Bruce Gates: A Career in Catalysis

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1. INTRODUCTION

The research of Professor Bruce Gates has addressed some of the most important and challenging problems in the field of catalysis in the last 50+ years. These include: how electronic properties of metal clusters change as they transform from organo-metallic complexes to atomically dispersed supported metal complexes or well-defined metal clusters; how the support can act as a ligand in supported metal catalysis; how the electronic pathways of hydrogenolysis and hydrogenation in sulfided oxide hydroprocessing catalysts, and strong acid catalysis. His contributions in all three areas are noteworthy and have been sustained over 50 years. The work of his group evolved from mainly catalyst synthesis and reaction studies to also incorporate sophisticated characterization techniques based on X-ray absorption spectroscopies and improved scanning transmission electron microscopic examination of catalytic surfaces. In the course of this work, he has addressed, and contributed to the solutions of some of the most significant and challenging problems in catalysis of the last half century.
2. OXIDE-SUPPORTED ATOMICALLY DISPERSED METAL COMPLEXES AND CLUSTERS

Catalysts with atomically dispersed metal complexes are synthesized by the reaction of metal complexes with oxides via stoichiometrically simple surface reactions. These supported metal complexes not only offer catalytic properties different from those of the bulk metal but also facilitate the investigation of the structure–performance relationships in supported metal catalysts owing to their simple, uniform structures. The electronic structure of metal complexes and clusters on oxides is influenced by the nature of ligands, including those provided by the support. Thus, it is crucial to identify the binding sites on oxides and to understand how the metal precursors react with these sites, and how the resulting supported species evolve under reaction conditions, both in terms of their nuclearity and ligand environment. The reports of supported species evolve under reaction conditions, both in terms of their nuclearity and ligand environment. The reports from the Gates Group on such supported metal complexes and clusters extend over the last four decades; the uniformity of supported metal catalysts owing to their simple, uniform structures. The electronic structure of metal complexes and clusters on oxides is in performance relationships in supported metal catalysts owing to their simple, uniform structures.

2.1. Organosmium Chemistry and Catalysis. Gates’s metal clusters work began at the CCST in the late 1970s with triosmium carbynols. The objective was to synthesize well-defined “molecular” metal clusters on metal oxide supports and employ them as catalysts. Osmium carbonyl clusters [e.g., Os₃(CO)₁₂] possess strong Os–Os bonds that confer stability at the high temperatures required for industrially relevant catalytic reactions (e.g., CO hydrogenation, water–gas shift). Extensive research on carbonyl clusters derived from Os₃(CO)₁₂ provided a basis to interpret their surface chemistry. Conventional high-surface-area metal oxide supports [e.g., Al₂O₃, SiO₂ and MgO] have acid–base and redox properties that influence the surface organometallic chemistry. Early research demonstrated that weakly acidic surface OH groups can oxidatively add to the metal centers sometimes resulting in cluster fragmentation, and basic surface OH groups (or oxide ions) can generate cluster anions by deprotonating hydrido carbynols or acting as nucleophiles toward CO ligands. Subsequent research revealed that the surface chemistry of anionic osmium carbonyl clusters on MgO parallels their rich solution chemistry. Infrared (IR) spectroscopy, solid-state nuclear magnetic resonance (NMR) spectroscopy, extended X-ray absorption fine structure (EXAFS) spectroscopy, and aberration-corrected scanning transmission electron microscopy (STEM) proved to be powerful complementary tools for characterizing the structures of supported metal complexes and metal clusters.

Deeba and Gates synthesized the supported triosmium clusters HOs₃(CO)₁₀(OM) (M = Al, Si, Ti or Zn) on SiO₂, Al₂O₃, TiO₂, and ZnO via oxidative addition of a surface hydridoxyl group [M–OH] across an Os–Os bond of Os₃(CO)₁₂ (Scheme 1). Later, the structure of HOs₃(CO)₁₀(OAl) on γ-Al₂O₃ was determined by EXAFS spectroscopy. This work initiated a highly successful collaboration with D. C. Koningsberger to more precisely characterize “molecular” organometallic species on metal oxide supports. Heating HOs₃(CO)₁₀(OAl) on γ-Al₂O₃ in vacuo or in inert gas at >373 K resulted in oxidative fragmentation and formation of Os(CO)₆[HOAl]{OAl}₁²⁻ complexes via reaction with surface hydroxy groups. X-ray photoelectron spectroscopy (XPS) and gas evolution measurements demonstrated the +2 oxidation state of Os. Knözinger and Zhou used infrared spectroscopy to characterize the complexes and document the reversible interconversion of the di- and tricarbonyl species:

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\text{Os(CO)₆}_{n}[\text{HOAl}][\text{OAl}]_{2} + \text{CO} \rightarrow \text{Os(CO)₆}_{n}[\text{HOAl}][\text{OAl}]_{2} \]

Early collaborative TEM work detected highly uniform ~0.6 nm scattering centers that were inferred to be 3-atom ensembles (groupings) of Os complexes on the γ-Al₂O₃ support. Later, the structures of Os₈(CO)₁₆[HOAl]{OAl}₁²⁻ complexes were determined by EXAFS spectroscopy.

Deeba et al. investigated CO hydrogenation catalysis by surface species derived from Os₈(CO)₁₆ on MgO. Formation of the analogous HOs₈(CO)₁₆(OMg) species was inferred from IR spectroscopy. Exposure of HOs₈(CO)₁₆(OMg) to air at 298 K resulted in oxidative fragmentation to Os₈(CO)₁₆(OMg)₄ complexes. The supported clusters and complexes were precursors of CO hydrogenation catalysts that produced C₁−C₄ hydrocarbons at 573 K and 3.2 MPa (4:1 H₂:CO). IR spectra of the used catalysts suggested retention/regeneration of molecular Os clusters. The novel stability of the clusters under reaction conditions was attributed to the strong basicity of the support.

Subsequently, Lamb and Gates demonstrated the formation of anionic Os₄ and Os₅ carbonyl clusters on MgO from a mononuclear precursor under catalytic CO hydrogenation conditions. The weakly acidic hydridocarbonyl complex H₂Os(CO)₄ chemisorbed on MgO to form [HOs(CO)₄]⁻. IR spectroscopy and solid-state C¹ NMR suggested that the anion interacted strongly with Mg₂⁺ via a µ−η¹ CO ligand. Extraction of surface-bound anions using [N(PPh₃)₂][Cl/CH₂Cl₂ yielded [N(PPh₃)₂][HOs(CO)₄] consistent with the redox condensation chemistry in solution:

\[2[H₂Os(CO)₄]⁻ + [HOs(CO)₄]⁻ \rightarrow [HOs(CO)₄][HOs(CO)₄]⁻ + CO + 2H₂\]
catalysts derived from Os₅(CO)₁₂ on MgO.³ That these specific Os carbonyl clusters were formed from [H₂Os(CO)₄]⁻ via redox condensation under reaction conditions is consistent with their solution chemistry.¹²−¹⁴ Thus, Gates’s research showed that strong basicity and a CO + H₂ atmosphere were keys to stabilizing molecular Os carbonyl clusters on a metal oxide support under high-temperature reaction conditions. The [H₂Os₅(CO)₁₂]⁻ /MgO was implicated in the catalysis, and [Os₁₀C(CO)₂₄]²⁻ /MgO was thought to be associated with catalyst deactivation.

Osmium cluster chemistry under high-pressure CO hydrogenation conditions was investigated by in situ IR spectroscopy.¹⁵ The observed transformations of Os carbonyl clusters on MgO under CO hydrogenation conditions are summarized in Scheme 2.

Gates’s research also demonstrated that molecular clusters were formed on Os/MgO and Ru/MgO catalysts for CO hydrogenation.¹⁶ Reductive carbonylation of H₂OsCl₆ on MgO in syngas (1:1 H₂:CO) at 548 K and 0.1 MPa resulted in the ultrastable carbido carbonyl cluster [Os₁₀C(CO)₂₄]²⁻. Reductive carbonylation of RuCl₃ on MgO under 1:1 H₂:CO at 498 K and 1.0 MPa yielded [Ru₆C(CO)₁₆]²⁻. The surface-mediated syntheses were followed by IR, and mononuclear carbonyl intermediates were observed. These were the first syntheses of high-nuclearity Os and Ru carbonyl clusters directly from metal salts.¹⁷ The capability of producing anionic carbonyl clusters from simple mononuclear species and lower nuclearity clusters [e.g., Os₃(CO)₁₂] on metal oxide supports was a new approach to metal cluster synthesis.¹⁷−¹⁹

2.1.1. Structural Elucidation of Supported Osmium Clusters and Complexes. There were many such investigations by EXAFS and STEM.²,¹⁸,²⁰−²⁴ The EXAFS-determined structure of [Os₃(CO)₁₁]²⁻ /MgO confirmed the triangular osmium framework (average Os−Os distance 0.289 nm) with 3.2 carbonyl ligands per Os atom. An Os−O bond distance of 0.216 nm was attributed to the metal−support interface, and the cluster was modeled as Os₃(CO)₁₁{OMg}. High-angle annular dark field (HAADF) STEM images revealed uniform scattering centers of radii 0.203 nm consistent with Os₃ clusters.²⁴ Atomic resolution aberration-corrected STEM and DFT calculations corroborated the EXAFS results (Figure 1).²⁰,²⁴ The essential features of trinuclear Os clusters on dehydroxylated MgO(110) are (1) each Os atom is located atop a column of Mg atoms; (2) each Os atom is bonded to either one surface O or to none; and (3) the triangular frame is tilted at 38° with respect to the surface.

When [Os₃(CO)₁₁]²⁻ /MgO was heated to 548 K in He and held for 2 h, X-ray absorption near-edge structure (XANES)
spectroscopy confirmed oxidation of the Os centers, and EXAFS provided evidence of cluster fragmentation.\(^{23}\) The quantitative EXAFS results were consistent with Os-\((\text{CO})_2\{\text{OMg}\}_n\) \((n = 3 \text{ or } 4)\) surface species. HAADF-STEM images (Figure 2a,b) of the mononuclear complexes on MgO(110) revealed Os atoms located directly atop columns of Mg atoms. This configuration results in 4-fold coordination by O atoms; however, it requires that the topmost Mg atom be removed. Thus, the Os-\((\text{CO})_2\) complexes were inferred to be located at Mg vacancies, as illustrated in Figure 2c. High-resolution TEM images of MgO-supported \([\text{Os}_5\text{C}(\text{CO})_{14}]^{2-}\) clusters that were synthesized by treating \([\text{Os}_5\text{C}(\text{CO})_{11}]^{2-}\)/MgO in flowing CO at 548 K and 1 atm revealed highly uniform scattering centers consistent with the expected cluster size (0.3–0.4 nm, Figure 3A).\(^{25}\) The image in Figure 3B shows a single-crystal MgO particle with the (111) planes \((d\)-spacing 0.244 nm) visible in contrast.

A family of anionic Os carbonyl clusters with nuclearities \(n = 3, 4, 5, 10\) was synthesized by treatment of Os-\((\text{CO})_2\{\text{OMg}\}_n\) \((n = 3 \text{ or } 4)\) complexes on MgO with CO at 548 K and 1 atm for 4 h.\(^{22}\) Aberration-corrected STEM images showed individual Os atoms in addition to the expected clusters (Figure 4). There was good qualitative agreement of the 2D image projections with the structural models, and intensity analysis verified the number of Os atoms in each cluster. The Os–Os distances in the supported clusters, as determined by EXAFS and HAADF-STEM, are in good agreement with crystallographic values for the molecular clusters in the solid state.

Gates et al. also extended the surface-mediated synthetic chemistry to Re and Mn, producing a series of supported rhenium clusters on \(\gamma\text{-Al}_2\text{O}_3\)\(^{26}\) and TiO\(_2\)\(^{27}\) and manganese clusters on MgO.\(^{28}\)

### 2.2. A Golden Age of Catalysis

By the early 2000s, there was a debate in the literature regarding the identity of the active sites of supported gold catalysts for low-temperature CO oxidation, and the catalytic activity was ascribed to numerous variables. The only consensus was that the preparation method of the samples had a great influence on their catalytic properties. Typical supported gold catalysts were synthesized by coprecipitation or deposition-precipitation methods using inorganic ionic salts \((\text{e.g., } \text{HAuCl}_4 \text{ and Au(PPh}_3\text{)(NO}_3\text{)})\) as precursors, which leave traces of undesired elements such as chlorine or phosphorus on the surfaces. Furthermore, the resulting high-surface-area supported catalysts contained structurally complex and nonuniform gold particles of various sizes and shapes. In an attempt to simplify the surface structure of the catalysts and by using the vast experience of the group with organometallic complexes, in 2001 Guzman and Gates reported the use of Au(CH\(_3\))\(_2\)(acac) as a precursor to synthesize structurally simple MgO-supported gold samples.\(^{29}\)

The mononuclear gold complexes were bonded to MgO through two surface oxygen atoms, as evidenced by the lack of Au–Au contributions in EXAFS spectra and the presence of a Au–O contribution with coordination number of \(\sim 2\). These species are schematically represented in Figure 5. Between 2001 and 2008 the same synthetic protocol was extended to prepare a family of mononuclear gold complexes on other metal oxides \((\text{i.e., } \gamma\text{-Al}_2\text{O}_3\text{, TiO}_2, \text{LaO}_2\text{, }\text{CeO}_2 \text{, and zeolite Y.})\)\(^{30–37}\) Special efforts were made to elucidate the reactions by which the organogold precursor reacted with surface hydroxyl groups on the supports to give nearly uniform surface species. The approach combined EXAFS and IR spectroscopies.

Advances in scanning transmission electron microscopy (STEM, in collaboration with Nigel Browning’s group) allowed confirmation of the presence of the mononuclear complexes and demonstrated the high uniformity of the samples.\(^{34,35}\)
Thermal treatments of the Au complexes in controlled atmospheres led to the formation of supported Au nano-clusters. These nanoclusters have the advantage (usually) of being much simpler in structure than typical supported Au catalysts prepared from inorganic salts. In fact, for the case of MgO-supported gold, it was proposed that structurally simple and nearly uniform Au₆ clusters could be obtained under specific treatment conditions. The structural simplicity of these gold nanoclusters made them ideal for extensive characterization and catalytic testing.

### 2.2.1. Role of the Oxidation State of Gold in the Catalysis.

In 2002, Guzman and Gates reported XANES spectra characterizing MgO-supported gold catalysts during CO oxidation that showed the simultaneous presence of cationic and zerovalent gold. This was the first report of direct physical evidence of both Au⁺ and Au⁰ in functioning supported gold catalysts.

Later, Guzman and Gates used an elegant combination of XANES spectra and TPR/TPO to correlate the catalyst activities with the relative fractions of zerovalent and cationic gold. This paper is among the most influential reports in the literature on gold catalysis, having been cited more than 400 times. The results showed that the fraction of cationic gold in functioning catalysts could be tuned by modifying the composition of the feed. Higher concentrations of CO led to the increased reduction of the gold with a concomitant decrease in reaction rate (Figure 6). In all cases, gold nanoclusters were present under reaction conditions at steady state.

### 2.2.2. Supported Mononuclear Gold Complexes.

Attempts were made to synthesize catalysts that contained only stable, supported mononuclear gold complexes. Such complexes on metal oxides are usually highly reactive, leading to the formation of gold nanoclusters during catalysis. However, Fierro-Gonzalez and Gates reported that zeolite NaY could stabilize the complexes under reaction conditions, at ambient temperature. Although this catalyst was not as active as those containing gold nanoparticles, it served as a good model to investigate CO oxidation catalysis, and was the first reported supported gold catalyst for CO oxidation that did not contain gold particles.

Effects of oxide supports on electronic properties have been intensively investigated in catalysis by supported metals. However, there exist few examples demonstrating how supports affect the coordination geometry of ligands on highly dispersed metals under reactive atmospheres, and this was one of them. Using time-resolved EXAFS to follow changes in bonding between the gold complexes and zeolite NaY (characterized by Au−O scattering pairs), it was observed that at short times the gold was bonded to approximately two zeolite O atoms, but at increasing time on-stream, a Au−surface O bond was broken and Au was coordinated to CO (Figure 7). The process was reversible and the data showed that the coordination of gold to supports can be tuned by changing the composition of the reactive mixture. Thus, the metal−support interface can be described in terms of identifiable chemical bonds, allowing analogies between catalysis on surfaces and in solution by organometallic complexes, a central interest of Prof. Gates’s research.

Gates has coauthored several reviews on gold catalysis. These papers illustrate the evolution in the research of CO oxidation catalyzed by supported gold. In the earlier reviews, Gates discussed the role of cationic gold in CO oxidation. The relevance of investigating functioning catalysts and the opportunities provided by structurally simple and uniform

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**Figure 5.** Schematic representation of a mononuclear gold complex bonded to the surface of MgO. Gold (yellow), carbon (gray), hydrogen (blue), oxygen (red), magnesium (green). Reprinted with permission from ref 46.

**Figure 6.** Correlation of the catalytic activity with the percentage and surface concentration of cationic and zerovalent gold (the concentrations of gold were calculated on the basis of the approximate surface area of MgO). Reprinted from ref 48. Copyright 2004 American Chemical Society.

**Figure 7.** Reversible transformation of a mononuclear Au complex on NaY during CO oxidation. Au is gold, carbon gray, hydrogen white, oxygen red, and silicon green. The time-resolved EXAFS (left) shows the increase in average Au−O distance and decrease in number of bonds as the transformation takes place. Reprinted from ref 43. Copyright 2005 American Chemical Society.
catalysts were emphasized. As the debate on the origin of the
catalytic activity of supported gold intensified, Gates pointed
out that this literature (although extensive) was fragmented
and did not lend itself to generalizations on the nature of the
active sites or explain the differences in the activities of
numerous catalysts. He pointed out that the evidence of
various surface species on functioning CO oxidation catalysts
was consistent with the possibility that multiple channels might
occur depending on catalyst structures and reaction conditions.
Thus, CO oxidation, apparently simple and prototypical, was
more of an “undiscriminating probe reaction” that did not
allow for the type of generalizations that were typically
expected.

2.3. Uniform, Small, and Simple Structures for
Establishing Structure–Property–Performance
Relationships. In similar fashion to the work discussed above,
the approach that Gates et al. typically employed was to use
organometallic precursors with sacrificial ligands mimicking
bidentate adsorption sites on supports. These ligands facilely
leave the complex upon reaction of the precursor, while other
ligands and the metal are chemisorbed to the support. The
types of metal precursors used include metal(L)2(acac) (acac
is acetylacetonato, and L is a reactive or nonreactive ligand,
such as π-bonded C2H4 or carbonyl, respectively). These types
of metal precursors were used to synthesize a series of
atomically dispersed supported metal complexes on a broad
range of supports.

For instance, Rh(CO)2 complexes were synthesized on
dealuminated zeolite Y by reacting Rh(CO)2(acac) with
partially dehydroxylated Y. A significant advance resulted
from use of a precursor with reactive π-bonded C2H4 ligands
instead of the nonreactive carbonyl ligands. They reacted
Rh(C2H4)2(acac) with highly dehydroxylated MgO and
obtained surface-site-isolated Rh(C2H4)2 complexes, as
evidenced by EXAFS and IR data. Because these Rh complexes
already possessed reactive C2H4 ligands, they provided a direct
entry into a catalytic cycle for C2H4 conversion and offered an
opportunity for facile conversion into other organic
ligands. These studies were later extended to Ir and Ru to
prepare analogous metal complexes with reactive ligands on
other supports, such as MgO and zeolites.

2.3.1. Supports Act as Ligands: Zeolites and Zeotype
Materials. Zeolites and supports like silico-aluminophosphates
(SAPOs) possess well-defined anchoring sites. Gates et al.
extended the work in zeolite-supported mononuclear gold
catalysts discussed above and synthesized a series of supported
metal complexes and clusters using metal precursors bearing
(acac) ligands. Zeolites and associated materials with larger
pore apertures, such as HY, Beta, HSSZ-53, or SAPO-37, allow
for facile mass transfer of metal precursors to acid sites inside
zeolite crystals, exchanging acac ligands with the anionic
oxygen ligands. When the pore aperture of a zeolite is
relatively small to the size of a metal acac complex, it forms a
mixture of physisorbed and chemisorbed metal complexes,
yielding broad νC=O bands. In this case, EXAFS characterization
provides only an average interatomic distance between
metal and oxygen atoms.

The uniformity of zeolite-supported metal-ethene complexes
is typically characterized by sharp νC=O IR bands, with a νC=O
fwhm of approximately 5 cm⁻¹ when the ethene ligands were
replaced by CO (Figure 8). The sharpness of the IR bands
is comparable to those of CO ligands on metal complexes in
solution and much narrower than for CO in isostructural metal
complexes on other metal oxides, including metal oxide nodes
in MOF. This high uniformity rivals that of molecular
catalysts in solution. A collaborative work with James Haw’s
group used variable-temperature 13C polarization MAS
NMR for Rh(C13C2H4)3 complexes anchored in zeolite HY and
demonstrated that [13C]ethene ligands undergo anisotropic
rotation at the same frequency at a given temperature that is
characteristic of the precursor compound (Rh(C2H4)2(acac)),
either in solution or crystalline. The rotational barrier for ethene ligands in the sample is sensitive to both
electronic and steric interactions. If the metal sites in the
sample were structurally diverse, it would map into a
distribution of rotational barriers for the ethene ligands
and some of the sites would yield sharp 13C components at each
temperature investigated.

The high degree of uniformity in these zeolite Y-supported
metal complexes results in close agreement between the
experimental data and calculations that is unattainable for
oxide-supported metal complexes, as demonstrated in collabora-
tive work by the Gates and the Dixon groups. In addition,
they presented an opportunity for a breakthrough in the
elicitation of preferential locations for binding with the
framework, through a collaboration with Nigel Browning’s
group to obtain atomic-resolution detail of Ir complexes and
clusters. Using low-dosing imaging techniques with aberration-
corrected HAADF-STEM, they demonstrated that the number of Ir complexes at the six-ring position (T6 sites) of
the zeolite is greater than that attached to the three-hollow
position next to the Al center (T5 sites). Aggregation of
Ir(C2H4)2 complexes, initially anchored near Al sites, forms Ir
clusters that preferentially attach to T6 sites. Later, it was
demonstrated that selective formation of Ir6(CO)12 followed
by decarbonylation led to the determination of the location of
Ir6 clusters within NaY supercages; 75% of the clusters were
present at T6 sites, and the rest were at T5 sites.

The Gates and Browning groups further demonstrated the
migration of atomic Pt species through zeolite K-LTL upon
This class of catalysts is relevant to industrial alkane dehydrocyclization. Some of the [Pt-(NH₃)₄]²⁺ complexes initially present in 12 member-ring (MR) channels of this zeolite migrated into 8 MR pores as a result of oxidation, forming Pt oxo species (Figure 10). After activation, the catalyst exhibits high activity for CO oxidation. Elucidation of the location of the metal sites provides insights into the detailed structures of complex porous catalysts, biological catalysts (enzymes), and other nanomaterials with three-dimensional structures.

### 2.3.2. Supports Act as Ligands: Other Metal Oxides

Typical oxide supports such as γ-Al₂O₃ and MgO contain various anchoring sites for metals, as demonstrated in work with Ir(C₅H₅)₂ complexes prepared by the reaction of Ir(C₅H₅)₂(acac) with MgO. Even when Ir(C₅H₅)₂(acac) complexes are reacted with MgO at low Ir loading (0.5–1 wt %), the metal populates different sites, as discerned using aberration-corrected HAADF-STEM (Figure 11). Broad IR ν(CO) bands were observed upon replacement of C₂H₄ ligands with CO. At a loading of 1 wt %, Ir complexes bond to the surface via two Ir−O bonds on average (EXAFS). But when the loading was lowered further to 0.1 and 0.01 wt %, the complexes preferentially populated edges and defect sites characterized by an Ir−O coordination number of 3. These tripod Ir(C₅H₅)₂ complexes are more stable and resist aggregation in flowing H₂ at 573 K more so than those bonded through 2 Ir−O bonds on faces. Gates et al. later extended the investigation, showing that treatment of MgO at 1273 K facilitates more precise identification of surface sites because of the enhanced crystallinity of the support. Through collaboration with teams at Minnesota and Northwestern, the Gates group extended the work on dispersed supported metal complexes by using MOFs as supports. They introduced sites with precisely defined structures by tuning MOF surface ligands and the density of MOF defects by postsynthetic treatments. Prospects and new opportunities for these MOFs as catalyst supports are summarized in a recent review paper.

### 2.4. Impacts of Ligands, Including Supports as Ligands

Taking advantage of the high degree of uniformity of atomically dispersed supported metal complexes, Gates et al. demonstrated the impact of subtle structural differences on the electronic and so the catalytic properties of Ir, Rh, and Ru. For example, they found that ethene ligands in Ir(C₅H₅)₂ complexes anchored in zeolite HY readily transform into ethyl ligands in the presence of H₂, whereas isostructural complexes on MgO were stable and hindered the activation of H₂. Rhodium dicarbonyl complexes anchored in zeolite HY readily transform into Rh(C₂H₄)(CO) in flowing C₂H₄, while the isostructural complexes on MgO do not. Moreover, Rh(C₅H₅)₂ complexes supported on MgO form ethane under a flow of ethene and hydrogen, while isostructural complexes on zeolite HY give butenes by dimerization, even in the presence of H₂. The supported mononuclear iridium carbonyl complexes can accommodate up to two ethene ligands in addition to one CO (Ir(CO)(C₅H₅)) and Ir(CO)-

![Figure 9](https://dx.doi.org/10.1021/acscatal.0c03568)

**Figure 9.** ¹³C CP-MAS spectra of the sample formed from[Rh-(C₂H₄)₂(acac)] and dealuminated zeolite Y, and then exchanged with ¹³C-labeled ethene. (a) Variable-temperature spectra. (b) Spectrum obtained at low temperature after heating and subsequent cooling of the sample, which demonstrates the results of a reverse-spillover reaction. The signal at δ = 5.7 ppm corresponds to ethane. Reprinted/redrawn with permission from ref 65. Copyright 2006 Wiley.

![Figure 10](https://dx.doi.org/10.1021/acscatal.0c03568)

**Figure 10.** (Left) STEM images showing site-isolated Pt atoms in KLTL zeolite in the a) oxidized and b) as-prepared samples. White features in blue circles indicate Pt atoms. Magnified views (c−e) of the highlighted regions in (b), containing one Pt atom each at A/B sites in (c), at C/E sites in (d), and at D sites in (e). Simulations (f, g) of the LTL zeolite in the [110] direction superimposed on the magnified views in (c−e), showing Pt atoms (green) at A/B sites in (f), C/E sites in (g) (purple), and D sites in (h) (red). Pt atoms are located right at the edge of the 12-membered rings of site D₁ between the two 12-membered rings of sites C/E and in the center of three 12-membered rings of sites A/B. (Right) Models of zeolite LTL with a) pore nomenclature as referred to the images on the left, and b) [Pt(NH₃)₄]²⁺ and c) PtO₂ located in the 8-membered ring at the C site. Pt−O bond distances determined by EXAFS were used with STEM images to determine the Pt atom locations. O red, T-site Si/Al purple, Pt green, N blue; H not shown for clarity. Reprinted/redrawn with permission from ref 68. Copyright 2014 Wiley.
and they catalyze hydrogenation of ethene instead of dimerization under identical reaction conditions. Because the IR νCO bands characterizing the Rh(CO)(C2H4) and Ir(CO)(C2H4) complexes are nearly the same, the electronic effect of CO on π-bonded ethene ligands was nearly the same for Rh and Ir, nonetheless the catalytic behavior differed greatly, and the Ir(C2H4)2 complexes have a substantially higher rate of H−D exchange. The explanation lies in a significant difference in electron density between Rh and Ir complexes when they incorporate reaction intermediates. The νCO frequency was 2063 cm−1 for the Rh carbonyl, inferred to be a reaction intermediate, but 2075 cm−1 for the iridium carbonyl Ir(CO)(C2H5). The difference in M−CO frequencies is an indication of different electron densities around the metals under reaction conditions, related to the differences in the bonding of ligands other than CO. The differences between Rh and Ir in bonding hydrogen and ethene affect the catalytic activities. Gates et al. further showed that chemisorbed Ru(C3H4)2(acac) complexes are substantially more reactive in activating ethene ligands than physisorbed Ru(C3H4)2(acac) complexes on zeolite HY, even though the Ru−O distances characterizing two species differ only slightly. Gates et al. treated such catalysts under reactive atmospheres to convert mononuclear complexes into small clusters in a controlled manner to study the effects of neighboring metal atoms. Supported Rh(C2H4)2 complexes were converted into Rh dimers via a stoichiometrically simple reaction in H2 (Figure 12, top). The presence of neighboring Rh atoms boosted the activation of H2, leading to a 60-fold enhancement in the hydrogenation rate of ethene (Figure 12, bottom). Selective poisoning of the dimers by CO resulted in high selectivity (100% selectivity at 97% conversion) for the partial hydrogenation of 1,3-butadiene to monoalkenes. A MgO support stabilized the Rh dimers, while larger clusters formed in zeolite HY, yielding more butane. Gates et al. also showed promotional effects of neighboring metal atoms in supported Ir. Dimers were synthesized from Ir2(μ-
OMe)2(COD)2 by H2 treatment at 353 K. The supported dimers retained their nuclearity under CO, H2, and C2H4 at 298−353 K and catalyzed ethene hydrogenation at a substantially higher rate than the MgO-supported Ir(C2H4)2 complex catalyst.

Atomically dispersed rhenium metals can be synthesized from H3Re3(CO)12 supported on γ-Al2O3, as for supported osmium. Gates et al. used this approach to synthesize Re3 (mononuclear Re) or larger clusters on the surface.26 They used the set of catalysts to elucidate how the cluster size and metal oxidation state of rhenium complexes and clusters influence their catalytic performance in hydrogenolysis of n-butane. The work showed that the activity increases as the Re−Re coordination number in the clusters increases. Re3 retained the average cluster size, showing the greatest resistance to reduction. In contrast, the mononuclear rhenium cations aggregate and form clusters approximated as Re3 during catalysis; they exhibit a substantially higher formal oxidation state than the "mononuclear" Re3, and much higher rates. The Gates group then extended the synthesis chemistry of supported Re to Mn, synthesizing a series of manganese clusters by anchoring Mn(CO)4 complexes on MgO.28

Surface defects on TiO2 serve as anchoring sites and enhance the dispersion of supported metals. Defects can be created by treatment of TiO2 under vacuum, in H2 by ion bombardment, or by exposure to an electron beam. Vacuum treatment can produce almost exclusively Ti3+ sites with less structural damage to the titania surface. Using IR and EPR, the Gates group and collaborators investigated how a Re3(CO)12H3 precursor reacts with defect sites on TiO2.27 The formation of surface defects was inferred to initiate on Ti4+ sites with OH groups, when TiO2 is heated to 773 K under vacuum. The bridging surface oxygen-Ti4+ bond is broken, an O− species is formed, leading to the reduction of Ti4+−OH to Ti3+−OH. When the Re precursor reacts with the TiOx, it donates a proton to a Ti3+ site, and the proton interacts with Ti3+−O−, forming an OH group. When the loading of the Re precursor is low (0.1 wt %), all the Re is present at the Ti3+ defect sites, bonded to the surface at a short Re−O distance. At higher loading (1 wt %), other sites are also populated with Re at longer Re−O distances.

The work on metal clusters also includes studies on supported Ir clusters. These were synthesized either by adsorption of ligated molecular Ir clusters with tetrahedral (Ir4) and octahedral (Ir6) frameworks, or by the treatment of single-Ir atom complexes under controlled reductive conditions following chemistry similar to that in the solution phase, as summarized in Figure 13.92 The formation of these clusters from single-Ir atom complexes was characterized by EXAFS and IR.77 The data demonstrated that the formation of Ir4 clusters from Ir(C2H4)2 in zeolite Y cages during a temperature ramp (to 353 K in H2) occurs first through conversion of π-bonded C2H4 into ethyl ligands and a decrease in Ir−C coordination number from ∼4 to ∼2. Then the structural transformation continues with a further decrease in Ir−C coordination number to ∼1 accompanied by the appearance of an Ir−Ir coordination shell. Stabilization of the coordination number of the Ir−Ir shell at 3 at the end of the treatment confirmed the formation of stable supported Ir4 clusters, with ethylidyne and disigma-bonded ethylene ligands. The results further demonstrated that these newly formed Ir4 clusters could be broken up into mononuclear complexes upon exposure to pure ethylene. Similarly, a more oxophilic binuclear tantalum cluster, formed from the mononuclear Ta(CH2Ph)5 by treatment in H2 at 423 K, undergoes fragmentation into mononuclear Ta complexes by replacing gas-phase H2 with C2H4.93

The significance of this work is that the structure and reactivity of atomically dispersed metal species is greatly influenced by subtle differences in the nature of ligands, including supports.

2.4.1. Catalytic Consequences of Structural Changes, Dependent upon Reaction Conditions, between Mononuclear Complexes and Multinuclear Clusters. Many recent reports show that the structure of metals in catalysts dynamically changes in response to different reaction conditions.
conditions such as partial pressures of reactant gases and temperature. Gates et al. have made major contributions to this field, demonstrating reversible interconversions between mononuclear Ir and Rh complexes and their corresponding metal clusters.\(^{77}\) For instance, Ir\(_4\) clusters in zeolite Y cages broke up into mononuclear Ir species during ethene hydrogenation under an ethene-rich composition (C\(_2\)H\(_4\)/H\(_2\) = 4) (Figure 14).\(^{94}\) When the feed composition was switched to

![Figure 14. EXAFS analysis of the changes in the coordination numbers of the catalyst formed from Ir(C\(_2\)H\(_4\))\(_2\)(acac) and dealuminated zeolite Y, obtained by fits with a three-shell model. The data show the conversion of clusters approximated as Ir\(_4\) to predominantly mononuclear Ir complexes, following a step-change in feed to the reactor/EXAFS cell from H\(_2\) to a mixture with C\(_2\)H\(_4\)/H\(_2\) = 4 (molar, indicated with a red background). After 35 min, the feed composition was switched to equimolar C\(_2\)H\(_4\) + H\(_2\) (green background). Later the feed ratio was switched to C\(_2\)H\(_4\)/H\(_2\) = 0.3 (dark blue background). Subsequent changes are indicated by the same color coding. Modified and reproduced from ref 94. Copyright 2009 American Chemical Society.](https://dx.doi.org/10.1021/acscatal.0c03568)

first equimolar and then to a H\(_2\)-rich (C\(_2\)H\(_4\)/H\(_2\) = 0.3) feed, the mononuclear species were converted into Ir\(_4\) clusters. The XANES data supported these changes and presented isosbestic points for the conversions of mononuclear Ir complexes and Ir\(_4\) clusters, indicating the conversion of one species into another. Complementary IR data using CO as a probe molecule further supported these structural changes.

Gates and co-workers further demonstrated that such interconversion of dominant surface metal species also leads to changes in reaction selectivity.\(^{95}\) Zeolite-supported Rh-(C\(_2\)H\(_4\))\(_2\) complexes yield mostly butenes in an ethene-rich mixture of C\(_2\)H\(_4\) and H\(_2\). When the ethene/H\(_2\) ratio was increased to 4, the supported Rh complexes remained mononuclear, and the yields of hydrogenated products ethane and butane increased. When the feed was switched to H\(_2\) small Rh clusters formed. The subsequent switch to an H\(_2\)-rich mixture (H\(_2\)/C\(_2\)H\(_4\) = 4) increased ethene conversion dramatically, and the hydrogenation selectivity became high because of facile H\(_2\) activation on metal sites. However, a reversal of the C\(_2\)H\(_4\)/H\(_2\) led to the rapid breakup of the Rh clusters, accompanied by a sharp drop in the rate of hydrogenation and an increase in n-butene formation.

Recently, Gates and co-workers also demonstrated that Rh(CO)\(_2\) supported in zeolite HY converts to Rh\(_4\)(CO)\(_{12}\) under conditions relevant to the water–gas shift reaction.\(^{96,97}\) The cluster formation results in the generation of CO\(_2\) and a zeolite proton, and the reverse reaction proceeds via a half-reaction that completes the cycle of the water gas shift. Rh\(_4\)(CO)\(_{16}\) formed along with Rh\(_4\)(CO)\(_{12}\) but only in low yield, although it is more stable than Rh\(_4\)(CO)\(_{12}\). The formation of Rh\(_6\)(CO)\(_{16}\) was hindered by trapping of Rh\(_4\)(CO)\(_{12}\) in the supercages and by the low rate of transport of the mononuclear rhodium species. However, the presence of water in the feed limited the oxidative fragmentation of Rh\(_4\)(CO)\(_{12}\) to supported Rh(CO)\(_2\) complexes by surface OH groups and instead formed Rh\(_6\)(CO)\(_{16}\).

In summary, the structure, reactivity, and catalytic properties of atomically dispersed metals are greatly influenced by subtle differences in metal nuclearity and ligand environment. Catalytically active centers undergo dynamical structural changes in terms of both at different operating conditions. Elucidating the impact of the subtle structural differences, however, is complicated when catalysts contain different surface structures. Uniformity and simplicity are the key for reaching an atomic level understanding of the structure–property–performance relationships of supported metal catalysts.

3. HYDROPROCESSING CATALYSIS

3.1. Hydrosulfurization. The pathways and kinetics of the reaction networks of hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and aromatics hydrogenation, and the role of the catalytic metals and supports, represented a major effort of the CCST during its early years. There was significant work on upgrading coal liquefaction products to transportation fuels. The work is still highly read today, as catalytic hydrosprocessing in the era of ultralow sulfur diesel and biomass valorization is as important as ever. Much of the work involved collaborations with George Schuit, who had been a principal developer of the Co–Mo HDS catalyst while at Shell, and Leonidas Petrakis at Gulf R&D. James Lyons of Sun Oil, and James Katzer and Mike Klein of Delaware also contributed. Together they wrote a series of papers extending over two decades examining reaction pathways/kinetics of all key model compounds in oil refinery and coal liquid hydprocessing, for Co–Mo, Ni–W, and Ni–Mo mixed sulfide/oxide catalysts, the ones most widely used today. The pioneering work on relative reaction rates of model compounds, the role of steric hindrance and molecular interaction with the catalytic sites is still relevant for catalyst design and also for upgrading biomass pyrolysis products to renewable transportation fuels.

In an early review, Schuit and Gates,\(^{98}\) highlighted the importance of the relative rates of HDS (hydrogenolysis at the C–S bond) and hydrogenation of both parent and intermediate compounds, and how the ratio of the two reactions greatly depends on the individual reactant (e.g., thiophene being more easily desulfurized prior to hydrogenation, but methyl substituents in one- and multiring thiophenes depress HDS), and the overall feed composition. The catalyst surface structures and the nature of the deactivation mechanisms, especially poisoning, were extensively reviewed.
On the basis of the existing evidence, Schuit and Gates postulated a four-layer model, with Figure 15 showing possible structures of the top two layers, for the working, sulfided Co–Mo/γ-Al2O3 catalyst. The Co3+ promoter is assumed to have penetrated the support (lowest layer), forcing some Al3+ ions to near the surface where they occupy tetrahedral positions. Some Co3+ also intercalates the subsurface layer, causing reduction of some Mo to Mo5+ or Mo3+, this reduction being critical to active site formation. A good promoter favors tetrahedral intercalation in MoO3. On the other hand, for Ni–W catalysts, intercalation of Ni3+ at the layer edges of the trigonal prismatic structure was more likely. These models proved to be of lasting value to the understanding of the catalysts.

There followed several studies, under realistic conditions (typically 548–598 K and 10–10.3 MPa),99 on model sulfur and aromatic compounds,100–102 which, along with TPD/TPR experiments111 and the work of others, led to a postulated reaction mechanism for the HDS of the thiophenic compounds.112 Where the intermediate compounds could not be obtained in pure form, they were synthesized in order to verify pathways. The dibenzothiophene and benzo[b]naptho[2,3-d]thiophene HDS/hydrogenation networks on Co–Mo/Al2O3 are shown in Figure 16.100,107 The key finding was how rapid the initial hydrogenolysis at the C–S bond is relative to competing aromatic hydrogenations,100,101 a result also found for methyl- and dimethyl-substituted (except those substituted at the 4- or 4,6-positions) dibenzothiophenes and benzothiophenes.102,103 Another key finding was that an optimal H2S/H2 ratio exists, to keep the catalyst in a sulfided state.108,110 However, at typical industrial conditions H2S was found to strongly poison the C–S hydrogenolysis reactions, while affecting hydrogenation to a lesser extent or not at all.101,104,106

The HDS and hydrogenation reactions both followed Langmuir–Hinshelwood-type saturation kinetics with respect to both the sulfur compounds and H2, but most likely on different types of sites.101,106,108 The hydrogenation sites were shown to be more acidic.106 The rate to a primary HDS product was characterized by saturation kinetics for the reactant but not for H2.104 Hydrogenation of the nonsulfur-containing aromatics also exhibited saturation kinetics with respect to reactants106 and was influenced by ring size, more rings resulting in greater than an order of magnitude increase in reactivity because of enhanced resonance stabilization of the larger adsorbate.105,106 However, the initial C–S hydrogenolysis rate cannot be simply related to ring size.109

The above observations and additional ones on H–D exchange in such catalysts led to a new proposed mechanism for HDS, where the adsorption of thiophenic compounds is multisite, the C1–C2 carbons pi-bond to an anion vacancy of the oxide, while the S atom, no longer part of an aromatic structure, bonds to another sulfur atom within the metal cation’s coordination sphere.112

### 3.2. Combined Hydroprocessing Operations on Coal Liquids

The model compound work led to more complex studies of HDS, HDN, and HDO of entire coal liquid fractions.113–118 A first step was to be able to understand and quantify such complex mixtures by functional group analysis using combined NMR, elemental and mass spectral analysis,119–122 after separation of the coal liquids into fractions by either LC or GC.124,125 The catalyst here was presulfided Ni–Mo/Al2O3. The HDN rates of the primary N-containing fractions varied as strong bases (e.g., quinolines, biphenylamines, acridine) < weak bases (e.g., imidazoles, amino-naphthols, quinolinol, indolines, carbazoles) < neutral resins (containing fewer N-containing compounds, but with carbazoles, quinolines, indanones, indoles, quinoxaline oxides, benzoazalidines).118 Both the reaction networks and the kinetics of HDN appeared complex, more so than in the HDS work, but some of this was ascribed to difficulties in maintaining constant dissolved H2 concentrations and equilibrium limitations on the HDN reactions. It was found that hydrocracking of biphenyl linkages, aromatic hydrogenations of the hydrocracking products, and methyl group scissions took place also.117

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**Figure 15.** Sulfided monolayers on a Co-promoted γ-Al2O3/Mo oxide. Left: surface layer is Al4/3[Al2O4], S2+ blue, O2− white, Mo3+ second layer open red, Mo5+ second layer hatched red. Right: surface layer is [Al2O4], S2+ blue, O2− white, Mo3+ second layer hatched red, Mo5+ second layer lined red, Al3+ second layer tetrahedral black. Reproduced with permission from ref 98. Copyright 1973 Wiley.

**Figure 16.** Left: reaction pathways for hydrogenolysis and hydrogenation in the reaction network for dibenzothiophene HDS. Redrawn with permission from ref 101. Copyright 1981 Wiley. Right: reaction network for benzo[b]naptho[2,3-d]thiophene and H2 with sulfided CoO-MoO3/γ-Al2O3 at 573 K and 7.1 MPa. Each reaction is approximated as first order in organic reactant; the numbers are the pseudo first-order rate constants in m3/(kgcat*s). Reproduced with permission from ref 107. Copyright 1980 Wiley.
For the neutral oils, HDS was the more important reaction, and here the reaction of DBT in the mixture was similar in rate to that of pure compound DBT\textsuperscript{111} and therefore unaffected by the PAHs present. As in the pure compound HDS work, HDS of the thiophenic compounds was shown to be about an order of magnitude faster than initial aromatic hydrogenation,\textsuperscript{113,115} except for 4-methyl dibenzothiophene, which is sterically inhibited. The 2-, 3-, and 4-ring aromatics that dominate the neutrals fraction are hydrogenated somewhat (the % of naphthenic carbon increases from ~16 to ~25% in 16 h), with evident equilibrium limitations.\textsuperscript{115} The phenolic compounds, concentrated in the weak acid fractions,\textsuperscript{114} undergo HDO at rates faster than for either aromatic hydrogenations, HDS, or HDN at typical conditions (350 °C, 12.2 MPa H\textsubscript{2}, 0.2 WHSV [gcat/(g feed* h)]). Both the HDO and HDS reactions were pseudo-first-order in the reactant, HDO about an order of magnitude higher rate constant than comparable HDS reactions, 10\textsuperscript{−4} L/(gcat*s) being typical.\textsuperscript{114,115,117} However, ethers and furans were far less reactive,\textsuperscript{115–117} either in the weak acids or the neutral oils (~20 times less here than phenolics). Tetralins, indans, cyclohexylbenzenes, cyclo- and dicycloalkanes, and two- and three-ring aromatics dominate the hydrosprocessing products of the weak acids.

The HDO pathways were further delineated in a series of hydrosprocessing studies of model coal liquid and heavy oil compounds, either by themselves or as a small group characteristic of compounds in the fractions discussed above. The catalysts were sulfided or oxidic Ni–Mo/Al\textsubscript{2}O\textsubscript{3} or Ni–W/Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{126–132} While both forms of Ni–Mo/Al\textsubscript{2}O\textsubscript{3} were active for HDO of 1-naphthol at 225 °C, the oxidic form was more so.\textsuperscript{127} Both forms deactivated with time on stream, and both could be regenerated. The HDO pathway is affected more than competing hydrogenation ones,\textsuperscript{127} with inhibition by both water and H\textsubscript{2}S possible, through association with active anion vacancy sites. The kinetics pathway on sulfided Ni–Mo/Al\textsubscript{2}O\textsubscript{3} (at 200 °C, 3.5 MPa H\textsubscript{2}) was traced for 1-naphthol HDO.\textsuperscript{128} There are two principal parallel pathways to tetralin, initial hydrogenation to a tetralone primary product (faster here, but not so at higher temperatures), or direct HDO to a naphthalene primary product.

Hydrogenolytic cleavage (hydrocracking) reactions readily take place on partially hydrogenated PAHs with five-carbon-member rings such as fluoranthene.\textsuperscript{129} The 3-ring compound fluorene is an order of magnitude less active for hydrogenation (poorer resonance stabilization), with essentially no hydrocracking observed with Ni–Mo and Ni–W catalysts.\textsuperscript{130} However, the addition of H-form zeolite to the catalysts greatly enhanced the hydrocracking reactions of linkages in partly saturated rings.\textsuperscript{126–130} For a compound that includes a five-carbon-member ring, the kinetics data were consistent with a mechanism initiated by six-member ring protonation, followed by a 1,5-hydride shift such that a C–C bond of the five-member ring can undergo β-scission, then a 1,3-hydride shift to a more stable benzyl cation, with cleavage of the biphenyl linkage.\textsuperscript{126,130} The latter part of the mechanism also holds for compounds with biphenyl linkages.\textsuperscript{128} Such a mechanism suggests that H\textsubscript{2} utilization rates will be less for compounds with five-member aromatic rings, because they will undergo less dealkylation after initial hydrogenolytic cleavage than do six-membered rings.

Girgis and Gates bridged the gap between hydrosprocessing an entire fraction of a coal liquid and that of model compounds, by examining reactions on sulfided Ni–Mo/Al\textsubscript{2}O\textsubscript{3} of simulated coal liquids consisting of small groups of PAHs and oxygen-, sulfur-, and nitrogen-containing heterocycles, typically at 350 °C, 17.3 MPa H\textsubscript{2}, and 0.8–1.0 WHSV.\textsuperscript{131,132} They confirmed the inhibition of aromatic hydrogenation by quinolines, the poor HDO reactivity of compounds such as dibenzofuran relative to phenolics, the general trend toward higher hydrogenation rate constants with number of rings, and the more reactive behavior of PAHs with five-carbon-member rings. PAHs with at least three six-carbon-member rings were shown to initially hydrogenate at bridging positions. Again it was found that many PAH hydrogenations (usually intermediates, not the initial reactants) are equilibrium-limited at these conditions.\textsuperscript{132}

The practical nature of the work was evident in the deactivation studies. The deposition of ferrous sulfide in the feed was identified as a principal deactivation mechanism in coal liquid hydrosprocessing.\textsuperscript{133} Coking was also shown to play an important factor, adversely affecting hydrogenation, HDS, and HDN reactions.\textsuperscript{134} Similarly, vanadium sulfide deposits were identified as poisons in heavy oil HDS,\textsuperscript{135} and for the hydrogenolysis of dibenzothiophene,\textsuperscript{136} while promoting secondary hydrocracking reactions.\textsuperscript{136} When spent Ni–Mo/Al\textsubscript{2}O\textsubscript{3} catalyst from residuum hydroprocessing was studied, it was found that coking was the primary cause for deactivation, because air-regenerated catalyst (still containing deposited Ni- and V-sulfides) recovered most of its hydrogenation, HDS, and HDN activity.\textsuperscript{137}

Much of the work on hydrosprocessing was summarized in a review of Girgis and Gates.\textsuperscript{138} In 1997, the HDS work was updated and summarized in a last review by Topsoe and Gates that emphasized the importance of alkyl-substituted dibenzothiophenes to the overall kinetics of deep desulfurization.\textsuperscript{139} This pioneering work formed a foundation for subsequent hydrosprocessing catalyst developments, developments needed to meet stringent specifications on fuels and emissions quality, as well as in upgrading renewable feedstocks to drop-in fuels designed to meet future greenhouse gas emission reduction targets.

3.3. HDO of Compounds Representative of Lignin-Derived Bio-oils. Leveraging his extensive experience in HDS/HDN/HDO of coal-derived feedstocks, Gates later returned to this area of research to elucidate reaction networks and catalyst functions in HDO of biomass-derived feedstocks. The research, with David Block, focused on the conversion of compounds representative of lignin and lignin-derived bio-oils. Prototypical compounds featuring methoxy and hydroxyl functional groups such as anisole\textsuperscript{140,141} and guaiacol,\textsuperscript{142,143} were used initially, with Pt/γ-Al\textsubscript{2}O\textsubscript{3} and HY zeolite catalysts. Results demonstrated that the metal function was responsible for the HDO and hydrogenolysis in guaiacol and anisole, with the alumina support or zeolite likely facilitating transalkylation.

One of the challenges determining conversion of bio-oils is the difficulty in quantifying the high yields of water formed in the conversion of oxygen-containing compounds. Gates worked with Susan Ebeler of UC Davis to develop methods to quantify water, including accurate measurements at low water concentrations.\textsuperscript{144} This work resulted in better online analysis of gaseous products, with multiple-detector GC used to identify and quantify reactants and products, complemented by full analysis of liquid-phase compounds, including water, by GC–MS and GC–FID.
A comprehensive experimental design enabled the development of an extended reaction network (more complete than any previously reported) shown in Scheme 3, accounting for all the kinetically important reaction classes in the conversion of prototypical compounds representative of lignin-derived bio-oils.\textsuperscript{145} Efforts to further elucidate reaction networks and understand reaction classes by catalyst function and functional group led to experiments with 4-methylanisole,\textsuperscript{146} cyclohexanone,\textsuperscript{147} furan,\textsuperscript{148} and eugenol.\textsuperscript{149} Gates et al. also identified the roles of the acid and metal functions of the bifunctional catalyst and the benefits of operating at higher pressures (6.9 MPa).\textsuperscript{150,151} The significance of this work is that it established a foundation to optimize catalysts in conversion of lignin-derived bio-oils for a particular application, by balancing these functions.

### 4. STRONG ACID CATALYSIS

#### 4.1. Polymer-Supported Acid Catalysts.

In collaboration with polymer science faculty at Delaware, Gates conducted novel research on structure–property relations of solid polymeric catalysts. This involved evaluation of how the catalytic properties depend upon intrinsic polymeric structure.\textsuperscript{152–154} Gates’s previous research was mostly on solid acidic sulfonated poly(styrene-divinylbenzene) catalysts,\textsuperscript{155–159} not films; therefore, this was an early example of his willingness to explore a new field in collaboration with experts outside of catalysis.

Industrial sulfonated copolymer catalysts are used (e.g.) in the production of isopropyl alcohol from propylene and water, and the reaction of methanol with isobutylene to give methyl-$t$-butyl ether. In the film work, a semicrystalline polymeric film was used to support the $-\text{SO}_3\text{H}$ groups; it was prepared by $\gamma$-radiation grafting of styrene onto commercial polyethylene, followed by sulfonation of the styrene.\textsuperscript{152,154} The polymer lamellae (plate-like crystals) were 20–60 nm thick and several hundred nm in length and width (Figure 17). The structure was manipulated to maximize catalytic potential, the rate data for isopropyl dehydration demonstrating sensitivity to changes induced by drawing (elongation under tensile stress): as the draw ratio was increased from 1 to 2.5, the activity increased but then decreased at higher draw ratios.\textsuperscript{153} The changes in catalytic activity induced by drawing did not result from formation of new surface sites.

A cluster of $-\text{SO}_3\text{H}$ groups is required for the reaction to proceed efficiently, as also found for the commercial resin catalysts (Figure 18).\textsuperscript{154} Gates et al. concluded that reactions could proceed between (i) amorphous chains and one crystalline surface, (ii) sites on the same crystalline surface, and (iii) within the amorphous regions. Clusters involving sites on the same lamellar surface would be unaffected at the low deformations observed for these materials. Therefore, structures of type (ii) and (iii) provide the catalytic sites having structures sensitive to deformation. The results from
this work suggest that polymer cross-linking in polymer-supported resins would affect rates in ways other than through diffusion rates and that reaction rates could be higher in certain cross-linked regions or on moderately cross-linked catalysts. This was shown by Gates et al. to be true with sulfonated poly(styrene-divinylbenzene), for both transesterification and alcohol dehydration reactions.\textsuperscript{157,160,161}

4.2. Zeolites. Research on H-form zeolites was mostly from Gates’s middle career. Some work was oriented toward advancing newer characterization techniques such as EXAFS or, with co-workers from Delaware and Los Alamos, 1-D and 2-D \textsuperscript{129}Xe NMR to study diffusion of metal ions and small molecules.\textsuperscript{162,163} There was also work on some H-form zeolite reaction pathways (e.g., methanol and t-butyl alcohol dehydration),\textsuperscript{164,165} where it was shown that the intrinsic (no diffusional influences) rates were independent of crystal size and that the shape of the zeolite (e.g., H-Mordenite) profoundly influenced shape-selectivity and molecular traffic control (e.g., how inerts trapped in pores could hinder reactions). Other work focused on acid catalysis on oxides similar to zeolites such as silicatized aluminas.\textsuperscript{166} However, the most influential paper here was the collaboration with Werner Haag of Mobil on strong-acid-catalyzed reactions of alkanes, the first to quantify and fully explain the product distributions in terms of two separate mechanisms, of that unimolecular and bimolecular cracking, simultaneously operating on zeolites such as HSM-5.\textsuperscript{167} With the unimolecular mechanism dominant in the limit of zero conversion (Scheme 4), they showed conclusively that zeolites could act as catalysts for the primary dehydrogenation of alkanes. Earlier work to establish the pathways was that of Bizreh and Gates.\textsuperscript{168}

Scheme 4. Schematic Representation of \textit{n}-Butane Cracking by the Unimolecular Pathway; Reproduced with Permission from Ref 167. Copyright 1992 Elsevier

The essentials of the chemistry were also used to show strong commonality (the differences resulting primarily from differing acid site strengths and deactivation rates) between H-form zeolites and other solid superacids such as sulfated zirconias for alkane cracking.\textsuperscript{169} The USY zeolite was 1−2 orders of magnitude less active than metal-promoted sulfated zirconia but with similar product distributions.

The culmination of this work was a review by F. Jentoft and Gates on protolytic and bimolecular cracking mechanisms.\textsuperscript{170} The evidence for alkanium ions in the former mechanism was explained, along with the support’s role in generating and stabilizing intermediates and transition states, and in alkoxide chemistry.

4.3. Superacid Catalysis and Sulfated/Tungstated Zirconias. Superacids have an acid strength greater than that of pure sulfuric acid. Liquid superacids often include the combination of a strong Bronsted acid with a Lewis acid, and are of interest as catalysts for hydrocarbon reactions such as isomerization, cracking, or alkylation at ambient conditions. A common liquid superacid is FSO\textsubscript{3}H-SbF\textsubscript{5}, capable of producing stable carbocations in solution.\textsuperscript{171} The advantages of solid catalysts for industrial application, easy separation from products, and potentially reduced corrosion motivate the search for solid superacid catalysts. In 1976, Gates et al. reported on the synthesis and activity of a solid catalyst with “superacid properties”.\textsuperscript{172} Two later papers more fully described the synthesis, characterization, and reactivity of these superacids.

The catalyst was synthesized by sublimation of anhydrous AlCl\textsubscript{3} onto a sulfonated poly(styrene-divinylbenzene) at 413 K. It appeared that AlCl\textsubscript{3} was anchored on a sulfonate group through an oxygen bridge. The prepared resins had a ratio of S:Al:Cl of 2:1:2, consistent with a HSO\textsubscript{3}AlCl\textsubscript{3} structure. The catalyst was active for cracking and isomerization reactions of \textit{n}-hexane at 358 K. Activity for \textit{n}-butane isomerization at 382 K was characterized by a high initial rate, comparable with those reported for solid SbF\textsubscript{5}/sulfonated Al\textsubscript{2}O\textsubscript{3}.\textsuperscript{173} However, the catalyst rapidly deactivated such that the number of turnovers per presumed active site was only 0.1. Loss of HCl was reported during reaction.

The catalytic chemistry occurring on aluminum chloride/sulfonic acid resin catalysts was further investigated by reacting either \textit{n}-butane or \textit{n}-pentane, with added HCl, at 343−416 K.\textsuperscript{174} The \textit{n}-butane was found to give almost exclusively disproportionation products propane and pentanes. The \textit{n}-pentane resulted in a much more complex product mixture consistent with isomerization, disproportionation, and the hexane disproportionation products undergoing subsequent β-scission. No olefins were observed. These findings were consistent with classical carbenium-ion mechanisms of hydride and methyl shift, β-scission, and C–C bond forming and breaking steps.

To gain more understanding of the effect of the strength of the Bronsted acid in these combination of Bronsted/Lewis acid catalysts, a series was synthesized reacting aluminum chloride with a number of solids with varying Bronsted acidity.\textsuperscript{175} Even a weakly acidic silica formed catalytically active sites. For the sulfonic acid resin catalyst, IR spectroscopy showed evidence of AlCl\textsubscript{3} reacting with sulfonic acid groups, presumably the OH groups, giving a Cl:Al ratio of between one and two. For this catalyst, the rate of \textit{n}-butane isomerization followed first-order (in butane) Langmuir−Hinshelwood kinetics. The appearance of the cracking products methane and ethane were taken to indicate that this catalyst was a superacid.

Other papers followed this approach of varying the Lewis acid component (AlCl\textsubscript{3}, SnCl\textsubscript{2}, TiCl\textsubscript{4}, BF\textsubscript{3}, and SbF\textsubscript{5}) with the same Bronsted acid.\textsuperscript{176,179} According to XPS, the Cl:Al ratio of a catalyst made from AlCl\textsubscript{3} is closer to 1; Figure 19 shows three structure that were proposed. The catalysts were much more active with HCl added to the feed, and an adsorbed HCl component (TPD suggesting 4 HCl/sulfonate group) was seen as an important part of the active site. The activity was also related to the acidity of the Lewis acid.

Research on solid superacids turned from polymers to oxide-supported acids.\textsuperscript{180−185} Gates re-entered superacid catalysis with a communication on a promoted sulfated zirconia catalyst,\textsuperscript{183} in collaboration with Sun Refining. They reported a sulfated 0.5% Mn−1.5% Fe ZrO\textsubscript{2} (FMSZ) that isomerized \textit{n}-
butane at 300 K. The catalyst was much more stable than metal halide–sulfonic acid resin catalysts and could be regenerated. The activation energy for FMSZ was similar to that for SZ, but the activity was 3 orders of magnitude higher, suggesting that the new catalyst had a higher concentration of active sites than did SZ.

Gates et al. investigated the catalysis of the interaction of FMSZ with light alkanes, especially n-butane. The isomerization of n-butane is significantly more difficult than that of (e.g.) n-pentane because it proceeds through the formation of a primary carbenium ion. An initial study of the kinetics of n-butane reaction on FMSZ found primarily isomerization with some disproportionation;\(^{184}\) the isomerization was 1–2 orders of magnitude faster.\(^{185}\) Products included traces of methane and ethane at 313–373 K.\(^{186}\) The activity first increased with time on stream, then decreased. The rate data were fit to a Langmuir–Hinshelwood rate equation consistent with a second-order reversible reaction; a C8 intermediate was suggested, because the product selectivities were similar to that for SZ and H-mordenite at 623 K, where a C8 intermediate for the n-butane reaction had been shown.\(^{187}\)

The invariant product selectivities at changing reaction conditions suggested that isomerization and disproportionation shared a common intermediate.\(^{185}\)

n-Pentane and n-hexane were also used to characterize the reactivity of SZ and FMSZ.\(^{188}\) For n-pentane, SZ produced only traces of isopentane at 313 K. The selectivity data suggested a unimolecular isomerization and a bimolecular disproportionation reaction. The rates for n-pentane isomerization were 3-fold higher than those for n-butane, and so did not reflect the need for the formation of a primary carbenium ion as during n-butane isomerization. The authors suggested there was more to the mechanism than acid catalysis. When Pt was added to FMSZ and H\(_2\) added to the feed, the isomerization activity at 273 K increased and the disproportionation activity decreased. During a low-temperature n-pentane reaction, the FMSZ catalyst changed color consistent with iron oxidation and thus consistent with a proposal of Mark Davis’s group\(^{190}\) that oxidative dehydrogenation was producing alkenes, which are then much easier to protonate.

Neopentane cracking was also used as a probe reaction to compare the FMSZ catalyst to both SZ and ultrastable Y (USY) zeolite.\(^{181}\) It was chosen as a test reaction because of the following: (1) neopentane would produce a relatively simple product distribution from cracking (methane and isobutene); (2) it would have a slow rate of hydride abstraction to form carbenium ions, because all hydrogens are on primary carbons; and (3) it typically gives a slow isomerization relative to cracking rate, reducing the complexity of the product distribution. For the isomerization of n-butane at 373–423 K, FMSZ is 3 orders of magnitude more active than SZ, but the initial rate ratio for neopentane cracking at 723 K was only 2 times higher, and only 1 order of magnitude higher than with USY. The product distribution for the zirconia catalysts was quite different from that of the zeolite. USY produced methane and butenes in a 1.5:1 ratio, but the zirconia catalysts produced about 97% methane and no measurable isobutene. However, the catalysts did deactivate, and the carbon balance was consistent with surface deposition of the butene product. The cracking kinetics for all three catalysts were first order with respect to neopentane, consistent with the Haag-Dessau unimolecular mechanism of cracking. Neopentane cracking on FMSZ did not show any differences in behavior from strong acids at higher temperatures, leading to the conclusion that “Perhaps there is more to the catalytic nature of the promoted sulfated zirconia” than superacid catalysis.\(^{191}\)

The reaction of n-butane on FMSZ at 498 K reinforced this conclusion, being consistent with conventional catalytic cracking,\(^{192}\) thereby suggesting that FMSZ behaves as strongly acidic (but not superacidic) at the higher-temperature conditions. The cracking rate to give methane for FMSZ at 723 K was about the same as that extrapolated from Kranil et al. with an HZSM-5 catalyst.\(^{167}\) The cracking selectivities for methane, ethane, and ethylene were consistent with the Haag–Dessau unimolecular cracking mechanism discussed previously.

Kinetics analysis for cracking of propane, n-butane, and isopentane on FMSZ showed a compensation effect,\(^{193}\) thought to relate all of these reactions because they all proceed through a carbonium ion transition state. For example, the product distribution for the reaction of propane at 523 K included ethane, ethylene, and propene,\(^{194}\) consistent with superacid solution chemistry. While SZ and FMSZ were both active between 523 and 623 K for cracking and disproportionation, USY was only active for cracking and dehydrogenation, at ≥673 K.\(^{169}\) The conclusion was that to the extent acidity is responsible for the activity, then the order of acidity is FMSZ > SZ > USY or HZSM-5.

By 1997 several groups had concluded that on SZ and FMSZ redox activity producing alkenes, which explains their high activity for n-butane isomerization.\(^{190,195,196}\) Gates et al. tested several catalysts and found that the dehydrogenation selectivity for an ethane reactant at 723 K followed USY > HZSM-5 > SZ > FMSZ, but all values were similar.\(^{197}\) The zirconia-based catalysts showed a high initial activity that rapidly decreased, then increased, then slowly decreased. The initial high activity produced ethene, methane and butane, while the subsequent high activity produced only ethene, hydrogen and methane. Interestingly, at 523 K FMSZ, the only catalyst of the four active at this temperature, rapidly deactivated with ethene and butane the only products. The kinetics data were consistent with a compensation effect. The data showed a clear difference between zirconia-based catalysts and zeolites, the former exhibiting chemistry consistent with superacidity. Methane, which cannot be dehydrogenated, reacts on FMSZ at 623−723 K to form ethane,\(^{198}\) which can be explained by several alternatives: (1) a minority of very strong acid sites are protonating the methane to form

\[\text{CH}_4 + \text{H}^+ \rightarrow \text{CH}_3^+ + \text{H}_2\]

\[\text{CH}_4 + \text{H}^+ \rightarrow \text{CH}_3^+ + \text{H}_2\]

\[\text{CH}_3^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 + \text{H}_2\]

\[\text{CH}_3^+ + \text{CH}_3\text{CH}_2\text{CH}_2\text{CH}_3 \rightarrow \text{CH}_3\text{CH}_2\text{CH}==\text{CH}_2 + \text{H}_2\]

**Figure 19.** Three plausible structures for the surface metal halide complex with sulfonate groups. Reproduced with permission from ref 178. Copyright 1984 Wiley.
carbonium ions; (2) oxidative formation of carbonium ions;\textsuperscript{195} or (3) coupling on the oxide surface.

Gates et al. also altered the promoter metals in SZ, testing Mn, Fe, Co, Ni, and Zn.\textsuperscript{199} Promoters were added to ZrO\textsubscript{2} at the same molar concentration as in FMSZ. The order of activity for the \( n \)-butane reaction was the following: Mn > Fe ≫ Co ≫ Ni ≫ Zn. All promoted catalysts showed a break-in period up to a maximum activity, and then deactivated. The products were isobutane for the SZ, Ni- and Zn-promoted SZ, but included propane and pentanes for Co-, Mn-, and Fe-promoted SZ (373 K). This again shows that superacid catalysis is insufficient to explain all the chemistry on metal promoted SZs.

In collaboration with Helmut Knözinger, Gates et al. employed several techniques to characterize the surface chemistry of the FMSZ catalyst.\textsuperscript{200} They found that the promoters were not always evenly distributed, with (e.g.) iron oxide domains in the catalyst. The oxidation states of the promoters were Fe\textsuperscript{III} and Mn\textsuperscript{II}. ESR showed hyperfine splitting for Mn\textsuperscript{II}, suggesting isolated manganese ions. The hyperfine splitting was not quenched by exposure to oxygen, indicating that the Mn was not on the surface. There was no observed interaction between Fe and Mn, and so the findings did not explain the exceptional activity of FMSZ over that of SZ promoted with an equivalent amount of either Fe or Mn.\textsuperscript{199}

Continuing this collaboration, Gates moved from SZ to tungstated zirconia (WZ) in 1998. It had been found that SZ could lose sulfur during \( n \)-butane isomerization at 523 K,\textsuperscript{201} and WZ was seen as a more stable alternative. WZ materials are strong acids but not superacidic. The WZ catalysts were characterized with Raman and IR spectroscopies during CO adsorption and with \( n \)-pentane isomerization.\textsuperscript{202} IR showed Lewis acid sites of coordinatively unsaturated Zr\textsuperscript{IV} ions and Bronsted sites associated with WO\textsubscript{5}. Similar to SZ, WZ showed a break-in period during \( n \)-pentane reactions. Carbonaceous deposits formed, and they were thought to be involved in active site formation and ultimately in generating the coke that deactivates the catalyst. Tungsten oxide was also supported on TiO\textsubscript{2}, and tested similarly.\textsuperscript{203} Tungstated titania was similar in activity to WZ but showed greater selectivity to alkenes. With the addition of Pt to the catalyst and H\textsubscript{2} to the feed, the catalyst became more stable, and its operation could be interpreted in terms of a bifunctional mechanism with dehydrogenation on the Pt metal and isomerization on the acid sites.

Following reports of reduced tungsten on WZ during catalysis, and of formation of new acid sites,\textsuperscript{204,205} the redox properties of WZ were studied by EPR and IR.\textsuperscript{206} Tungsten on ZrO\textsubscript{2} was reduced to W\textsuperscript{5+} by \( n \)-pentane at 523 K, with formation of Cs radicals. It was inferred that W\textsuperscript{5+} is a stoichiometric redox initiator on WZ catalysts, perhaps similar to sulfate on ZrO\textsubscript{2} and that the Cs radicals react with the surface in a one-electron transfer that leads to a surface carbenium ion.

The addition of iron sulfate or nitrate to a Pt-promoted WZ catalyst and the addition of H\textsubscript{2} to the feed produced an active and stable pentane isomerization catalyst.\textsuperscript{207} Pt without iron produced a stable catalyst with 95% selectivity (523 K) and adding iron increased selectivity.

The reaction paths on Pt-promoted WZ were elucidated by observing the \( n \)-pentane reaction with or without H\textsubscript{2} in the feed, and by prereduction of the catalyst.\textsuperscript{208} The Pt was assumed to act either (1) as a site for dehydrogenation and hydrogenolysis, giving alkenes that isomerize on acid sites with hydrogenolysis products C1 and C4 or C2 and C3;\textsuperscript{209} or (2) as a locus for hydrogen spillover that then affects reactions on the acid sites.\textsuperscript{210} Four reaction paths, A–D, were hypothesized to explain the reaction chemistry. Paths A and B are considered to occur on the tungsten oxide surface and are depicted in Figure 20. Path A is the formation of a stable polyalkenyl that

\begin{itemize}
  \item Path A
  \item Path B
  \item Path C
  \item Path D
\end{itemize}

\texttt{Figure 20. Reaction paths A and B for isomerization on the tungsten oxide surface. Redrawn with permission from ref 208. Copyright 2003 Elsevier.}

\texttt{Figure 21. Activation of alkanes on WZ catalysts with the formation of a bronze like surface cluster. Reprinted with permission from ref 212. Copyright 2003 Elsevier.}

then protonate alkenes. Monomolecular isomerization is more prevalent if there is spillover hydrogen to facilitate desorption of the isomer and inhibit the formation of polyalkenyls. Paths C and D would occur on the Pt, and are dehydrogenation and cracking to form byproducts, or hydrogenolysis to also form byproducts, respectively. The reactions in these paths depend upon Pt dispersion and hydrogen availability.

The significance of the work was that while it was shown that solid superacids capable of forming carbenium ions from alkanes could be made, and that while the initial cracking reactions on such catalysts could proceed via the unimolecular pathway, many other complications ensued even at low conversion. As the product pool evolved, the chemistries became more consistent with the classical carbenium-ion mechanisms of acid catalysis, and alkene addition to the pool could be accelerated by the presence of dehydrogenated alkanes in catalysts such as tungstated or sulfated zirconia.
5. GATES’S ROLES IN EDUCATION AND SERVICE TO THE CATALYSIS COMMUNITY

Gates’s first textbook “Chemistry of Catalytic Processes” with Jim Katzer and George Schuit (McGraw-Hill, 1978) was among the first to address key industrial catalytic processes (including cracking, reforming, catalysis by transition metal complexes, partial oxidation, and hydrodesulfurization) from the dual viewpoints of science and engineering. His second textbook “Catalytic Chemistry” (1992) was an outgrowth of an undergraduate-graduate class at Delaware that taught catalytic chemistry as a unified subject comprising homogeneous, enzymatic, and heterogeneous catalysis.

The Center for Catalytic Science and Technology, founded by Gates and James Katzer in 1978 and still going strong at the University of Delaware, was groundbreaking in many ways. The Center arose from the interactions of its founders with industrial catalysis practitioners (no initial Federal “Center” grant) and was heavily reliant on industrial subscription. Researchers from sponsoring companies participated in much of the work, and more than half the alumni took initial employment at sponsoring companies. It has inspired countless imitators since.

Gates (initially working with D. C. Koningsberger) played a significant role in popularizing and explaining X-ray absorption spectroscopy to the catalysis community. This work took several forms, including practical publications on low-cost transmission (ultimately fluorescence as well) cells capable of both vacuum and atmospheric operation at elevated temperatures and in reactive atmospheres. There were several iterations of this design, the first appearing in 1996, with subsequent improvements. Gates worked closely with Simon Bare on the DOE co-ACCESS laboratory at SSRL and was an early advocate of high-energy resolution fluorescence-detected XANES (HERFD-XANES) for catalyst characterization. An early EXAFS review by Gates and Koningsberger of work on a wide range of supported metals and complexes addressed how the technique could be used to interpret metal–support interactions of both precursor complexes and (usually after reduction) small metallic clusters. Alexeev and Gates later wrote a review specifically focused on the EXAFS of supported metal complexes and clusters. This work covered both conventional metal oxide and zeolite supports, included guidance on error assessment in structural calculations, compared XRD and EXAFS structural calculations, and showed that different M−O (at the support interface) bonds often result from differently hydroxylated surfaces.

Gates served as an Editor of Advances in Catalysis from 1995 to 2014, much of that time with Helmut Knözinger. He has contributed to the catalysis community in many other ways, traveling the world giving many plenary lectures (29 in addition to the Burwell lectureship, and many other invited seminars) on his research and broader vision of catalysis, serving on many high-level advisory boards and panels (e.g., the Department of Energy’s Basic Energy Sciences Advisory Committee from 2003 to 2017), and in thorough and incisive reviewing of others’s work (50 reviews a year on average). He never disdained publication of more accessible material designed to reach a wider audience, such as a series of short publications in CHEMTECH on polymer supports, supported metal clusters, multifunctional catalysts, or chapters in the “Handbook of Heterogeneous Catalysis” on ion-exchange resin catalysts, supported metal clusters and hydrocarbon reaction mechanisms. He also contributed to the 2016 catalyst benchmarking practices effort. He has consulted for several companies, has served as a Director of the North American Catalysis Society since 1997, and was cochair of its 2009 North American Meeting.

As an avid herpetologist, Gates is probably the only catalysis researcher ever to publish in the journal of the Global Gecko Association on his observations of the Namibian native shown in Figure 22.

Figure 22. Gecko Pachydactylus scherzi Mertens, 1954.

■ SUMMARY

Bruce Gates has made landmark contributions to the field of Catalysis, in atomically dispersed supported metal complexes and metal clusters, hydroprocessing, catalysis by strong acids, and in new catalyst characterization techniques. His work is characterized by unrelenting intellectual rigor, focus on the most important problems in catalysis, use of the most powerful physical methods available, and careful writing of seminal manuscripts and reviews. We hope we have illustrated the progression of his thinking and accomplishments in these areas, efforts that we note are continuing. We wish him a happy 80th birthday and good health and happiness for the future.

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Notes
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