeolite unit cell size, the latter being used as a fingerprint for catalyst acidity and reactivity in FCC units.[122] Jim's research group carried out kinetic studies of a series of commercial USY and RE-USY catalysts, calcined, and steamed under different conditions. Kinetic studies were conducted at low temperature to focus on hydride transfer and oligomerization/β-scission reactions. As illustrated in Figure 5, the TOF of paraffinic products of isobutane conversion depended exponentially on the Brønsted acid site density. In agreement with these experimental results, MKA determined that rates of hydride transfer reactions and β-scission processes also depended exponentially on Brønsted acid site density. As a result, the composite activation energies (i.e., composite energies of transition states of elementary steps relative to the gaseous reactant) for these reactions had a linear relationship with Brønsted acid site density. These relationships hold regardless of whether the site density was modified by RE cations or not (REUSY-C, USY-C), by being steamed under different severity conditions (USY-S2, USY-S1), or both (REUSY-S1). In addition, MKA showed that a Brønsted acid site in Y zeolite catalysts in the presence of other such sites was significantly more effective for hydride transfer and catalytic cracking than an isolated site, in contrast with previous reports in the literature. Accordingly, MKA of isobutane conversion made evident that a critical parameter determining activity and selectivity of USY and RE-USY catalysts, calcined and steamed, was the Brønsted acid site density, which depends on framework aluminum content and therefore on the extent of dealumination during steaming. Jim's research group reached the conclusion that the role of RE cations was to ensure the retention of high Brønsted acid site density during hydrothermal conditions, such as in FCC regenerators, where steam would dealuminate the USY zeolite framework and reduce this site density. Jim's research group proposed that increasing the Brønsted acid site density in USY zeolite leads to larger zeolite elasticity, which induces an increased stabilization of cationic transition states and, therefore, lowering composite activation barriers for hydride transfer and β-scission steps. In this case, it was also suggested that changes in zeolite properties were mostly reflected on the stabilization of the transition state because MKA showed that the heats of adsorption on USY-based catalysts were not kinetically significant.

It is noteworthy to recognize the collaboration established by Jim with Prof. Manos Mavrikakis at UW. The synergy of their collaboration has been shown in research of CO oxidation;[213] methanol and ethanol decomposition on transition metals;[170,214−216] low-temperature WGSR on Cu, Pt, and Pt−Re catalysts;[185,217−221] ethylene glycol reforming over Pt;[222] reduction of NO by hydrogen on Pt(111);[223] H_2O_2 decomposition over Pd;[224] and formic acid decomposition on Au and Pt catalysts.[225−228] Application of DFT calculations in MKA provides better parameter estimates for reaction intermediates and transition states, enhances the predictive ability of MKA, and facilitates the development of BEP correlations. For instance, the correlation between the energy of the transition state and the energy of the final state for C−C and C−O bond-breaking steps on metal surfaces was used to study the selectivity of ethanol decomposition on the close-packed facets of 10 metals.[170] The combination of these BEP-type correlations with a second linear scaling correlation to relate the binding energy of molecular adsorbates to the binding energy of the atom through which it adsorbs was an original and powerful approach to make an adequate description of kinetic data of ethanol decomposition on transition metal surfaces.[170] This theoretical approach reduces the cost of DFT calculations required for identifying reactivity descriptors of complex reactions[168,170,214,216] and contributes to finding reactivity trends to enhance catalytic performance and fundamental understanding to design catalysts for complex reaction networks based on first principles.[160,195,205−207]

The development of a full MKM may be computationally intensive and time-consuming, often making it impractical for rapid analyses of experimental data. To solve this issue, Jim's research group recently suggested the maximum rates analysis (MRA) of elementary steps as an analytical methodology to determine which transition state and adsorbed intermediates are kinetically significant.[229] This approach is exact for reaction schemes where the stoichiometric coefficients of the constituent steps are equal to unity and the most abundant adsorbed species are in quasi-equilibrium with the gas phase. MRA initially evaluates the surface coverages of adsorbed species to identify which surface species are expected to be abundant. Subsequently, the maximum rates of the constituent steps are calculated. The overall reaction rate and the degree of rate control ($X_{RC,i}$) of the constituent steps are then calculated using analytical expressions. Accordingly, steps with finite $X_{RC,i}$ are kinetically significant in determining catalyst performance, and detailed DFT calculations are carried out for only these species; however, more approximate methods are used for the remaining species. This approach minimizes the DFT calculations and computational time needed in the development of a MKM, as it was recently shown for the case of WGSR.[162,229]

To make predictions about improvements in catalyst performance, Jim's research group extended MRA to generalized reaction kinetics rate expressions. They suggested that by writing the rate expression in terms of transition states and adsorbed intermediates, such that the reaction order and apparent activation energy are in agreement with experiments, it is possible to apply scaling relationships to guide experimentalists in the search toward an improved catalyst. It was also suggested that when only small improvements in catalytic rates can be achieved by changing the binding energy of the reference species within the scope of scaling relations, then other catalytic materials that do not obey the scaling relations need to be considered to improve reaction rates.[230,231]

Ever since Jim pioneered the MKA, there has been lively interest of research groups around the world as a standard tool to investigate model and industrial reaction systems.[157−159] As Professor Boudart foresaw in the foreword of Jim's microkinetic book, slowly but firmly, MKA has become a standard tool in the area of heterogeneous catalysis that can be applied to understand surface chemistry of catalytic reactions.

7. AQUEOUS PHASE REFORMING OF BIOMASS

During the development of the MKM approach, Jim followed a fundamental thought process based on chemical intuition and experience with related catalytic processes (termed "catalytic reaction synthesis by analogy").[110,232] The results of this thought process were reaction schemes against which he could consolidate the information derived from diverse experimental and computational techniques. This led to the development of microkinetic models that not only extracted fundamental knowledge about the system but also served as tools for extrapolation of this information to other reaction conditions and to other catalytic reactions involving related reactants, reaction intermediates, and/or products.[9,155,232] During the late 1990s, as advances in biotechnology and increasing oil prices drove society to consider alternative sources for fuels and chemicals, Jim was able to leverage this thought process to pioneer several research discoveries related to the conversion of biomass-derived molecules to fuels and chemicals.

One of the first projects during this "biomass conversion era" involved studying the catalytic conversion of lactic acid into different chemicals. This project was funded by Cargill as they were interested in the range of products that can be produced from lactic acid which was being produced via a commercial fermentation technology. Doug Cameron, a former UW Professor, had recently left UW to become the director of biotechnology at Cargill. Doug encouraged Jim to start using his knowledge of catalysis to convert biomass-based feedstocks. Just as he had done his entire career, Jim attacked the lactic acid project at several different length scales and in several different ways with a team of different graduate students. His group first started studying the adsorption of oxygenates (including methanol, ethanol, and trifluoroethanol) on silica[153] to measure the heats of adsorption of these oxygenates and the fundamentals of how these oxygenates adsorb on the surface. In parallel, model compounds (acetic acid, ethanol, 1,2 propanediol) were used to measure the rates and product selectivities at various conditions on Pt-based catalysts (already known as effective alkene/alkyne hydrogenation catalysts) and to quantify the intrinsic kinetics of the reaction. Finally, these experimental data were combined with DFT calculations and interrogated against simplified mechanisms synthesized from the data and from analogous reactions. The result of these studies was a microkinetic model describing organic acid hydrogenation that identified three surface intermediates (and six associated reactions) as essential chemical features that dictated the selectivity of organic acid hydrogenation and that directed future researchers toward the potential of alloy catalysts for influencing the binding energies

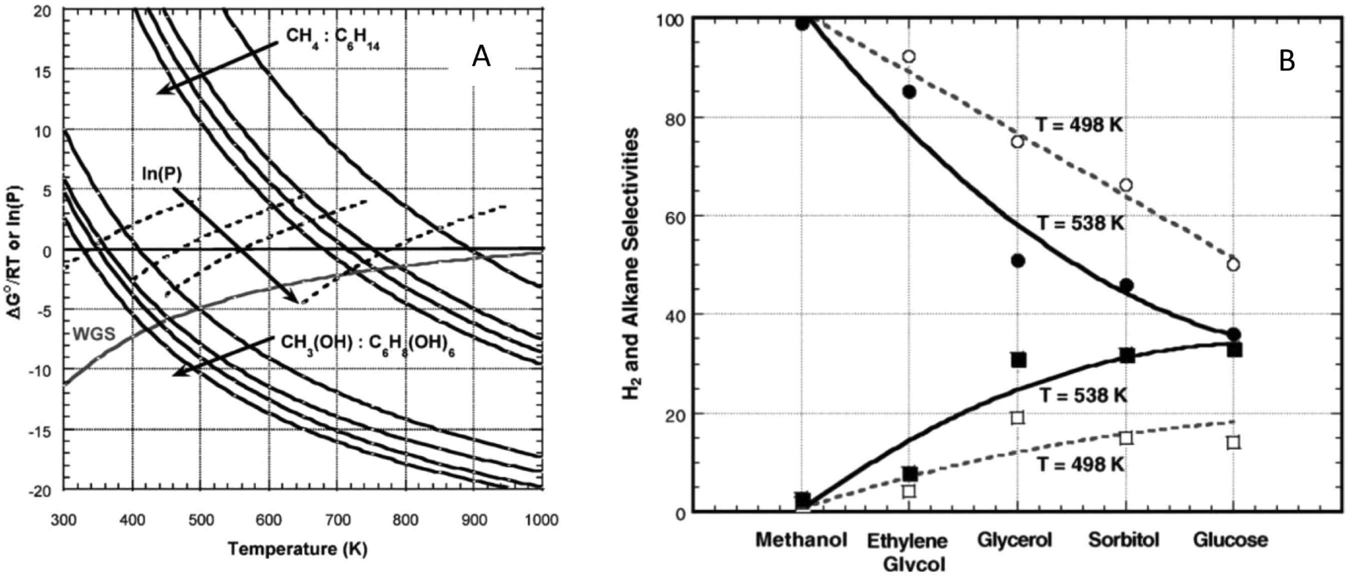

Figure 6. (A) $\Delta G^{o}/RT$ vs temperature for the production of CO and H_2 from vapor-phase reforming of CH_4, C_2H_6, C_3H_8 and C_6H_8; $CH_3(OH)$, $C_2H_4(OH)_2$, $C_3H_5(OH)_3$ and $C_6H_8(OH)_6$; and water−gas shift. Dotted lines show values of ln (P) for the vapor pressures vs temperatures of $CH_3(OH)$, $C_2H_4(OH)_2$, $C_3H_5)OH)_3$ and $C_6H_8(OH)_6$ (pressure in units of atm) and (B) Selectivities vs oxygenated hydrocarbons. H_2 selectivity (circles) and alkane selectivity (squares) from aqueous-phase reforming of 1 wt % oxygenated hydrocarbons over 3 wt % Pt/Al_2O_3 at 498 K (open symbols and dashed curves) and 538 K (filled symbols and solid curves). Panels A and B reproduced with permission from refs 235 and 236, respectively. Copyright 2002 Nature Publishing Group and Copyright 2005 Elsevier.

of these intermediates as a means to control overall reaction selectivity.[178,233]

In the early 2000s, the hydrogen economy began to draw interest from leaders within both the political and scientific spheres.[234] This interest also inspired the Dumesic group to begin to think about hydrogen production from biomass-derived renewable resources. While existing steam reforming and gasification technologies had already been demonstrated to exhibit high hydrogen productivity, they suffered from the drawbacks of requiring multiple steps, requiring high temperatures and high energy requirements. To solve these issues, Jim drew from his chemical intuition and his experience with analogous catalytic reactions to piece together a new reaction network to produce hydrogen from carbohydrates. By understanding the role of the water gas shift reaction (WGS) in hydrocarbon reforming and by recognizing that the small oxygenates he had recently studied could be produced from glucose (in dilute aqueous solutions), Jim designed a process in which aqueous feedstocks of biomass-derived molecules were processed under liquid-phase conditions. The first step in his research methodology was a thermodynamic analysis[235] which showed that carbohydrates and other polyols selectively formed fuel grade hydrogen (with ppm levels of CO) and carbon dioxide at low temperature (lower than 250 °C) and with water (and other low vapor pressure species) in the liquid phase as shown in Figure 6A. These analyses also indicated that the hydrogen could be produced in a single catalytic reactor because coupling between reforming and WGS reactions occurred on the catalysis surface. To demonstrate this concept of Aqueous Phase Reforming (APR), a high-pressure continuous reactor was built to convert short chain polyols (e.g., methanol, ethylene glycol, etc.) to hydrogen at high selectivities (>50%) over Pt-based catalysts, and the results from this work were presented in the first Nature paper[235] that was published in this area. While the hydrogen selectivity decreased with increasing polyol size (i.e., from ethylene glycol to sorbitol), decreasing H/C ratios (e.g., sorbitol vs glucose), and increasing polyol concentration (e.g., > 1 wt %), the proof of concept demonstrated that hydrogen could be produced from a renewable source with low concentrations of CO or alkane as shown in Figure 6B.

After this initial discovery, the majority of the Dumesic group began to work on different aspects of APR. The group studied the selectivity changes with other Group VIII-X metals and with various supports.[237] However, catalyst stability in the aqueous-phase was a major concern. The base metals (Ni, Cu, and Co) typically leached or deactivated, while Ru produced large amounts of methane and Pd showed low activity. Most metal oxide supports (SiO_2, Al_2O_3) underwent phase changes and decreased in surface area under these high-temperature water environments.[238] The Dumesic group began to use their full range of characterization and kinetic tools to study the reaction fundamentals as a means to design improved catalysts.[66] Jim also cofounded with Randy Cortright, his first startup company, Virent Energy Systems, to commercialize this technology.

The intrinsic kinetics of model compounds were studied over Pt catalysts[239] to demonstrate that the mechanism of APR most likely involved (1) C−H and C−C bond cleavage steps to form hydrogen and adsorbed CO and (2) critical steps of the WGS reaction which converted adsorbed CO into CO_2 and more hydrogen.[239] These studies also revealed that the increase in alkane production with increasing polyol size and/or decreasing H/C ratios resulted from more favorable C−O cleavage of highly dehydrogenated surface species. The mechanism was further probed using spectroscopic techniques to identify CO as the most abundant surface species (and also a poison) on Pt during the reaction, while also identifying new methods and techniques (i.e., ATR-IR and capping of hydroxyl groups) to reduce interference from liquid water and high extents of adsorption of catalyst supports.[240]

These fundamental discoveries produced insights into the reaction mechanism that, in turn, inspired the search for bimetallic catalysts to improve activity and selectivity. Toward this goal, and in parallel with the fundamental studies, the Dumesic group designed and built a high-throughput reactor to rapidly screen multimetallic catalysts for APR. The result of this study led to the development of Raney Ni−Sn catalysts that had similar activity and selectivity to Pt for APR reactions[65,241] but were more stable under aqueous conditions than supported catalysts. It was demonstrated that the addition of Sn to Raney Ni abated the formation of methane by decorating defect sites on Ni and/or by decreasing the number of surface Ni ensembles which facilitate the C−O cleavage steps necessary for methanation, as also observed for analogous reactions.[65,241] Similarly, the high-throughput studies identified more active Pt and Pd bimetallic catalysts[242] wherein alloying the Pt and Pd with Fe, Ni, or Co increased the catalysts activity by 5−9 times.[242]

As the work on APR proceeded, Jim began charting new directions in the area of biomass conversion that were derived from the knowledge generated from these APR studies. Specifically, the formation of coke over the acidic supports during APR initiated the study of aqueous phase dehydration/hydrogenation (APDH) to produce alkanes that were suitable for the current transportation infrastructure. In this process, larger oxygenates such as glucose and sorbitol were converted to C_1−C_6 alkanes on silica−alumina supported Pt catalysts in a single catalytic reactor.[243] To extend this concept to fuel range hydrocarbons, Dumesic first observed that heterocyclic aldehydes (e.g., HMF) were intermediates that formed via dehydration of glucose and sorbitol over acid sites. To increase hydrocarbon chain length, the group incorporated an intermediate aldol condensation step with acetone to produce higher hydrocarbons (C_9−C_{15}), suitable as components for diesel fuel.[244] This discovery was disruptive in multiple ways. First, it advanced biomass conversion technology from a small subset of feedstocks (e.g., small polyols) to other carbohydrates that comprise the most abundant components of biomass. Second, it produced molecules that could serve as “drop in” replacements for current transportation fuels (i.e., linear alkanes), which mitigated the “lack of infrastructure” argument that opponents of the hydrogen economy often touted. Third, it inspired the next two branches of the Dumesic group biomass research tree.

The formation of intermediate molecules and the observation that alkanes formed a separate organic phase that simultaneously removed products from the reactor served as the basis for a research direction that targeted the formation of HMF and its derivatives as platform molecules and alternate fuels using phase modified reaction-extraction processes (discussed in sections 8 and 9). Simultaneously, APR research pivoted to study integrated reforming/upgrading processes for the production of gasoline and diesel range alkanes. Combined reforming/upgrading strategies had their roots in the critical discovery from APR that Pt selectively formed H_2 and very strongly adsorbed CO from small oxygenates. If these adsorbed CO molecules could be released from the surface, then a stream of synthesis gas (H_2/CO) could be produced for subsequent Fischer−Tropsch synthesis (FTS). Furthermore, the energy from exothermic FTS could be supplied to endothermic reforming steps for an overall process that was almost energetically neutral.

Initial experiments focused on glycerol conversion (as a means to upgrade biodiesel coproduct streams) at atmospheric pressure on several Pt-based catalysts, and these studies identified carbon-supported Pt as stable and active catalysts for the selective production of synthesis gas.[245] However, coupling with FTS required reforming glycerol at lower temperatures (~200 °C) where the Pt catalysts exhibited much lower activity because of the high coverage of Pt by CO at low temperatures and high CO partial pressures. To combat this issue, Jim combined previous knowledge about analogous reactions (i.e., hydrocarbon reforming) with emerging knowledge (i.e., DFT studies on Pt-alloys as fuel cell anodes)[212] to identify that alloying Pt with Ru and Re will make an excellent catalyst for selective syngas production from small oxygenates because (1) it was already used as an industrial reforming catalyst and (2) Re and Ru exhibited the ability to lower CO binding energies on Pt. Carbon supported Pt−Re was demonstrate to be an optimum catalyst for glycerol reforming under conditions that could be coupled with FTS for the production of diesel range alkanes in a single reactor.[246,247]

Subsequent experiments proceeded to identify the effects of process conditions and catalyst composition for Pt−Re catalysts on glycerol reforming, and during these studies, it was discovered that as the feed molecule increased in size (i.e., glycerol versus sorbitol), the selectivity shifted away from synthesis gas and toward a mixture of small oxygenated molecules (e.g., ketones, aldehydes, and organic acids with 4−6 C atoms).[248−250] This mixture was ideal for subsequent upgrading to fuel range alkanes via a variety of C−C bond formation and deoxygenation steps (as had been previously identified during APDH). Specifically, aldol condensation and ketonization were used for C−C bond formation between aldehydes/ketones and acids, respectively.[251−254] Additionally, C−C bond formation between unsaturated molecules over acid catalysts was used to obtain higher hydrocarbons. In total, this work identified pathways to convert polyols and sugars to fuels via simple, two-step processes that was flexible depending on the feed (e.g., glycerol vs sorbitol) and on the desired product (gasoline, jet, diesel fuels).

Indeed, the conversion of small oxygenates and sugars to hydrogen and conventional fuels was an interconnected project stretching from lactic acid hydrogenation to 1,2 propanediol through integrated sorbitol reforming with subsequent C−C bond formation to form gasoline, diesel, and jet fuel components. The foundation of the project stretched back to the development of the MKM approach to catalysis research, and its impacts extended through the development of multiphase systems for lignocellulosic biomass processing. As graduate students and postdocs conducting this research at the time, it may have been difficult for us to see the interconnections of each single research project beyond a 1 or 2 year window before and after our own time in the group. However, reflecting on this work 20+ years later, it becomes clearly evident that Jim was not simply conducting catalysis research as usual. Rather, his research plans were a purposeful vision that was driven by his very strong chemical intuition and experience combined with his unique talent to synthesize new reaction networks via analogy. Jim was very involved in all aspects of the research typically visiting the laboratories several times a day. Often, he would ask his graduate students when they would have a certain result and then go into the laboratory at that time and watch as the peaks came out of the gas chromatograph. He would then ask the student if the

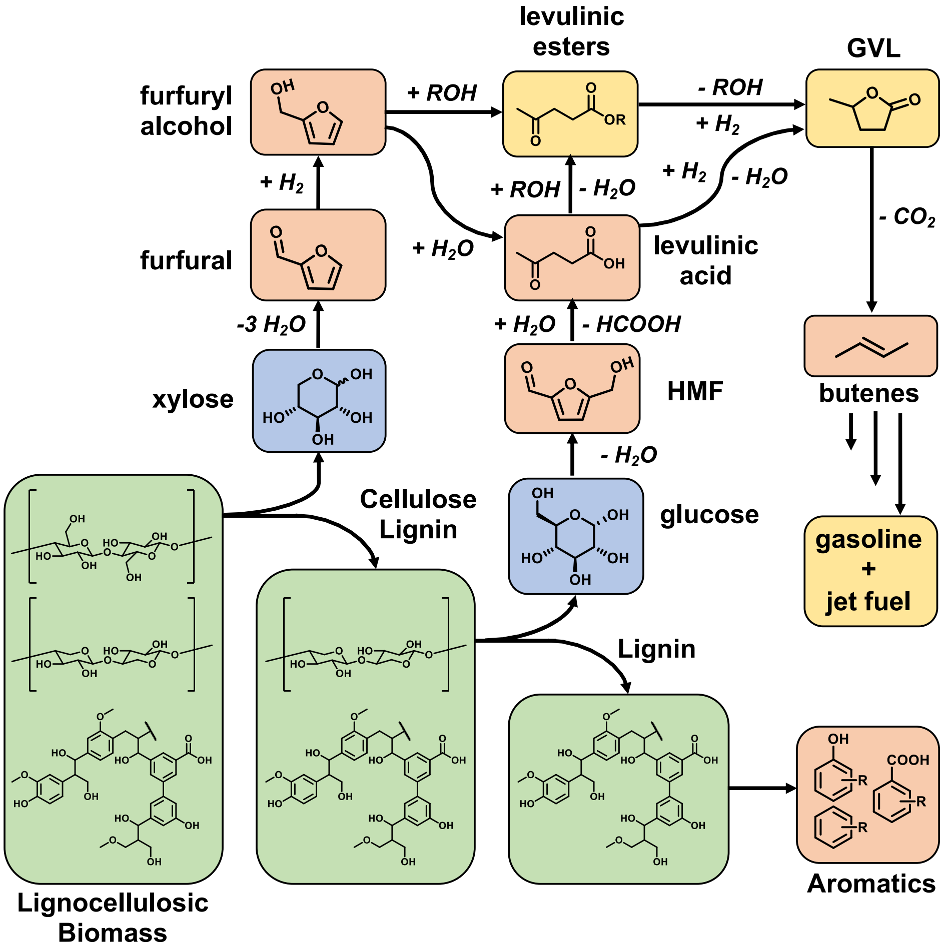

Figure 7. Roadmap for the conversion of lignocellulosic biomass to value-added chemicals via platform molecules. Reproduced with permission from ref 264. Copyright 2012 Elsevier.

experiment was successful and what that meant in terms of the selectivity or reaction rate. He was constantly analyzing and developing models to explain the experimental data that were collected in the laboratory. He taught both the undergraduate and graduate kinetics class, and these classes would be focused on developing MKM of the reactions that he was studying in the laboratory. For Jim Dumesic, the teaching and research mission of the university were the same.

8. CATALYTIC PRODUCTION OF BIOBASED CHEMICALS: A JOURNEY TOWARD HIGH SELECTIVITY, ACTIVITY, AND STABILITY

The concept of an integrated biorefinery to produce chemicals and fuels from sustainable resources, matching the petroleum refinery in scale and diversity, gained increasing attention at the turn of the 21st century. Biorefining technologies were dominated by a few well-known chemistries, and many processes did not meet the price-performance targets required for widespread commercial use. Jim recognized early on that thermocatalytic routes offered an attractive complement to enzymatic strategies to diversify the portfolio of biobased products, which led to the APR work described in the previous section. In developing this work, the Dumesic group showed that the effective conversion of lignocellulose with inorganic catalysts requires overcoming a new set of challenges. The high oxygen content of biomass components translates into low thermal stability and high boiling points, thus necessitating processing at low temperatures and in condensed phases, often composed of high-ionic-strength aqueous solutions. Most inorganic catalysts developed for the petrochemical industry lack the activity and stability required to work effectively under these conditions. Further, given the narrow margins imposed by the high price of biomass feedstocks, compounding selectivity losses during each step in a complex catalytic sequence could quickly lower overall product yields under the threshold of economic viability. This required developing new strategies to maximize selectivity while streamlining processing to reduce the number of unit operations during lignocellulose deconstruction and upgrading. This also led to collaborations with Professor Christos Maravelias who developed process models and did techno-economic analysis (TEA) of approaches outlined by the Dumesic group.

Jim extended Boudart's concept of "kinetic coupling" that states the rate of an elementary steps can impact the reversibility of preceding steps.[255] Ultimately, this concept leads to the conclusion that catalyst design cannot be easily divorced from process development. Given that biomass-derived molecules are highly reactive, many challenges exist not only for selective activation of C−O, C−H, and C−C bonds but also for product recovery and feedstock preparation.[256] Accordingly, Jim extended Boudart's concept to also include coupling among active sites on a single catalyst surface or on multiple heterogeneous catalysts,[252] coupling of multiple chemical reactions (that could be catalyzed by either heterogeneous or homogeneous catalysts),[257] and coupling of multiple phases within a reactor.[258]

Figure 7 depicts the chemical conversion roadmap used by the Dumesic group to guide research on production of fuels and chemicals from C_5 and C_6 sugars. These pathways rely on a subset of platform chemicals that serve as stable nodes in complex reaction networks, akin to how mountain climbers use base camps to rest and regroup while ascending a difficult summit. Accordingly, the Dumesic group developed a comprehensive body of work focusing on the production of 5-hydroxymethylfurfural (HMF), furfural, levulinic acid, and γ-valerolactone (GVL) as gateway molecules for the production of a wide range of fuel and chemical precursors using integrated multistep catalytic strategies. At the writing of this manuscript, several chemical companies are commercializing performance advantaged biomass-based chemicals that are based on concepts studied by the Dumesic research group.

HMF and furfural are versatile platform molecules generated from the acid-catalyzed dehydration of hexoses and pentoses, respectively. Their diverse functional groups allow access to dozens of value-added products via oxidative, reductive, and C−C coupling reactions.[259] However, in monophasic aqueous systems using traditional Brønsted acid catalysts, the relative rates for desired sugar dehydration compared to undesired HMF rehydration and polymerization reactions limit the system to high selectivities only at low conversions. Informed by kinetics analyses, the Dumesic group used aqueous-phase additives, including dimethyl sulfoxide and poly(1-vinyl-2-pyrrolidine), to suppress side reactions, as well as water-immiscible solvents (e.g., methylisobutylketone) to generate biphasic systems capable of continuously extracting HMF and arrest product degradation.[260] HMF yields were strongly correlated to the partition coefficient of HMF in the immiscible solvent, but alas, those solvents capable of forming two-phase systems with water showed poor HMF partitioning into the organic phase. This problem was solved using the salting-out effect—a phenomenon in which dissolved ions alter the intermolecular forces in a solution, increasing the immiscibility between species—to generate biphasic systems with solvents, such as propanol and tetrahydrofuran, that have high affinity to HMF but would form monophasic solutions under standard conditions.[261,262] Optimized conditions using an aqueous phase saturated with NaCl, HCl as the catalyst, and 2-butanol as the immiscible solvent led to 82% HMF selectivity at 87% fructose conversion at 180 °C. At the time, this result represented a record HMF yield for a system that did not use high-boiling aprotic solvents (e.g., DMSO). High furfural yields were also obtained from xylose dehydration in analogous biphasic systems.[263]

The use of simple biphasic systems with salt-saturated aqueous solutions to generate furan-derivatives in high yields allowed accessing other important chemistries. Downstream, supported Cu−Ru bimetallic catalysts generated 2,5 dimethylfuran via selective HMF hydrodeoxygenation;[261] Pd-based catalysts produced the dialcohol 2,5-dihydroxy-methyl-tetrahydrofuran (DHMTHF) via selective carbonyl hydrogenation;[265] Rh−Re bimetallic alloys yielded 1,2,6 hexanetriol via selective ring-opening;[266] and solid acids produced *p*-xylene derivatives via acid-catalyzed cycloadditions between furanic dienes and olefinic dienophiles.[267] Upstream, a glucose-to-fructose isomerization step was required to maximize yields from cellulose given that direct glucose dehydration resulted in low HMF yields even in the best biphasic systems. Base catalysts promote aldose isomerization, but these catalysts quickly deactivate in the presence of the Brønsted acids needed for sugar dehydration. Recognizing the innate ability of water-tolerant Lewis acids to promote intermolecular hydrogen transfer reactions, Dumesic demonstrated that Al-based salts,[268] lanthanide salts,[269] as well as Sn-containing porous solids,[270] not only were effective catalysts for isomerizing aldoses into ketoses but also that this interconversion could be kinetically coupled with the sugar dehydration reaction in a single reactor, ultimately allowing the production of furan-derivatives from C_6 and C_5 polysaccharides with high yields.[271]

The availability of furfural and HMF naturally led to the development of catalytic strategies to generate levulinic acid and its hydrogenation product, GVL.[272] The Dumesic group used a combination of liquid chromatography−mass spectrometry (LC-MS) measurements, isotopic labeling studies, nuclear magnetic resonance (NMR) spectroscopy, and ab initio quantum chemical calculations to elucidate the major reaction pathways in furfuryl alcohol hydration, revealing a geminal diol species as a key intermediate in levulinic acid production.[273] These insights enabled an approach to maximize levulinic acid production in aqueous,[274] organic,[275] and biphasic[276] systems using various solid acid catalysts. The hydrogenation and subsequent lactonization of levulinic acid produces GVL.[277] Although this reaction is readily performed by a variety of late transition metal catalysts, not all catalysts could withstand long-term operation in the solvent media containing the levulinic acid substrate. The Dumesic group devised appropriate hydrogenation catalysts that were compatible with upstream reaction cascades starting from cellulose and hemicellulose processing, ultimately resulting in a comprehensive body of work on kinetically coupled reaction cascades to selectively produce GVL from polysaccharides.[278]

Building on these successes and the relative ease of producing LA and GVL, in 2010, the Dumesic group first published an integrated approach to produce liquid alkane transportation fuels based on the ring-opening and decarboxylation of GVL over amorphous $SiO_2-Al_2O_3$ followed by oligomerization of the resulting butenes over Amberlyst 70.[279] Notably, this process included intermediate separation steps designed to remove water (which inhibits the oligomerization catalyst) and CO_2 (which could be conveniently concentrated and sequestered). This approach that considers together multiple reactions and separations, typified the Dumesic group's work during this era. For example, following up on the importance of GVL as a biomass-derived platform chemical, the Dumesic group developed a process by which GVL could be produced directly from cellulose and corn stover in a biphasic reactor, whereby the biomass was hydrolyzed to LA using a homogeneous acid catalyst (e.g., H_2SO_4), the LA was converted to GVL by hydrogenation, and the GVL extracted into an alkylphenol solvent.[258] Importantly, the H_2SO_4 could be recycled in this process since the product of biomass deconstruction (e.g., LA) was removed by liquid−liquid extraction, while the hydrogenation of LA to GVL was used to further improve the partition coefficient of LA into the organic phase. Reinforcing the notion that process design and catalyst design must be linked in such systems, this process necessitated several advances in C═O hydrogenation catalysis: a reduced metal catalyst that was stable in the presence of H_2SO_4 for LA hydrogenation in the aqueous phase (achieved by the formation of RuRe bimetallic nanoparticles),[257] one that would not saturate the aromatic ring

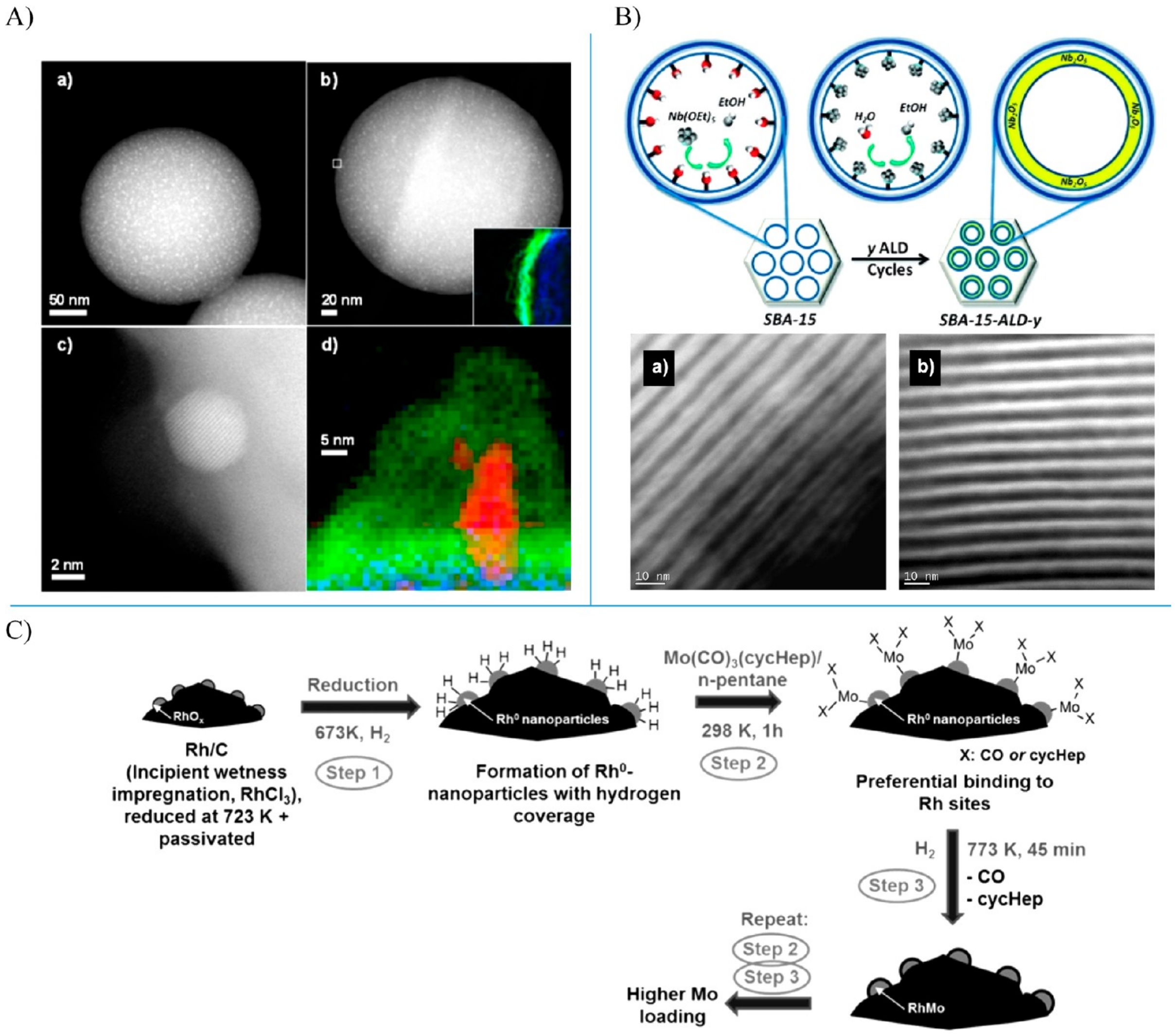

Figure 8. Dumesic approach to developing stable catalysts by controlled synthesis methods for the liquid-phase catalytic processing of biomass-derived molecules. (A) STEM images of overcoated nanoparticles by ALD to mitigate Cu sintering and leaching (a) reduced Cu/spSiO_2; (b) 30ALDAlO_x/Cu/spSiO_2 (inset EDS map of spSiO_2 particle border); (c) aluminum oxide overcoated Cu particle for 30ALDAlO_x/Cu/spSiO_2; (d) EELS map of aluminum oxide overcoated Cu particle (corresponding color and element: green, Al; blue, Si; red, Cu). (B) Schematic illustrating the synthesis of hydrothermally stable mesoporous Nb_2O_5 by ALD; (a) STEM image of niobium oxide coated SBA-15-ALD-30 and (b) SBA-15. (C) Schematic of the CSR method to produce supported RhMo bimetallic nanoparticles with uniform size and composition. Panel A reprinted with permission from ref 307. Copyright 2014 American Chemical Society. Panel B reprinted with permission ref 308. Copyright 2011 American Chemical Society. Panel C reprinted with permission from ref 315. Copyright 2014 Elsevier.

of the alkylphenol solvent (achieved by forming RuSn bimetallic nanoparticles),[280] and one that operated in the absence of precious metals via transfer hydrogenation chemistry (achieved using Zr-based solid Lewis acids).[281] The same sort of process can be used to produce LA and GVL from the xylan as well.[276]

This coupling of active sites, reactions, and phases ultimately led to the discovery by the Dumesic group that it is possible to make GVL and furfural using GVL as a solvent,[278,282,283] which ultimately led to a long-running investigation of solvent effects on catalytic reactions (discussed in Section 9). Indeed, the unique reactivity of GVL as a solvent enabled the Dumesic group to make substantial advances in longstanding problems in biomass conversion. For example, by using GVL as a solvent and H_2SO_4 as a catalyst, the Dumesic group showed that it is possible to recover sugars from lignocellulose in quantitative yields and sufficient purity as a feedstock for fermentation processes.[284,285] This approach is enabled by the ability of GVL to preferentially stabilize transition states for desirable reactions while destabilizing transition states for degradation reactions and by this ability of GVL to fully solubilize all components of biomass. Moreover, because GVL is an excellent lignin solvent, the Dumesic group was able to show that the same technology can be used to recover lignin monomers in high yields, coupled with mild hydrogenation.[286] In 2012, Jim Dumesic, Brent Shanks, and David Martin Alonso started the company GlucanBio to commercialize this technology.[287]

The simultaneous consideration of both process and catalyst design also led Jim to explore new biomass conversion research areas that had received little attention previously. Notably, in collaboration with Brent Shanks at Iowa State, Jim developed a new route to produce sorbic acid and a number of other high-value specialty chemicals, all starting from a fermentation-derived molecule called triacetic acid lactone (TAL).[288] This development recognized that while selective C−O bond activation (as required for upgrading many biomass-derived species, such as sugars) is notoriously challenging for heterogeneous chemical catalysis, biocatalytic processes are much more efficient at such reactions.[289,290] While TAL is produced by fermentation, Dumesic also showed that enzyme-derived species, such as cortalcerone, can also be converted to high-value chemicals.[291] Notable about the cortalcerone work is not only the coupling of chemical and enzyme catalysis but also the coupling of Brønsted and Lewis acid catalysis in a single material, can again be used to minimize the concentration of reactive intermediates leading to high selectivities. More generally, the approach combining chemical and biological catalysis that Jim and Brent Shanks pioneered ultimately led to the development of a number of new routes to biobased chemicals by allowing for selective conversion of biomass to new platform chemicals,[292−297] as well as to the recognition that improved catalyst designs were needed to address deactivation because of impurities present only in fermentation-derived feedstocks.[298,299]

Jim's approach to mitigate catalyst deactivation caused by feedstock impurities, corrosive reaction environments, and high-temperature liquid-phase catalytic processing conditions required for biomass conversion,[300−303] involved designing and synthesizing nanostructured materials through nonconventional catalyst synthesis methods, including atomic layer deposition (ALD)[304−308] and controlled surface reactions (CSR), as illustrated in Figure 8.[309,310] The replacement of supported precious metal (e.g., Pd) catalysts with earth-abundant base-metals (e.g., Cu) is highly desirable for the cost-effective implementation of biomass conversion technologies.[300] However, a challenge with supported base-metal (e.g., Ni, Cu) nanoparticles is their tendency to undergo irreversible deactivation processes such as sintering and leaching under liquid-phase biomass processing conditions.[305,311−313]

Jim's innovative approach toward stabilizing base-metal nanoparticles involved the growth of atomically controlled porous thin-layers of metal oxides over supported base-metal (e.g., Cu) particles by ALD (Figure 8A).[307] The Dumesic group and collaborators at Argonne National Laboratory combined kinetics studies, advanced-materials characterization (e.g., scanning tunneling microscopy, solid-state NMR, operando XAS, scanning transmission electron microscopy), and DFT calculations to elucidate the interaction between ALD overcoats and metal nanoparticles and its effect on catalyst reactivity and stability.[305−307,312] These studies revealed the selective coating of under-coordinated metal atoms at step edges and defect sites of base-metal nanoparticles was key to blocking sites susceptible to initiating particle leaching and sintering phenomena.[314] Furthermore, ALD-modified catalysts showed remarkable activity and stability as a function of time-on-stream in the conversion of biomass-derived furans.[305−307,312] In another ALD application, the Dumesic group studied the conformal coating of mesoporous silica with metal-oxides to impart both hydrothermal stability and functionality (e.g., acidic sites) to the support (Figure 8B).[308] In this work, the deposition of NbO_x functionalities by ALD prevented the hydrolysis of Si−O−Si bonds by capping surface silanols of SBA-15,[308] thus resulting in a highly ordered mesoporous niobium oxide structure with remarkable stability in liquid water at 473 K.[308] The addition of Pd nanoparticles on the niobium oxide surface resulted in a bifunctional catalyst with both activity and stability in the catalytic conversion of GVL to pentanoic acid.[308] Overall, these studies demonstrate applying ALD enhanced catalyst stability either by titrating undercoordinated atoms of supported base-metals, thus mitigating nanoparticle coalescence, or protecting hydrolyzable bonds, thus mitigating support dissolution. A more thorough discussion of ALD and catalysis is given in a review article that was written by Jim Dumesic and collaborators.[313]

Jim's vision of developing active, selective, and stable catalytic materials to increase product yields in biomass transformations also led to the design, synthesis, and characterization of well-structured bimetallic catalysts with uniform particle size and composition.[310,315] The Dumesic group, in collaboration with the groups of Professors Abaya Datya, Robert Davis, and Matthew Neurock, determined that catalytic materials composed of a reducible metal (e.g., Rh, Pt) combined with an oxophilic metal (e.g., Re, Mo) result in highly active and selective catalysts for the hydrogenolysis of biomass-derived oxygenated hydrocarbons.[250,266,316] However, because of the wide distribution of nanoparticle sizes and compositions obtained from the conventional catalyst synthesis method employed (e.g., incipient wetness impregnation), establishing structure−function relations is extremely difficult.[266] Early studies by Basset et al. demonstrated the preparation of supported bimetallic particles by reacting organometallic $Sn(n\text{-}C_4H_9)_4$ precursors with the surface of oxidized or reduced Rh, Ru, and Ni particles supported on silica.[317,318] Through a similar approach, known as CSR, Dumesic tailored the deposition of oxophillic promoters (e.g., Mo) on precious metal particles (e.g., Rh, Pt) supported on carbon to produce bimetallic particles with uniform particle size and surface composition for the hydrogenolysis of biomass-derived oxygenates (Figure 8C).[315] In the CSR method, the interaction between the organometallic precursor of the oxophilic promoter and the reduced precious-metal particle is optimized as a function of organometallic precursor ligands and its concentration. In collaboration with the groups of Professors Jeffrey Miller and Fabio Ribeiro, Jim's group used characterization (e.g., in situ XAS, STEM/EDS, CO chemisorption) and kinetic studies conducted on the hydrogenolysis of biomass-derived cyclic ethers to elucidate that the active site of catalyst synthesized by CSR is composed of reduced oxophilic metal species (e.g., Mo) located at the surface of small ensembles of supported metal nanoparticles (e.g., Rh, Pt).[315] The oxophilic metal species facilitated acid-catalyzed ring-opening reactions, whereas the precious metal catalyzed the hydrogenation of unsaturated reaction intermediates.[266,315] The bifunctional nature of the catalyst also demonstrates Dumesic's unique approach toward the coupling of active sites between reactions to minimize reactive intermediate formation, which lead to carbon deposition.[256,319]

9. LIQUID-PHASE SOLVENT EFFECTS

As Jim was developing processes for the conversion of lignocellulosic biomass to fuels and chemicals, it became evident that the solvents used in these processes had a profound impact on the productivity of the process. Using his experience from MKM, APR, and biomass upgrading, Jim judiciously used various solvents to improve the performance of processes to effectively and efficiently convert carbohydrates obtained from lignocellulosic biomass to platform chemicals and drop-in fuels.[259,320] Jim's work, over the past decade, has shown that careful selection and tuning of the solvent composition can result in substantial control over the activity and selectivity of a reaction.[303] Understanding the phys-

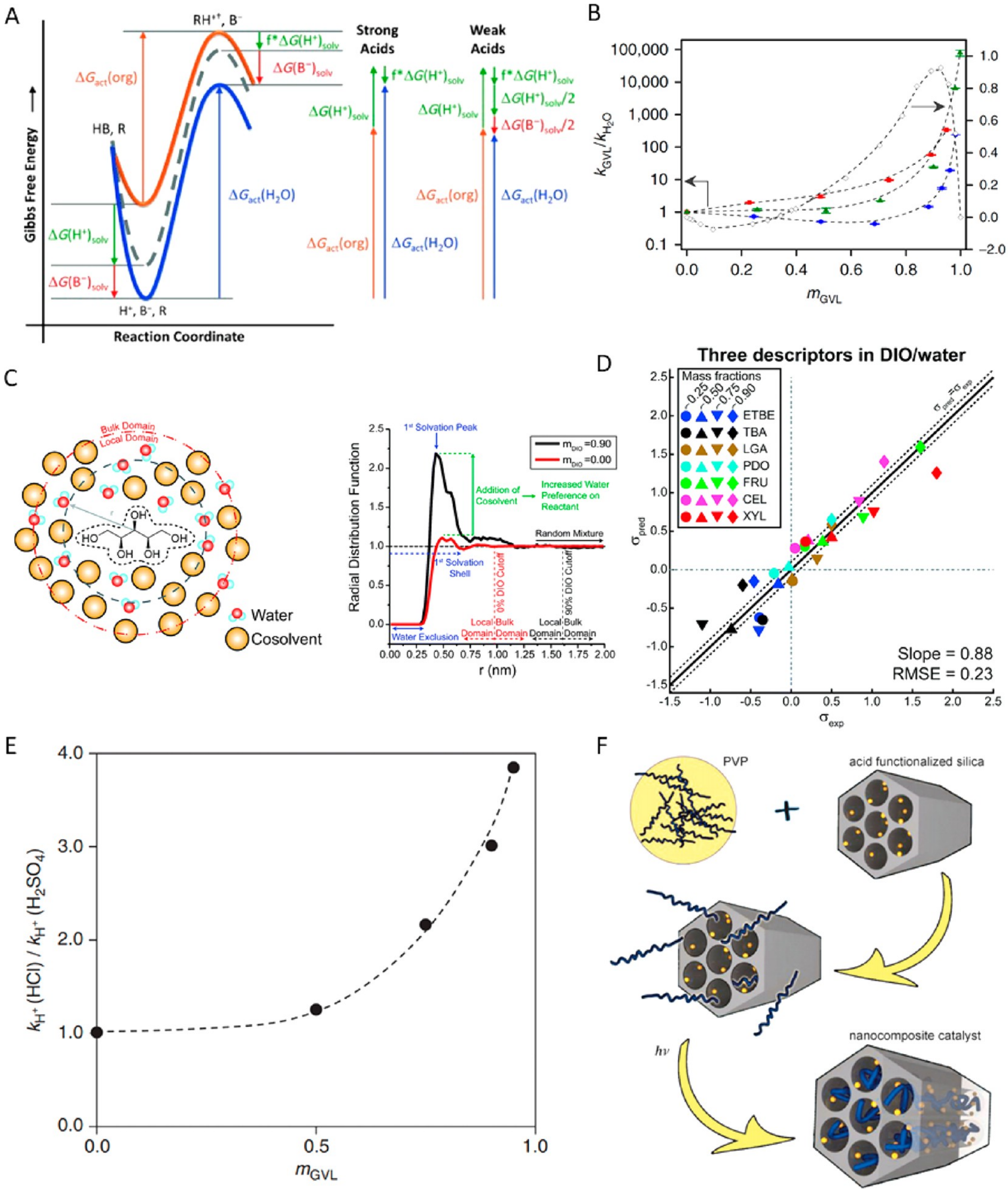

Figure 9. Solvent effects in acid catalyzed dehydration reaction. (a) Schematic representation of the Gibbs free energy surface in water and polar aprotic organic solvent for the conversion of reactant R into product P catalyzed by a Brønsted acid. Reproduced with permission from ref 338. Copyright 2018 Nature Publishing Group. (b) Ratio of the rate constants in the organic solvent to the rate constant in water for dehydration of tert-butanol (blue), 1,2-propanediol (green), and fructose (red). Reproduced with permission from ref 338. Copyright 2018 Nature Publishing Group. (c) The radial distribution function for xylitol in a mixed solvent and its schematic description. Reproduced with permission from ref 345. Copyright 2018 Royal Society of Chemistry. (d) Parity plot showing the application of kinetic solvent parameters obtained using the multidescriptor correlation (σ_{pred}) for seven reactants in dioxane/water mixtures. Reproduced with permission from ref 345. Copyright 2018 Royal Society of Chemistry. (E) Ratio of the rate constant for fructose dehydration using HCl to H_2SO_4 with varying GVL solvent concentration. Reproduced with permission from ref 340. Copyright 2019 Nature Publishing Group. (F) Schematic showing intercalation of PVP into the ordered mesopores of acid functionalized silica forming a tailored microenvironment for enhanced dehydration rate. Reproduced with permission from ref 343. Copyright 2013 Wiley-VCH.

icochemical origins of solvent effects has been the cornerstone in developing processes that have originated from the Dumesic group including fractionation of lignocellulosic biomass to soluble carbohydrates,[287,321−323] dehydration of carbohydrates to highly sort-after platform chemical like furfural and 5-hydroxymethylfurfural (HMF),[265,324−327] depolymerization of lignin to valuable aromatic chemicals,[286,327,328] and upgrading of HMF to polymer precursors and dyes.[329,330]

In early 2000s, Jim used a biphasic reaction mixture composed of solvents with different polarities to selectively extract the unstable yet desired products from the aqueous layer using organic solvents such as GVL, THF, butanol, *sec*-butylphenol, and methyl isobutyl ketone and by addition of salts to the aqueous phase.[258,260,261,263,331,332] An example of this approach is the selective production of 5-hydroxymethyl furfural (HMF) from fructose as described in the previous section. However, downstream separation of the organic and aqueous layer can become cumbersome and may lead to solvent losses. Jim, using his chemical intuition, simplified the process by introducing a monophasic solvent mixture comprising a polar aprotic solvent and water.[287,324,333,334] This monophasic solvent system performed similar to the biphasic reaction mixture. For example, using GVL-H_2O (90 vol % GVL) as a solvent system, HMF was obtained with 80% selectivity at 90% fructose conversion leading to a 72% HMF yield which is comparable to the 73% yield obtained in the biphasic system.[324]

To fully understand solvent effects at a fundamental level, Jim drew from his microkinetic experience to put together a theory that could explain the observed increase in reaction rate and improved activity and selectivity in dehydration reactions with polar aprotic solvents.[335] Jim designed detailed kinetic experiments to clearly show that the increase in the activity for dehydration reaction in polar aprotic solvents was due to the decrease in the activation energy of the dehydration step.[336] These experiments proved that the hydronium ion of a strong acid (i.e., the catalyst in dehydration reactions) was stabilized to a greater extent in water than in polar aprotic solvents while the same effect was marginal for the transition state of the reaction (see Figure 9A), leading to an overall reduction of the activation energy of the dehydration step in polar aprotic solvents. Following his meticulous nature, Jim designed experiments with a series of homogeneous acid catalysts spanning a wide range of pK_a values. With these experiments, it was shown that the solvation effect on the reaction rate is a function of both the proton reactivity and the proton availability.[336] This clearly explained the increased activity observed for strong acid (conjugate base has no effect) and marginal activity improvement observed for weak acid (conjugate base had large effect leading to low proton availability). Jim's philosophy was to first gain the fundamental knowledge, and once a clear picture of the fundamental principle was obtained, he would immediately think about using this knowledge to solve practical and pertinent problems. For example, an issue for biomass-derived carbohydrate upgrading to furans is the separation of homogeneous mineral acid from the product mixture. Having demonstrated that the strong acids significantly improved dehydration activity, Jim designed experiments to show that the same behavior also holds for solid Brønsted acid catalysts, and a process was designed to use solid Brønsted acid in a continuous flow packed bed reactor which eliminated the issue of acid neutralization and separation.[333,336,337]

As the work on relative stabilization of the reactants and transition state proceeded, Jim began to work on identifying descriptors that could predict the potential applicability of a solvent for dehydration reactions. Of particular interest were binary solvent mixtures comprising a polar aprotic solvent and water. Jim's strategy was to combine molecular modeling with experimental data to get a clear picture of the role of the solvent, and he collaborated with Professor Matthew Neurock at University of Minnesota to work on this challenging problem. In this fruitful collaboration, the Neurock group performed classical and ab initio molecular dynamics simulations and the Dumesic group performed experiments to guide and validate the modeling work. It was shown that the rate of an acid-catalyzed dehydration reaction is a function of the binary solvent composition as well as the extent of solvation of the initial and transition states.[338] Using his experience in catalytic dehydration reactions, Jim designed a series of experiments with a wide range of substrates, including tert-butanol (1 hydroxyl group), 1,2-propanediol (2 hydroxyl group), and fructose (6 hydroxyl group), and different aqueous solvent mixtures of polar aprotic cosolvents, including GVL, THF, acetonitrile, 1,4 dioxane, and dimethyl sulfoxide, to gain further understanding of the role of the solvents in dehydration reactions. This study showed that the dehydration rate correlates well with the heat of mixing of the solvent components, and the extent of solvation of the initial state (i.e., solvation of substrate) increases with the increasing hydroxyl groups (i.e., hydrophilicity) which in turns leads to enhancement in the dehydration rates (see Figure 9B). The reaction rate was higher for solvent composition with endothermic enthalpy of mixing and lower for solvent composition with exothermic enthalpy of mixing. This study demonstrated that the enthalpy of mixing can be used as reliable descriptor to identify solvent composition for maximum improvement in dehydration rate, especially for the case where the substrate molecule is highly solvated.

The Dumesic group, in collaboration with Professor Reid Van Lehn at UW, conducted a subsequent study using molecular dynamic simulations and experimental data to reveal that the water molecule preferentially orients around the substrate molecules, like fructose, creating a "hydrophilic domain", and that the average lifetime of the hydrogen bond formed between the substrate molecule and water molecule was increased with decreasing water content of the solvent.[339] Furthermore, Jim outlined experiments to clearly show that the change in the reaction rate correlates with the accessible surface area of the reactant covered by the hydrophilic groups; for example, tert-butanol with one hydroxyl group has lower accessible surface area of the reactant covered by the hydrophilic groups leading to minimal rate enhancement with mixed solvent systems, whereas fructose with six hydroxyl groups has a higher accessible surface area of the reactant covered by the hydrophilic groups leading to high rate enhancement in mixed solvent systems (see Figure 9C). By combining all these experiments, the following correlation was developed to predict the rate enhancement achieved by using a mixed solvent compared to water:

$$log_{10}\left(\frac{k_{\mathrm{org}}}{k_{\mathrm{H_2O}}}\right) = A + B(\Gamma) + C(\tau) + D(\delta)$$

where $k_{\mathrm{H_2O}}$ and k_{org} are the rate constant in water and in the solvent system composed of water and a polar aprotic solvent, respectively; *A, B, C, D*, are constants; Γ is the local density of water near the reactant; τ is the average hydrogen bond lifetime between the reactant and neighboring water molecules; and δ is the accessible surface area occupied by hydrophilic groups on the substrate. The above equation predicted the rate enhancement for a variety of substrate in dioxane water solvent system as shown in Figure 9D.

While studying the effect of polar aprotic solvents on dehydration rates, Jim observed that an additional rate enhancement is achieved by introducing inorganic salts to the reaction mixture. Among these salts, chlorides had the most significant impact on the dehydration rate. Reaction kinetics studies of the Brønsted acid-catalyzed dehydration of fructose showed that the use of catalytic concentrations of chloride ions leads to a 10-fold increase in the activity.[340] Jim, in collaboration with Professor Robert Rioux at Pennsylvania State, devised calorimetric experiments to first eliminate the possibility that the substrate (fructose) was stabilized or destabilized by the presence of catalytic amount of the chloride ions. Thus, it was identified that the promoting effect of chloride ion was either through stabilization of the transition state or by entropic contributions to the activation free energy. To ascertain the mechanism by which the chloride ion improved the reaction rates, Jim designed a set of very clever experiments wherein he studied the effect on the rate enhancement caused by changing the catalyst from H_2SO_4 to HCl at various solvent (GVL) concentration as shown in Figure 9E. It was found that the increase in the rate constant was linearly correlated with the increase in the formation of a "chloride transition state". To further explore this idea, Jim collaborated again with Professor Matthew Neurock, to use ab initio molecular dynamic simulations to explore the effects of chloride ions on the kinetics of the acid-catalyzed dehydration of fructose.[340] These simulations showed that at high solvent concentrations, the chloride anion is localized within the hydrophilic domain near fructose and stabilizes both the oxocarbenium ion intermediate as well as the transition state for deprotonation, providing a clear picture of the chloride ion effect on acid-catalyzed dehydration reactions.

As the work on acid-catalyzed dehydration of fructose proceeded, Jim studied the effect of solvent on the relative stability of different isomers of fructose in various solvent systems. Using ^{13}C NMR, it was shown that fructose tautomer distribution was shifted to the furanose form in polar aprotic solvents like DMSO and NMP and was shifted to pyranose from in water.[341] Since the furanose from is more easily dehydrated than pyranose form,[342] it was shown that the improved HMF selectivity in polar aprotic solvents is partly due to the shift in the equilibrium tautomer distribution. The solvent enabled tuning of the reactant configuration is an effective strategy, and Jim used this solvent property to engineer a tailored microenvironment wherein PVP was incorporated within the pores mesoporous silica (see Figure 9F). This engineered microenvironment provided an abundance of pyrrolidone groups in the confined space favoring the formation of furanose tautomer of fructose.[343] Further, the engineered microenvironment led to an increase in HMF selectivity to levels achieved only with biphasic systems and high-boiling aprotic organic solvents. Additionally, the solid catalyst was easily recovered, and HMF was easily obtained from the low-boiling, single-phase solvent.

Building on the progress made in controlling the dehydration rate and in influencing the relative stability of different isomers of fructose by judiciously choosing a solvent system, the Dumesic group studied fructose dehydration to HMF in acetone/water solvent system. High HMF yields of >90% were obtained with this solvent system. Additionally, HMF was easily separated from this low boiling solvent system with high recovery (96%) and purity (~99%).[326] During this time, interest in the production of polymer and plastic from renewable resources grew and Jim drew from his past experience with aldol condensation of HMF with acetone to selectively produce the HMF−acetone−HMF dimer (HAH), a high molecular weight $\alpha-\omega$ diol that is a potential precursor to functional polymers and organic pigments. Specifically, HAH can be used for the production of conductive polymers due to the connected p-orbitals with delocalized electrons. To further broaden the application of HAH, Jim used a solvent system composed of isopropyl alcohol and water to selectively reduce HAH to produced compounds that can be used as a cross-linking agent in paints, coating, and epoxy resins.[330,344]

The application of solvents in acid-catalyzed dehydration reactions started with a simple idea of extracting a highly reactive molecule from the reaction medium to an organic layer and due to Jim's persistence and his innate ability to see connections between seemingly unrelated phenomena led to a clear understanding of solvent effects that will surely enable others in this and related fields to utilize and further build on this fundamental knowledge.

CONCLUSIONS

During the past 40+ years, James A. Dumesic has had a tremendous impact on the field of heterogeneous catalysis in several different areas as described in this Account. His early work was focused on identification of the active sites using in situ spectroscopy tools. He then began working on microcalorimetry to measure the energetics of adsorbed species. This was combined with vibrational spectroscopy and density functional theory to develop a better understanding of monometallic, bimetallic, and metal-oxide catalysts. In the early 1980s, he developed microkinetic analysis to combine this mechanistic information with kinetic data to understand more about the working catalysts. These tools have now become commonplace in the catalysis fields. In the 1990s, he started to study oxygenate conversion over different catalysts which later led to developing new catalytic approaches for biomass conversion into fuels and chemicals. He started applying techno-economic analysis to guide the fundamental work thereby working in areas that are commercially of interest. Several of the biomass conversion technologies that Jim developed are being commercialized. He has also developed new synthesis approaches including atomic layer deposition and controlled surface reactions to prepare well-characterized catalysts. He has studied dozens of reactions throughout his career. His approach has always been to first look at the fundamental surface chemistry that occurs in the reaction and to try to develop an understanding of the relationship between the catalyst structure and properties. This knowledge is then applied to different reaction classes to push the boundaries of catalysis and then develop new catalytic processes for the sustainable production of fuels and chemicals.

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