

A Career in Catalysis: Mark E. Davis

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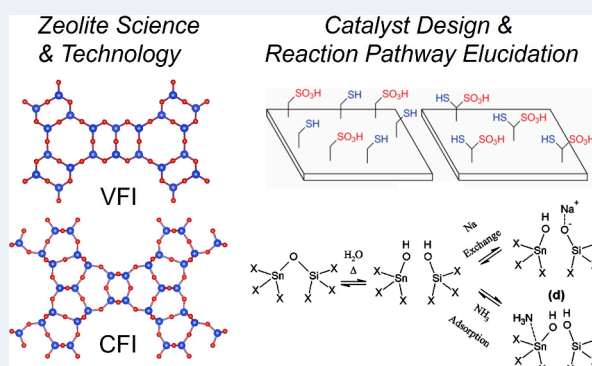
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ABSTRACT: Mark E. Davis led an independent research program from 1981 to 2023, beginning at the Virginia Polytechnic Institute and State University (VPI) and then transitioning to the California Institute of Technology (Caltech). His research program was marked by exceptional creativity, breadth, and depth. With classical training in reaction engineering, Davis developed expertise in experimental heterogeneous catalysis and led work in this discipline for more than 40 years. His name is synonymous with zeolites, and today, he is one of the most widely recognized experts in zeolite synthesis, characterization, and catalysis in the world. Early work at the VPI focused on zeolites and catalysis with supported metal coordination complexes. His creativity was evident at the earliest stages of his career, with the development of supported aqueous phase catalysts and the world's first crystalline, extra-large pore molecular sieve, both reported in the late 1980s. A move to Caltech saw a significant expansion of his zeolite synthesis program and the rapid acceleration of a multidecade collaboration with Dr. Stacey I. Zones of Chevron. At Caltech, his work expanded to include studies of molecular recognition and catalysis with organic/inorganic hybrid materials, and he developed a large, parallel program in drug delivery. His work on catalysis heavily emphasized zeolite catalysis, including major thrusts on the conversion of sugars in the liquid phase and methanol in the gas phase. Numerous new zeolites and molecular sieves were discovered throughout the four decades of the Davis laboratory, highlighted by a successful, multidecade quest to prepare a chiral zeolite with enantioselective catalytic properties. Davis is one of the most decorated researchers of the last four decades. He is one of only 21 living people currently elected to all of the US National Academies (Engineering, Science, Medicine) and elected as a Fellow of the National Academy of Inventors. He was the first engineer to win the NSF's Alan T. Waterman Award and is one of only two researchers (to date) to win the International Zeolite Association's Donald Breck Award twice (1989, 2019). Awards from the ACS (Ipatieff, Murphree, and Somorjai Awards), AIChE (Colburn, Professional Progress Awards), and North American Catalysis Society (Emmett Award) are among his accolades.

KEYWORDS: zeolite, zeotype, molecular sieve, catalyst, enantioselective catalysis, MTO, isomerization, sugar



INTRODUCTION

Much has been said about the elitist process of hiring and promoting graduates from within their own ranks at the top US universities. Empirical data and analysis show that this trend persists, perhaps discouraging graduates from other universities from pursuing their dreams.¹ While no process, program, or system involving decision-making by people can be completely free from bias, the pursuit of scientific knowledge remains focused on uncovering universal truths of the world. In this light, from a meritocracy point of view, Prof. Mark E. Davis' (MED) career path and accomplishments exemplify the American Dream, as he rose to prominence through the strength of his contributions to scientific knowledge and his engineering advancements.

Mark earned his BS (1977), MS (1978), and PhD (1981) degrees in chemical engineering from the University of Kentucky, where he simultaneously competed on the track team. After graduating with his Ph.D., he joined the faculty in chemical engineering at the Virginia Polytechnic Institute and State University (Virginia Tech or VPI) and rose to prominence before moving on to a position as Full Professor at the California Institute of Technology (Caltech). He

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achieved this by sheer brilliance, coupled with a knack for mentoring, without the benefit of a prototypical foundation in the field in which he excelled and where he ultimately built the foundation for his career, zeolites, and catalysis. Indeed, he started as an Assistant Professor in chemical engineering at Virginia Tech teaching and researching what he learned during his Ph.D. studies—numerical modeling of chemical reactors.²

This Account details the career of Prof. Mark Edward Davis, Emeritus Professor at the California Institute of Technology (Caltech), from the perspective of his contributions to porous materials, catalysis, reaction engineering, and related areas of chemical engineering (Figure 1). Mark was such a prolific



Figure 1. Mark E. Davis, Warren and Katharine Schlinger Professor of Chemical Engineering, Emeritus at the California Institute of Technology.

researcher and scholar that his career ultimately grew far beyond this scope, including a second, parallel career as a researcher in drug delivery, which simultaneously produced dozens of papers, several start-up companies, and an array of graduates populating universities, hospitals, and industry making contributions in this wholly separate field from catalysis. Today, MED stands as one of the most decorated scholars in the history of chemical engineering in the United States. He is one of only 24 individuals elected to all three National Academies (Sciences, Engineering, Medicine).³ Over 10 years at VPI and 32 years at Caltech, Mark and his team of students, postdocs, and collaborators published 468 papers and produced 130 US (and numerous international) patents, to date. Over this span, 10 MSs and 61 PhDs graduated after studying under his guidance (Table 1), while 45 postdoctoral researchers and 20 visitors performed research in his laboratories (Table 2).

■ FOUNDATIONS AT VIRGINIA TECH

After earning his PhD under the guidance of Prof. John Yamanis at Kentucky,² Mark joined Virginia Tech as an Assistant Professor in the Fall of 1981. He continued contributing to numerical modeling of reactors, the subject of his doctoral work, for four years after his graduation.^{4–12} In

Table 1. Graduates of the Mark Davis Laboratory from 1981–2024

| Virginia Tech | |
|-----------------------------------|--------------------------------------|
| Michael D. Burnett, MS, 1983 | Paul E. Hathaway, PhD, 1989 |
| Kathleen M. Richter, MS, 1984 | Consuelo Montes de Correa, PhD, 1989 |
| Edward J. Rode, PhD, 1985 | Man-Hoe Kim, PhD, 1992 |
| Jill Schnitzer, MS, 1985 | Michael J. Annen, PhD, 1992 |
| Joseph A. Rossin, PhD, 1986 | Suk Bong Hong, PhD, 1992 |
| Renato Sprung, PhD, 1987 | Valerie L. Young, PhD, 1992 |
| Juan P. Arhancet, PhD, 1989 | |
| Caltech | |
| Kam To Wan, PhD, 1994 | Ryan K. Zeidan, PhD, 2007 |
| Raul F. Lobo, PhD, 1994 | Eric L. Margelefsky, PhD, 2008 |
| Sandra L. Burkett, PhD, 1995 | Heather K. Hunt, PhD, 2009 |
| Charles B. Khouw, PhD, 1995 | Brendan C. Mack, PhD, 2009 |
| John E. Lewis Jr., PhD, 1996 | John Carpenter, PhD, 2009 |
| Christopher B. Dartt, PhD, 1996 | Raymond H. Archer, PhD, 2009 |
| Peter R. Seidel, MS, 1996 | Christopher A. Alabi, PhD, 2009 |
| Wayez R. Ahmed, MS, 1996 | John C. McKeen, PhD, 2009 |
| Matthew Helmkamp, MS, 1996 | Jonathan Chung Hang Choi, PhD, 2011 |
| Shervin Khodabandeh, PhD, 1997 | Jonathan Zuckerman, PhD, 2012 |
| Jack Geilfuss, MS, 1997 | Jelena Culic-Viskota, PhD, 2012 |
| Yushan Yan, PhD, 1997 | Devin Wiley, PhD, 2013 |
| John F. Nagel, PhD, 1997 | Han Han, PhD, 2013 |
| Kenneth R. Carlgren, MS, 1999 | Yashodhan Bhawe, PhD, 2013 |
| Christopher W. Jones, PhD, 1999 | Ricardo Bermejo-Deval, PhD, 2014 |
| Alexander Katz, PhD, 1999 | Mark A. Deimund, PhD, 2015 |
| Paul A. Wagner, PhD, 1999 | Joshua J. Pacheco, PhD, 2015 |
| Suzie H. Pun, PhD, 2000 | Joel E. Schmidt, PhD, 2015 |
| Patrick M. Piccione, PhD, 2001 | Andrew J. Clark, PhD, 2016 |
| Lin Luo, PhD, 2001 | Dorothy W. Pan, PhD, 2016 |
| Bekah Main Mellema, MS, 2002 | John Birmingham III, MS, 2016 |
| Andrea P. Wight, PhD, 2004 | Marat Orazov, PhD, 2016 |
| Jonathan M. Gallownia, PhD, 2005 | Yuewei Lucy Ji, PhD, 2016 |
| Jeremy D. Heidel, PhD, 2005 | Stephen Kramer Brand, PhD, 2017 |
| Stephen R. Popielarski, PhD, 2005 | Emily Wyatt, PhD, 2018 |
| Hyunjoo Lee, PhD, 2005 | Steven Lee, PhD, 2018 |
| John F. Murphy, PhD, 2005 | Jong Hun Kang, PhD, 2019 |
| Swaroop Mishra, PhD, 2006 | Faisal Alshafei, PhD 2023 |
| Derek K. Bartlett, PhD, 2007 | Youngkyu Park, PhD 2024 |

this time, he authored a textbook on *Numerical Methods and Modeling for Chemical Engineers*,¹³ the first of two textbooks he authored. However, in these early years, some of Mark's innate personality traits began to pull him in new directions. Mark is a deeply curious person, and he is inherently ambitious, seeking to work on grand, important problems. Most importantly, Mark believes in his ability to learn new things, either through self-study or via collaboration and partnership with others, and he is not intimidated by dogma. These traits will appear repeatedly in this Account, most prominently when he launched his drug delivery research program in the mid-1990s.

While an Assistant Professor at Virginia Tech, Mark began a long-standing friendship with David Cox, who began work as an Assistant Professor at Virginia Tech in 1986, that included collaborations in the area of surface science.^{14–16} He also established a fruitful collaboration with an inorganic chemist, Brian Hanson,¹⁷ and began a deep dive into the field of catalysis, learning organometallic and coordination chemistry and key features of active sites in catalysts. Research in catalysis and reaction engineering in this period in the United States was shaped by the oil crisis of the late 1970s, and catalytic

Table 2. Post-doctoral Fellows, Visitors (V), and Lecturers (L) Affiliated with the Mark Davis Laboratory from 1981–2024 Organized by Approximate Year of Departure from the Laboratory

| | |
|---------------------------------|-------------------------------|
| Ligia Sierra, 1989 | Allen W. Burton, 2001 |
| Chi L. Lin, 1990 | Christopher Dillon, 2001 |
| David Young, 1991 | Theresa M. Reineke, 2002 |
| Ela Mielczarski, 1991 | Joseph H. Holles, 2002 |
| Michelle Goeper, V, 1993 | Isao Ogino, V, 2003 |
| Hong-Xi Li, 1993 | Victor Diakov, 2004 |
| Michael Tsapatsis, 1994 | Christoph M. Fougret, 2004 |
| Cong-Yan Chen, 1994 | Alexandre Blanc, 2005 |
| David P. Serrano, V, 1994 | Jennifer L. Anthony, 2005 |
| Tatsuya Okubo, V, 1994 | Rozamond Sweeney, 2007 |
| Miguel Cambor, 1994 | Maria P. Lambos, V, 2008 |
| Frederic Vaudry, 1995 | Noemi Linares Perez, V, 2008 |
| Hubert Koller, 1995 | Hiroko Okatsu, V, 2009 |
| Yoshihiro Kubota, 1995 | May Pang Xiong, 2009 |
| Clemens C. Freyhardt, 1996 | Alejandra Nieto Pena, V, 2009 |
| Masahito Yoshikawa, V, 1996 | Yuriy Roman-Leshkov, 2010 |
| Katsuyuki Tsuji, V, 1998 | Manuel Moliner-Marin, 2010 |
| Larry W. Beck, 1998 | Fanny Eriksen, V, 2011 |
| Takahiko Takewak, V, 1999 | Eranda Nikolla, 2011 |
| Hector Gonzalez, 1999 | Michael Trudsliev, V, 2011 |
| Javier Garcia Martinez, V, 1999 | Flavien Lucas Morel, V, 2011 |
| Hiroshi Yamashita, V, 1999 | Kammei Rai, V, 2012 |
| Hiroshi Kominami, V, 1999 | Rajamani Gounder, 2013 |
| Osamu Chiyoda, V, 1999 | Bingjun Xu, 2013 |
| Masaki Okamoto, 1999 | Ben W. Boal, 2015 |
| Peter-Paul Knops-Gerrits, 1999 | Michiel Dusselier, 2015 |
| Wen Li, 1999 | Raimund Walter, V, 2017 |
| Jose Geraldo Nery, 2000 | Sarah Mojarad, L, 2017 |
| Patricia Andy, 2000 | Dana Levine, 2018 |
| Axel Brait, 2000 | Matthew J. Kale, 2018 |
| Brian P. Santora, 2001 | Viktor J. Cybulskis, 2018 |
| Nathalie C. Bellocq, 2001 | Marcella Lusardi, 2021 |
| Veronique Dufaud, V, 2001 | Donglong Fu, 2023 |

methods aimed at improving the efficiency of oil production were of great interest. Zeolites are used as catalysts to produce a significant part of the fuel used in transportation. To this end, he developed an early interest in zeolites and started a new research direction on the use of zeolites as supports for organometallic compounds with a focus on reactions distinct from conventional catalytic cracking, for which zeolites were already known. Mark emphasized hydroformylation catalysis.^{18–24} In parallel, Mark began to teach himself and develop methods to make, modify, and characterize different zeolites and molecular sieves.^{25–28} While there are over 250 known crystalline zeolite and wholly inorganic (ALPO, SAPO, metallosilicate, etc.) molecular sieve topologies today, in the mid-1980s there were only ~90 structures known, with most having only 8-, 10-, or 12-membered ring (MR) pore openings accessible. As such, Mark saw the potential for innovation in the creation of new zeolite structures, including extra-large pore crystalline structures, incorporation of unconventional framework heteroatoms, and creation of chiral zeolite structures. He also began a focus on application of advanced characterization techniques to the elucidation of zeolite structures as well as synthetic pathways, for example, electron spin resonance and nuclear magnetic resonances spectroscopies (ESR and NMR).^{14,15,29–40}

Mark published his first papers on zeolite synthesis in the mid-1980s, including studies of ZSM-5 synthesis with mixed organic cation structure directing agents (OSDAs),⁴¹ SAPO versions of faujasite zeolites,²⁷ Co-containing ZSM-5,²⁸ gmelinite and ZSM-12 using a polymer OSDA,⁴² and a SAPO sodalite framework.¹⁵ But it was Mark's discovery of VPI-5,⁴³ a molecular sieve with pores much larger than any other material of this type known at that time (Figure 2, left), that established him as a leading zeolite expert at an early career stage. In many ways, this discovery was a career-defining event. Occurring in the decade after the gasoline shortages caused by the Iranian revolution of 1979, this discovery was hailed as a huge success, because it opened the door to new, large-pore materials that were projected to be able to significantly increase the yields and reduce the costs of the gasoline and diesel fuel obtained by catalytic cracking. This is because fouling of the zeolite catalyst and the need for its subsequent continuous regeneration represent one of the main costs incurred in the catalytic cracking process, and fouling could potentially be reduced by increasing the pore size of the zeolite. The discovery of VPI-5 was significant, and when he and his team were able to reproducibly prepare the material and succeed in its structural characterization, they published the findings in the journal *Nature*.⁴³ This was the first of 10 original research publications in *Science* or *Nature* from Mark's laboratory.^{43–52} In addition to its potential as a catalyst in fuel and petrochemical manufacturing, the discovery of VPI-5 also opened the door to efficient materials for gas storage, e.g., methane, as well as applications in the pharmaceutical field, since the pores could accommodate large molecules. Thus, Mark's team devoted significant effort to fully characterize and to modify VPI-5 to make it more stable.^{45,53–57}

While at Virginia Tech, Mark's research interests began to expand beyond classical heterogeneous catalysts, zeolites, and molecular sieves. For instance, the team published seminal work in base catalysis using alkali-exchanged low silica zeolites.^{58–60} Buoyed by his experience working on zeolite-supported transition metal catalysts, he sought to extend his contributions to the field of homogeneous catalysis, with a particular emphasis on compounds soluble in water.^{61–67} This work led to the invention of supported aqueous phase catalysts (SAPC), whereby porous silica supports were loaded with a thin layer of water containing water-soluble homogeneous catalysts (Figure 2, right). This work describing a new general class of catalysts, and a new hydroformylation catalyst, specifically, was also published in *Nature* around the same time as VPI-5,⁴⁴ cementing Mark's reputation as a leading innovator in catalysis. This work led to Mark's first patents associated with his research, one comprising compositions of matter and another comprising methods of manufacture.^{68,69} In subsequent years, these hydroformylation catalysts were characterized in detail, and this platform was extended to other types of reactions, including Wacker oxidation.^{70–73} The concept of a heterogeneous catalyst based on a thin liquid film on a solid support was later expanded by others in the creation of supported ionic liquid phase catalysts (SILPs).^{74,75}

By the end of his time on the faculty at Virginia Tech, Mark had established several of his career-defining personality traits: a willingness to take risks and venture into new areas of science, a focus on grand challenges as well as core research directions, and an emphasis on zeolite synthesis, characterization, and catalysis. He was the first engineer recognized with NSF's Alan T. Waterman Award in 1990 and was nationally

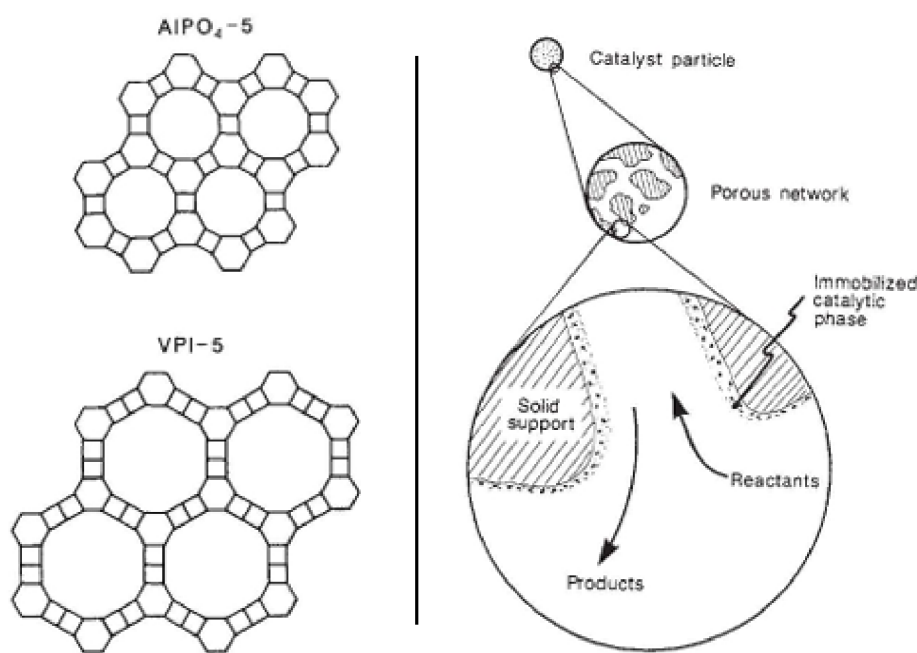


Figure 2. VPI-5 was the first extra-large-pore, crystalline molecular sieve (left), shown in comparison to the large-pore $\text{AlPO}_4\text{-5}$ (AFI) structure. Supported aqueous phase catalysts allow for utilization of water-soluble homogeneous catalysts in heterogeneous catalytic systems (right). Reproduced from ref 43 (left) and 44 (right) with permission from Springer Nature. Copyright 1988 and 1999.

recognized as a research innovator already at this early career stage. With this foundation, Mark moved west to Pasadena, CA, starting as a Full Professor at Caltech in 1991.

■ A MOVE TO CALTECH

Mark's transition to work at Caltech in 1991 opened a new era for his distinguished scientific career. While he continued working in the fields in which he excelled at Virginia Tech, e.g., reaction engineering,⁷⁶ supported aqueous phase catalysis,^{44,63–65,70–72,77–79} chemical vapor deposition,¹⁶ and adsorption,³⁴ as well as the synthesis of zeolites and zeolite-like materials,^{45,80–84} he significantly expanded his research interests to nearly all aspects of zeolite science and technology, and made many additional significant contributions.

At Caltech he established one of the best zeolite research laboratories in the world. It was a great honor and a once-in-a-lifetime experience for many of his mentees to work under his supervision. His pioneering work on the synthesis of new zeolites using organic structure directing agents (OSDAs)^{85–89} and insight into the crystallization mechanism of zeolite formation (Figure 3, left)⁹⁰ led to the discovery of many new zeolites in the early years at Caltech. Using organosilicon compounds as OSDAs for the synthesis of zeolites with targeted properties is another example of Mark's scientific creativity.⁹¹

Mark continued to collaborate with leading scientists to support his interest in learning novel techniques that he felt would advance his scientific pursuits. Supporting the structure direction concept from the thermodynamic aspect, Mark's collaboration with Prof. Alexandra Navrotsky, then at Princeton University, on the thermochemical study of the stability of microporous and mesoporous materials via high-temperature solution calorimetry revealed that there is very little energetic limitation to the possibility of synthesizing various framework structures. Thus, the self-assembly of these materials is

controlled geometrically and kinetically via structure direction.^{92,93}

Mark's remarkable friendship and collaboration of 30+ years with Dr. Stacey Zones at Chevron was another notable component of his career that can be traced back to the time of Mark's transition from Virginia Tech to Caltech. This ongoing collaboration began at the International Symposium on Innovation in Zeolite Materials Science held in September 1987, in Nieuwpoort, Belgium, where they first met. Since then, together they have developed a long-term joint research program on zeolite synthesis, characterization, and applications, coauthored more than 50 scientific publications plus many patents, and made pioneering contributions to zeolite science in numerous ways. An early manifestation of this successful collaboration was the determination of the crystallographically complex structures of the 10-/12-membered ring (MR) zeolites SSZ-26, SSZ-33, and CIT-1 (CON) (Figure 4, top).^{52,94} As reported in this Account below, under this joint program, they together mentored and inspired many collaborators and young students/scientists, including many of us after graduation, well beyond the Caltech and Chevron boundaries.

Mark's zeolite research advanced further from the traditional aluminosilicate zeolites at Caltech, from AlPO_4 's and SAPO's to other heteroatom-containing molecular sieves such as borosilicate (B-SSZ-24),⁸⁸ zincosilicate (VPI-7 (VSV) and VPI-9 (VNI)),^{81,95} and titanosilicate (Ti-ZSM-5 and T-ZSM-48) molecular sieves,^{96–100} in search of new framework structures, compositions, properties, and applications. For example, the early 1990s saw a concerted focus on creating novel, environmentally benign technologies for hydrocarbon oxidation, including 1-hexene and *n*-octane oxidation using aqueous hydrogen peroxide as the oxidant over titanosilicate zeolites.¹⁰⁰ This contributed significantly to our better understanding of the structure–property–catalysis relation-

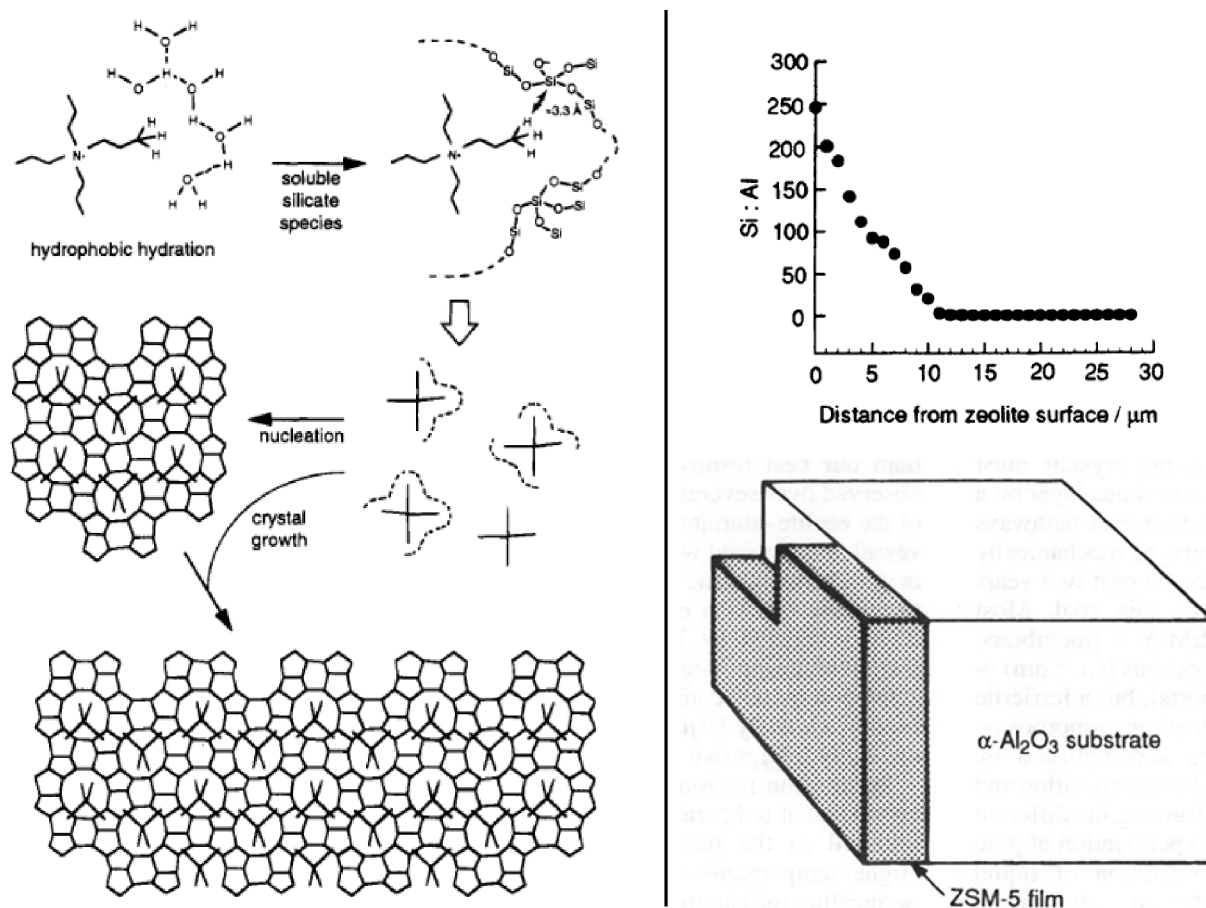


Figure 3. Davis has developed mechanistic insights into the synthesis of numerous zeolites and molecular sieves, with a prototypical example being his early studies of the mechanism of tetrapropylammonium ion directed synthesis of MFI zeolites (left). The group was among the first to explore zeolite membranes for separation applications (right), with several former mentees further elaborating this field. Reproduced from ref 89, Copyright 1995 by the American Chemical Society (left) and reproduced with permission from ref 111, Copyright 1995 by the Royal Society of Chemistry (right).

ships of these molecular sieves and the associated reaction mechanisms.

Mark's group was among the first that investigated Mobil's MCM-41/48 type mesoporous materials (Figure 4, bottom),^{101,102} including their physicochemical properties and their synthesis using organic molecules and self-assembled organic aggregates as OSDAs.^{103–106} The results from a combination of Raman spectroscopy, ¹⁵N NMR spectroscopy, and other techniques revealed that the inorganic wall of these mesoporous materials resembles amorphous oxides rather than crystalline molecular sieves in terms of the local structure and bonding and that randomly ordered rod-like organic micelles interact with silicate or aluminosilicate species that then spontaneously assemble into the long-range ordered structure characteristic of these mesoporous materials. Accordingly, new mesoporous materials were synthesized, for example mesoporous alumina,¹⁰⁷ and a range of applications for these materials was envisioned.

Through collaboration with his colleague at Caltech, George Galvas, Mark was also among the early researchers studying polycrystalline zeolite films as membranes for gas separations (Figure 3, right).^{108–111} This work extended to fundamental studies of diffusion in single crystalline zeolite membranes, where the group tested large FER zeolite single crystal materials as membranes.¹¹² As a testament to Mark's creativity and broad impact, it should be noted that there is a robust

research thread on zeolite and silicate films and membranes beyond the scope of this catalysis and reaction engineering-focused Account that continues to be pursued by several MED mentees.^{113–117}

Fundamental research on catalysis aiming to elucidate industrial applications has long been one of the ultimate goals in Mark's research. This drive is diversely exemplified in Mark's publications on alkane and alkene oxidation using aqueous hydrogen peroxide as an oxidant over titanosilicate molecular sieves,^{118,119} naphtha reforming over platinum-containing molecular sieves,^{120,121} alkane isomerization over nonzeolitic solid superacid catalysts,¹²² and base-catalyzed alkylation of toluene with methanol over cesium-containing FAU zeolite catalysts.^{35,59,123} These latter studies represented some of the earliest investigations of base catalysis using zeolites, which are a class of catalysts that are most widely known for their acidic properties. Mark also continued to innovate in supported homogeneous catalysis, with further elaboration of the SAPC concept to include asymmetric catalysis.¹²⁴

■ DIVERSIFICATION OF RESEARCH

In the latter half of the 1990s, Mark undertook a significant new direction in his research, adding a thrust to nanomaterials for drug delivery. Beginning with the recruitment of the first graduate student to work in this area, Suzie Hwang Pun, in

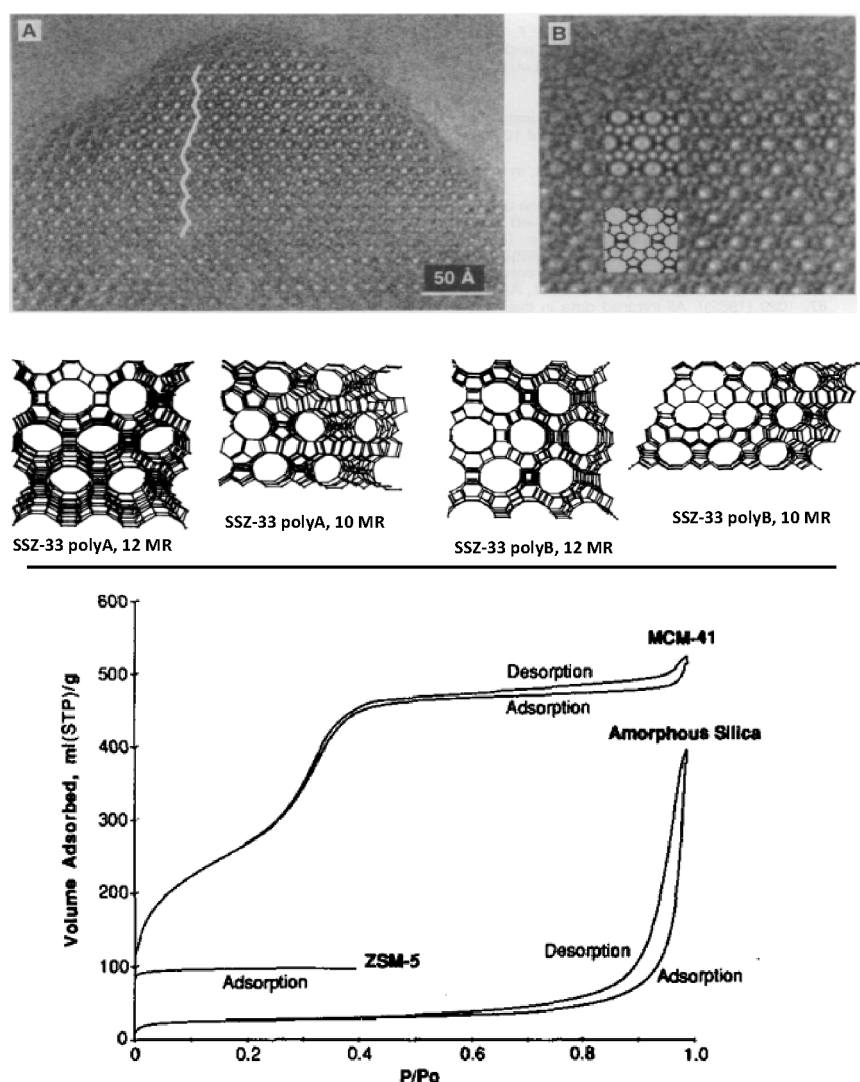


Figure 4. The group elucidated the structure of many new zeolites first synthesized at Caltech, Chevron, or elsewhere, including the CON family of materials, with SSZ-33 shown here, featuring HREM images and structural projections (top). The group was among the first to explore the MCM-41 ordered, micelle-templated mesoporous materials developed by Mobil, demonstrating how the porosity (bottom), structure, and synthesis mechanisms differ from zeolites. Reproduced from ref 52 (top) with permission from the American Association for the Advancement of Science. Copyright 1993. Reproduced from ref 104 (bottom) with permission from Elsevier (bottom). Copyright 1993.

1996, Mark went on to produce an innovative body of work in the design of materials and methods for nonviral drug delivery (Figure 5, right).^{125,126} Stemming from this work, Davis founded 4 start-up companies, including Inert Therapeutics, Calando Pharmaceuticals, Avidity Biosciences, and Dantari Pharmaceuticals. Addition of this new research thrust, however, did not dilute the energy he poured into his research on porous materials and catalysis, and his foundational programs continued to grow and thrive.

Mark continued to deeply focus on elucidating a mechanistic understanding of zeolite and porous material synthesis. This included a continued focus on the thermodynamics of zeolite synthesis and new investigations into ALPO or SAPO structures as well as crystalline, microporous pure silica materials.^{93,127,128} An overall goal was elucidation of the complete pathway from fully soluble molecular species to porous crystalline materials, and the tetrapropylammonium (TPA⁺)-directed synthesis of MFI structures was identified as an ideal target system for comprehensive characterization. From this platform, additional syntheses using a wider array of

components were also undertaken, for example, with variation of the organic OSDAs or the presence or absence of inorganic cations. ¹H–²⁹Si CP MAS NMR studies elucidated the importance of hydrophobic hydration spheres created by the OSDA in the aqueous media,⁸⁹ and studies of the partitioning of organic cations used as OSDAs between octanol and water provided new insights into the role of OSDA hydrophobicity¹²⁹ in zeolite synthesis.¹³⁰ Structure-direction with polycationic OSDAs and the role of net charge on the kinetics and particle size resulting from the zeolite synthesis was investigated.¹³¹ X-ray scattering and TEM imaging were combined to follow the evolution of zeolite nuclei to larger zeolite structures.^{132–134} Mechanisms of structure direction in zeolite synthesis has been a long-standing focus of the Davis laboratory.¹³⁵

In addition to the focus on important, known zeolites like ZSM-5, Mark also continued to pursue the synthesis of novel zeolite and molecular sieves, continuing a focal direction from his VPI days. His team uncovered the structure of the zincosilicate VPI-8 (VET),¹³⁶ which contained a novel

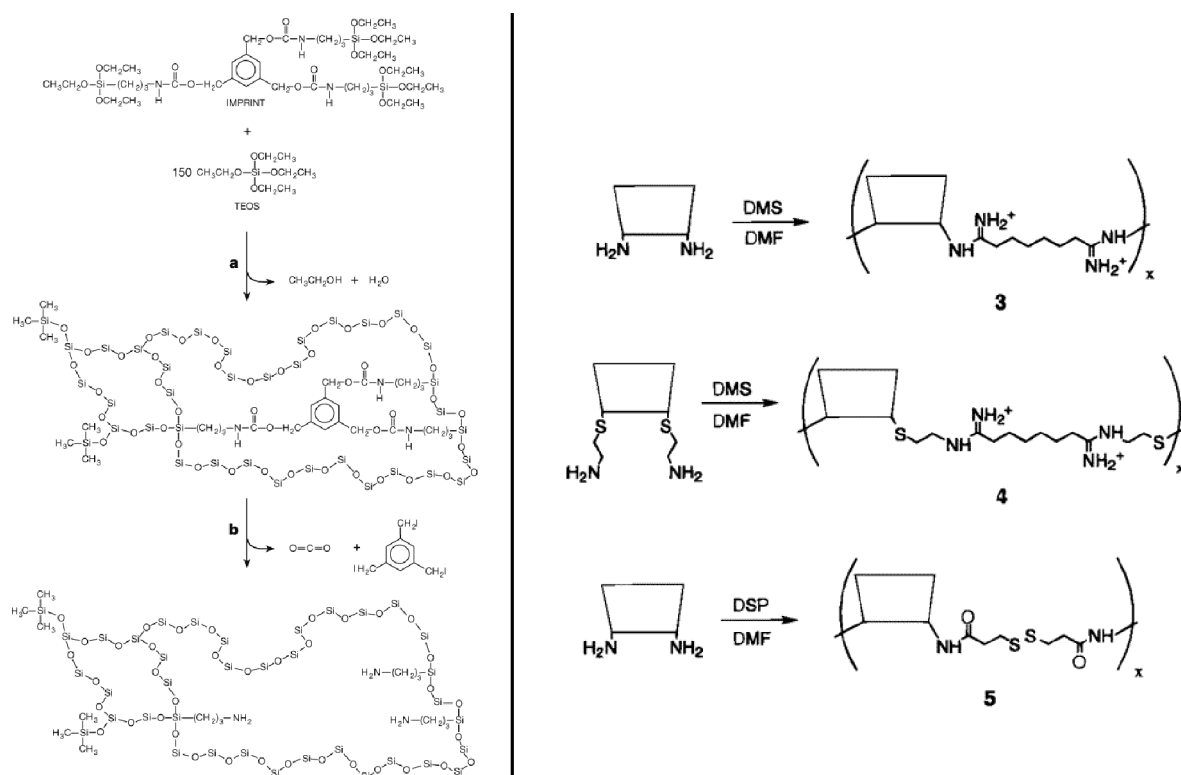


Figure 5. The Davis group designed a variety of organic/inorganic hybrid catalysts in the 1990s and 2000s, with a focus on the spatial positioning of active sites, catalytic cooperativity, and shape-selectivity (left). Materials design extended to wholly organic species as well, for example, with the launch of the new research thrust on nanomaterials that facilitate drug delivery in 1996. The group's first polymers designed for drug delivery, based on cyclodextrin building blocks, are shown (right). Reproduced from ref 50 with permission from Springer Nature (left). Copyright 2000. Reproduced from ref 126. Copyright 1999 American Chemical Society (right).

“pinwheel” framework building unit. In collaboration with others, the structure of zincosilicate VPI-9 (VNI) was also elucidated. New zeolites were discovered at Caltech, as well, including zincosilicates. CIT-6 was synthesized and demonstrated to be the zincosilicate form of the commercially important zeolite Beta (BEA).¹³⁷ In 1995, Mark reported the synthesis of the first zeolite with intersecting 10 MR and 12 MR pores that was not an intergrowth of two structures, CIT-1 (CON).¹³⁸ Structurally related to SSZ-26 and SSZ-33 (Figure 4, top), which Mark and collaborators had previously characterized in detail,⁵² the CON family of zeolites remain important materials today, 30 years later.

Working with collaborators who originally discovered the zeolite, Mark's team elucidated the structure of the first extra-large-pore zeolite, UTD-1, in 1996.⁴⁷ The following year, the group characterized this novel aluminosilicate in detail,¹³⁹ and in parallel they reported the structure of the 14 MR zeolite CIT-5,¹⁴⁰ which contained straight, one-dimensional pores, like UTD-1. As the team's experience in zeolite structure elucidation grew, the ability to solve structures of even complex, highly faulted materials was demonstrated, for example, in the case of zeolite SSZ-31.¹⁴¹ The team elucidated the structure of zeolites with occluded organic molecules using single-crystal X-ray diffraction (FER, pyridine),¹⁴² as well as electron diffraction (SSZ-48, SFE),¹⁴³ in the latter case, with collaborators. Host–guest interactions were further elucidated in studies of OSDA-containing zeolites SSZ-35, SSZ-36, and SSZ-39.¹⁴⁴ Additional SSZ zeolites were also characterized, and the SSZ-35 and SSZ-44 zeolites were shown to contain unique structures including intersecting 10 and 18 MRs.¹⁴⁵ All

of the SSZ materials were discovered at Chevron by Stacey Zones and/or his collaborators, and the strong focus on this array of materials demonstrates the long-standing, continued collaboration between Mark and this corporate zeolite laboratory.

The team also tackled the synthesis of abundant natural zeolites that had proven difficult to synthesize in the laboratory. Heulandite and other natural zeolites were successfully synthesized using ion-exchanged precursor materials, for example, with CIT-3 being a calcium aluminosilicate with the HEU topology.¹⁴⁶ Similarly, CIT-4, the first synthetic analogue of brewsterite (BRE), was prepared using a strontium-ion-mediated synthesis.¹⁴⁷

As one of the leading laboratories in the world working on zeolites, catalysis, and reaction engineering, Mark's lab hosted many visitors over the years. This included eminent scientists passing through the area, longer-term sabbatical visitors, and visitors who worked in the laboratories alongside the students and postdocs. In the mid to late 1990s, there was a large contingent of Japanese researchers from both industry and academia who worked in the laboratory and made strong impacts on the group (Table 2). Prof. Michel Boudart was another eminent visitor in the 1990s, and during his stay, he suggested that he and Mark should write a textbook on kinetics and reaction engineering. Mark came to know Boudart well during Mark's sabbatical at Stanford in 1989, and based on Boudart's suggestion, Mark worked on a new reaction engineering textbook throughout the decade. This text came together in the late 1990s in tandem with his brother, Prof. Robert J. Davis of the University of Virginia, who contributed

in place of Prof. Boudart, who was in declining health. The textbook, originally published in 2002, *Fundamentals of Chemical Reaction Engineering*,¹⁴⁸ continues to be widely used and is accessible via free download from the Caltech library. That Mark was able to complete this text while he was launching a parallel program in drug delivery and as he served as Executive Officer of Chemical Engineering at Caltech (1999–2004) demonstrates the remarkable breadth of his capabilities.

Also in the latter half of the 1990s, the group took on a new research direction focused on the creation of organic active sites in porous materials. This thrust included a critical evaluation of the field of “molecular imprinting,” which was focused on creating precise, three-dimensional active sites for molecular recognition or catalysis in organic and inorganic materials.¹⁴⁹ Early work on silica materials¹⁵⁰ and organic polymers¹⁵¹ led to high fidelity imprinted silica materials that displayed the precise organization of multiple organic functional groups around an imprinted cavity (Figure 5, left).⁴⁹ In parallel, the group was focused on incorporating organic active sites into crystalline zeolites and molecular sieve structures. The ability to remove OSDAs from siliceous zeolites via solvent treatment¹⁵² enabled the synthesis of organic-functionalized molecular sieves (OFMSs) containing framework Si–C bonds and pendant organic functional groups within the micropores of the molecular sieve.⁴⁸ The team demonstrated the creation of both acid¹⁵³ and base¹⁵⁴ catalytic sites from the incorporated organic functional groups in these materials.

THE NEW MILLENNIUM

Throughout the 1990s and into the new century, new OSDA structures were continuously explored for zeolite syntheses, including diethoxyethyltrimethylammonium ions,¹⁵⁵ decahydroquinolinium cations,¹⁵⁶ and sparteine derivatives,¹⁵⁷ among others. Considering that most new OSDAs are complex and costly, a strategy to reduce the cost of the OSDAs was developed. In a new approach, after zeolite synthesis, the OSDA was disassembled within the zeolite pores to allow the removal of fragments, allowing the OSDA to be reassembled and reused in additional zeolite synthesis (Figure 6, top).^{50,158}

Organic–inorganic hybrid materials continued to be investigated intensively, with the work focusing on creating tethered organic active sites on mesoporous silica. Much of this work took inspiration from enzymes, which use a myriad of strategies, from the accurate alignment of functional groups to specialized molecular transport mechanisms, to enable specific reactions under mild conditions. Recognizing this intricacy, Mark sought to design catalysts with precisely positioned functional groups to harness the catalytic cooperativity. In these cases, cooperativity was defined as the combined action of multiple catalytic entities working together to achieve reaction rates beyond what each could achieve individually. Thiol and sulfonic acid groups were organized on SBA-15 using designed organosilane molecules.^{159–161} In one example, the distance between thiol and sulfonic acid sites was systematically controlled using mercaptoalcohol linkers (Figure 6, bottom).¹⁶² Reaction rates and regioselectivities in the synthesis of bisphenol A and Z could be modulated by the cooperative interactions of the two types of active sites. In another example, acidic and basic functional groups, which cannot coexist in solution as active catalytic sites, were immobilized on SBA-15 together.^{163,164} The coexisting amine

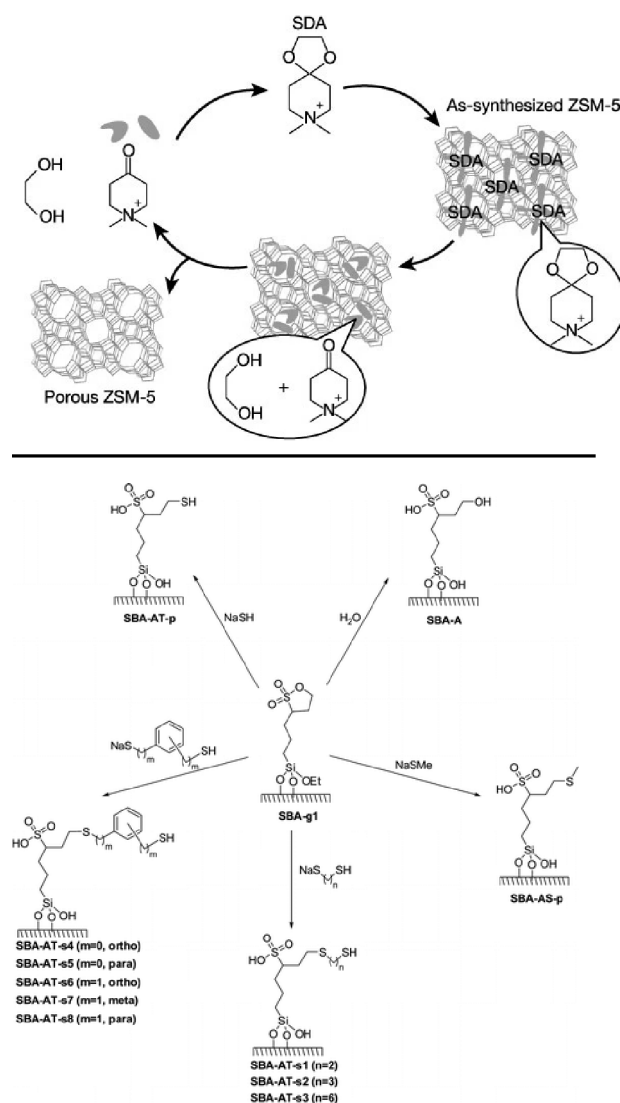


Figure 6. Davis continued to innovate in zeolite synthesis in the new millennium, for example, introducing degradable, recyclable structure-directing agents (top). Cooperative catalysis with designed organic–inorganic hybrids coupling sulfonic acids and thiols yielded new insights into cooperative catalysis (bottom). Reproduced from ref 50 (top) with permission from Springer Nature. Copyright 2003. Reproduced from ref 161. Copyright 2007 American Chemical Society (bottom).

and sulfonic acid groups were shown to catalyze the aldol condensation more effectively than acid or basic sites alone.

In collaboration with BP, the selective oxidation of light alkanes was thoroughly investigated. Vanadium was incorporated into the AFI framework to create VAPO-5, which was used for the oxidative dehydrogenation of propane with high selectivity toward propylene.¹⁶⁵ The research also explored mixed oxide materials,¹⁶⁶ leading to new catalysts. When H₃PMo₁₂O₄₀ was treated with an appropriate niobium/vanadium precursor and pyridine, the resulting NbPMo₁₂pyr or NbPMo₁₁Vpyr material oxidized butane or propane selectively, forming maleic acid.¹⁶⁷ The role of each component was subsequently elucidated.^{168,169} These catalysts were also effective for oxidative dehydrogenation of ethane to ethylene and acetic acid.¹⁷⁰

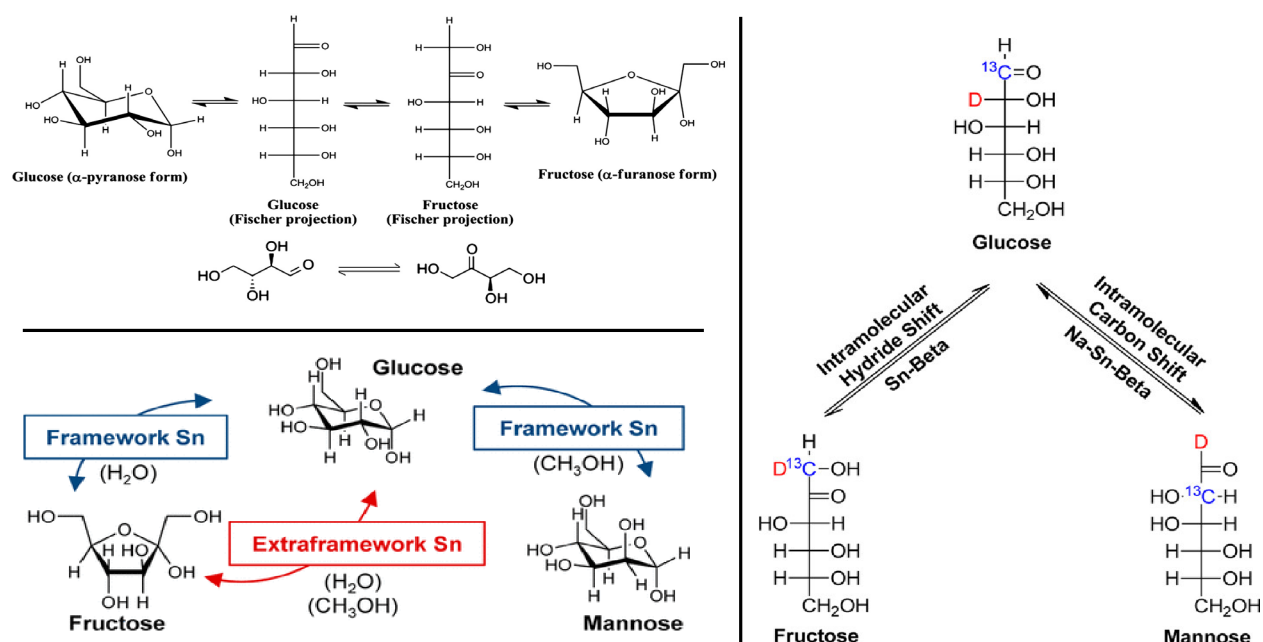


Figure 7. Catalysis in liquid media with Lewis acid molecular sieves was a major theme from 2010. Sugar isomerization (top left) rates and selectivities were impacted by the structure of active sites, pore hydrophobicity, and reaction conditions (right, bottom left panels). Reproduced from ref 182 with permission from the National Academies (top). Copyright 2012. Reproduced from references 184 and 187, with the American Chemical Society (middle, bottom). Copyright 2014, 2012.

In the latter part of the 2000s heading into the 2010s, Mark explored additional application areas for zeolites and molecular sieves and set out in new directions, targeting novel energy sources. In collaboration with Prof. Yushan Yan's group, the proton conductivity of acid-functionalized zeolites or MCM materials was modulated, targeting fuel-cell applications.^{171,172} Also with the Yan group, zeolite thin films and powders were investigated for their low- k dielectric properties.^{173–175} In thermochemical water splitting, a field in which Mark has launched a start-up company, HGenium, his group demonstrated a system that utilizes redox reactions of Mn(II)/Mn(III) oxides at a moderate temperature of ~ 850 °C to generate hydrogen and oxygen from water.¹⁷⁶ Later work explored different combinations of metal oxides with a spinel structure (Mn_3O_4 , Fe_3O_4 , and Co_3O_4) and alkali carbonates (Li_2CO_3 , Na_2CO_3 , and K_2CO_3) in thermochemical cycles for both water splitting and CO_2 reduction.¹⁷⁷ Mark's interest in thermochemical hydrogen production dated back 30 years from this work,¹⁷⁸ demonstrating his persistent interest in key themes in chemistry. This trait of dogged persistence is further personified below.

NEW DIRECTIONS IN LONG-STANDING INTERESTS

As the second decade of the 21st century approached, the group continued to innovate in areas of long-standing interest. Two focal areas were Lewis acid molecular sieves and zeolite/molecular sieve synthesis. In 2009, Mark was invited to join the Catalysis Center for Energy Innovation (CCEI), one of the Department of Energy's Energy Frontier Research Centers (EFRCs) that focused on the thermochemical conversion of lignocellulosic biomass. Leveraging prior work on titanasilicate molecular sieves in the 1990s, the Davis lab sought to develop solid Lewis acid catalysts for sugar isomerization reactions that could facilitate efficient conversion of sugars to platform chemicals, such as 5-hydroxymethylfurfural (HMF)—a de-

rivative produced by the acid-catalyzed dehydration of C6 carbohydrates. To optimize HMF yields, cascade sequences were sought, with a pivotal step being the isomerization of glucose to fructose (Figure 6, top left), preceding its dehydration into HMF. The group investigated Lewis acid zeolites as plausible isomerization catalysts that could potentially be compatible with the requisite acidic conditions for dehydration.

Characteristically, Lewis acid zeolites feature tetrahedrally coordinated metals (M^{4+}) with open coordination sites within the silica matrix.¹⁷⁹ Notably, Sn-containing zeolites with a Beta topology, synthesized in fluoride media, showed remarkable performance during glucose isomerization in aqueous systems and was able to efficiently achieve equilibrium conversions to fructose.¹⁸⁰ The Sn-Beta catalyst did not show signs of deactivation after multiple cycles or after calcination and maintained activity in highly acidic aqueous environments with rates and selectivities equivalent to those obtained without added acid.

Having an isomerization catalyst that could operate in the presence of homogeneous acids set the stage for a two-pronged approach to glucose conversion into HMF: isomerizing glucose to fructose, then dehydrating the fructose to HMF. The group demonstrated the capability of Sn-Beta zeolites used in conjunction with homogeneous Brønsted acids in biphasic systems to effectively dehydrate saccharides into HMF with high yields.¹⁸¹ This was one of the first examples wherein a heterogeneous Lewis acid and a homogeneous Brønsted acid collectively optimized glucose-to-HMF conversion, mitigating excessive byproduct generation.

At the time of discovery, it was not precisely known how the Sn active sites could effect this transformation. Mark's group, using a combination of NMR and isotopically labeled glucose molecules, demonstrated that glucose isomerization proceeds via an intramolecular hydride shift.¹⁸² This pathway is similar to the one observed in Meerwein–Ponndorf–Verley (MPV)

reduction reactions involving a six-membered transition state between the Lewis acid, the carbonyl group, and the adjacent hydroxyl group in the carbohydrate. Contrastingly, analogous experiments with base catalysts such as NaOH revealed an alternative mechanism involving proton abstraction and enolization, clearly distinct from the hydride shift pathway.

Complementary characterization of the Lewis acid sites through solid-state NMR and probe-molecule spectroscopy established structure–activity relationships for the molecular sieve catalysts (Figure 7).^{183,184} Early parallels were drawn to MPVO and Baeyer–Villiger chemistry on Sn-Beta, with “open” Sn sites appearing to enable a 1–2 hydride shift (1–2 HS) mechanism.^{185,186} The isotopic tracing also revealed a surprising change toward a 1–2 carbon shift (1–2 CS) mechanism in glucose isomerization in methanolic solutions for some, but not all, samples of Sn-Beta.^{187–189} Such samples produced the glucose epimer mannose instead of fructose as a primary product. A subsequent effort revealed that exchanging the silanol of the open Sn site with alkali or quaternary ammonium cations leads to this switch in selectivity.¹⁸⁴ The study of minor byproducts revealed that sites associated with the 1–2 CS also enable rapid realdol reactions of sugars that, when combined with a size-selective 1–2 HS catalyst such as Sn-MFI, form a tandem catalytic system that selectively produces lactic acid or alkyl lactates at temperatures significantly lower than reported for purely 1–2 HS materials.¹⁹⁰ Additional diversity in Lewis acid catalyzed reaction mechanisms and primary products were achieved in forming sorbose by Ti-Beta via a 1–5 hydride shift¹⁹¹ and various direct reactions of disaccharides,¹⁹² illustrating the rich possibilities of chemistries that such catalysts can enable.

Beyond the local active site structure, the impact of defect density and the corresponding transition to hydrophilicity was also quantified.¹⁹³ Materials that are synthesized in hydroxide rather than fluoride media exhibit hydrophilicity, and correspondingly, the turnover frequency for glucose isomerization is orders of magnitude lower. The importance of the pore environment has subsequently been observed for other reactions by other groups.^{194,195}

The group demonstrated applications of Lewis acidic zeolites outside of sugar isomerization as well. The team showed that Lewis acidic zeolites could convert ethylene and 5-hydroxymethylfurfural to terephthalate-like aromatics, providing a route for 100% biomass-derived PET.^{196,197} Later work in the group demonstrated the ability of Zn-Beta (CIT-6) to directly make terephthalate esters from dimethyl-FDCA.¹⁹⁸

In parallel with the Lewis acid, liquid phase work, the group delved into more traditional gas/vapor phase hydrocarbon catalysis with a focus on the role of the zeolite topology, synthesis method, and active site distribution influencing the ultimate catalytic performance. A particular interest was placed on small-pore (8 MR) molecular sieves, which possess narrow micropore openings in the range of 3–4 Å, exhibiting remarkable shape-selectivity in catalytic applications involving small molecules. Mark extensively documented his accounts on these small-pore molecular sieves in his review paper published in 2018.¹⁹⁹ FER has nonintersecting 8 and 10 MRs, and the group showed that controlling the zeolite synthesis conditions could yield Brønsted acidic aluminum in both channel systems, or predominately in either the 8 or 10 MR channels.²⁰⁰ In the conversion of methanol to olefins (MTO), the group systematically investigated three different small-pore zeolites (AFX, CHA, and LEV) that contain different size cages, at

similar crystal sizes and Si/Al ratios, showing that ethylene selectivity decreases as the cage size increases and that an intermediate cage size is ideal for maximizing the production of light olefins (Figure 8, top).²⁰¹ Further MTO work

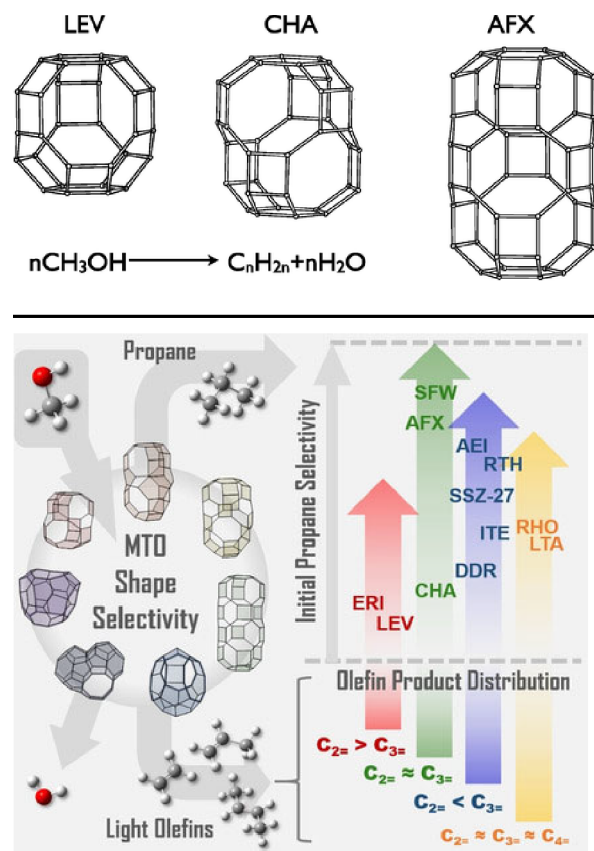


Figure 8. MTO catalysis with small-pore zeolites was a recurring theme in the MED group and with collaborators. The role of cage size on light olefin selectivity (top) was probed using a trio of catalysts, with later work expanding the scope to many new small-pore zeolites discovered at Chevron. Catalysis in liquid media with Lewis acid molecular sieves was a major theme from 2010. Reproduced from ref 201 from the American Chemical Society (top). Copyright 2012. Reproduced from ref 209 with permission from John Wiley and Sons (bottom). Copyright 2018.

demonstrated that a cage large enough to accommodate an aromatic intermediate was necessary for a framework to be active for MTO catalysis.²⁰² In the chabazite (CHA) system, his research team observed a noteworthy resemblance in the MTO behaviors between SSZ-13 zeolites and SAPO-34 zeolites, the latter being characterized to possess isolated acid sites.²⁰³ Mark also sought to enhance the catalytic lifetime of SSZ-39 (AEI) by employing a steaming process to reduce the acid site density.²⁰⁴ Steaming proved to be an effective technique for reducing framework Al sites in small-pore zeolites, especially in the case of low-silica zeolites such as CHA, RHO, and KFI-type materials that were synthesized without the use of OSDA cations.²⁰⁵ Always with an eye toward practical catalysis, Davis showed that low-cost aluminosilicate CHA synthesized without an organic OSDA could be prepared that performed similarly to the commercially used SAPO-34.²⁰⁶ Finally, it is noteworthy that during the investigation of the influence of the specific OSDA isomer in the synthesis of SSZ-39,²⁰⁷ his team also proposed a novel

method for the synthesis of high-silica gmelinite (GME)-type zeolite, which he named CIT-9.²⁰⁸

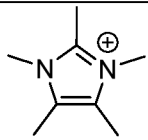
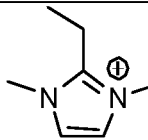
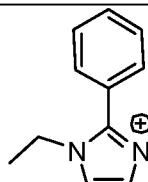
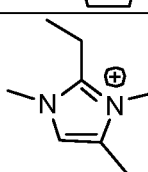
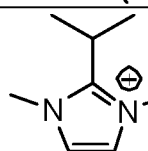
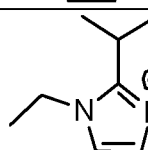
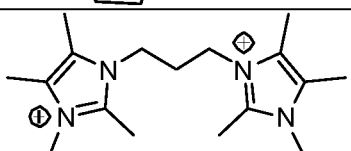
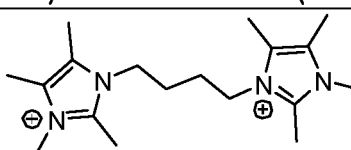
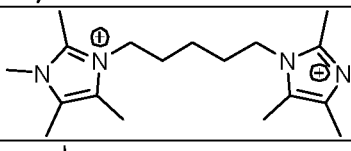
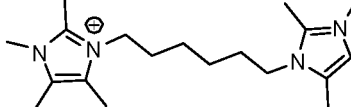
Working again with Zones, the team compiled MTO reaction results for several recently discovered SSZ-series small-pore zeolites such as SSZ-28, SSZ-98, SSZ-99, SSZ-104, and SSZ-105. The outcome of this collaboration led to an intermediate conclusion that the topologies of small-pore/cage-type zeolites could be categorized into four distinct groups based on the distribution of light olefin products ($C_{2=}$, $C_{3=}$, and $C_{4=}$) from the MTO reaction (Figure 8, bottom).²⁰⁹ Mark's group postulated that the topology of cages plays the primary role in determining the resulting olefin selectivity distribution during MTO catalysis, being more important than framework elemental composition. Based on experimentally observed MTO behaviors of various zeolites and $AlPO_4$ -based molecular sieves with 14 different topologies (LEV, ERI, CHA, AFX, SFW, AEI, DDR, ITE, RTH, SAV, LTA, RHO, KFI, and UFI), the team introduced the first global shape selectivity theory for the MTO reaction, coined the "cage-defining ring theory." This theory suggests that the second longest axis of the cage regulates the evolution of the hydrocarbon pool intermediates and the resultant olefin selectivity distribution.²¹⁰ Because narrow-cage molecular sieves (LEV and ERI) often exhibit high selectivities for heavier products, contradicting initial predictions, the team synthesized a series of ERI-type molecular sieves with varying acid site densities, encompassing SAPO-17 and SSZ-98 zeolites.²¹¹ The work showed that within narrow-cage molecular sieves, the acid site density significantly influences the rate of formation of aromatic intermediates responsible for the formation of ethylene, which is the expected main product of narrow-cage molecular sieves.

■ A FOURTH DECADE OF INNOVATIONS IN ZEOLITE AND MOLECULAR SIEVE SYNTHESIS

Mark's interest in the fundamentals of zeolite synthesis never waned, and the group continued to innovate on their own and in collaboration with Zones and others. The group demonstrated the synthesis of aluminophosphate and germanosilicate LTA using a large, triquatery OSDA, that contained imidazolium ions,²¹² with the same OSDA also producing germanosilicate ITQ-24 (IWR).²¹³ High-silica LTA has long been a target in zeolite synthesis, first reported as ITQ-29 in 2004 by Corma and co-workers,²¹⁴ and in 2015, Davis reported a method to synthesize all-silica and aluminosilicate (high SAR) LTA using a benzylimidazolium OSDA.²¹⁵ His team also revealed that configurational isomers of imidazolium-derivative OSDAs, which incorporated one or two methylbenzyl pendant group(s), exhibited the capability to crystallize various frameworks in the germanosilicate and high-silica aluminosilicate systems.²¹⁶

The success in using imidazolium-based OSDAs led to testing a library of mono-, di-, and triquatery imidazoliums across a range of zeolite synthesis screening reactions (Table 3). The pentamethylimidazolium OSDA, which crystallized STW in the pure-silica and germanosilicate systems, produced small-pore RTH-type zeolites in the aluminosilicate system.^{217,218} The team reported a novel 8/10 MR framework CIT-7 (CSV),²¹⁹ a high-silica heulandite (HEU) material CIT-8,²²⁰ IWV-type zeolites,²¹⁷ and a series of *rth*-type layered structures, CIT-10, CIT-11, and CIT-12,²²¹ using imidazolium-based diquats with flexible $(CH_2)_n$ linkers with varied lengths. This led to the discovery of a simple method to

Table 3. A Family of Imidazolium OSDAs Produced a Wide Array of Zeolite Frameworks Including Some New Structures

| OSDA | Frameworks |
|--|----------------------|
|  | STW, RTH |
|  | STW, ITW, MTW |
|  | MFI |
|  | STW |
|  | MTW, STF |
|  | STF |
|  | CIT-7, CIT-8, PREFER |
|  | CIT-7, CIT-8 |
|  | CIT-7, CIT-8, IWV |
|  | CIT-8, BEA, STF |

synthesize aluminosilicate RTH using a pentamethylimidazolium OSDA.²²² Further work showed a number of other monoquatery imidazoliums could be used to synthesize RTH, along with a number of other known zeolites, depending on the synthesis conditions.²¹⁸ The RTH zeolites showed

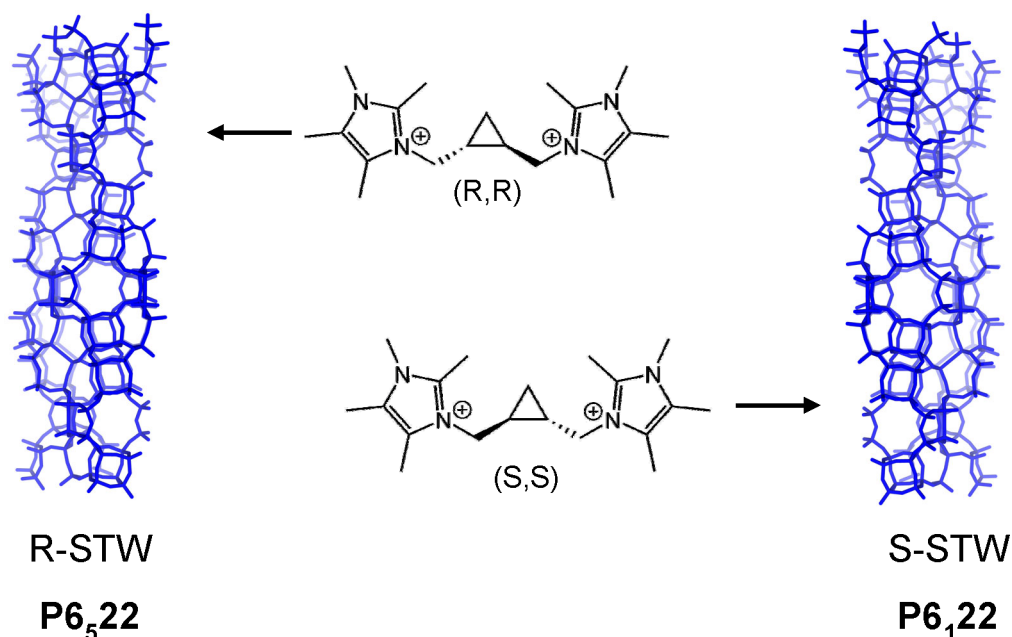


Figure 9. Illustration of the synthesis of enantioenriched STW samples using enantiopure, chiral OSDAs. Adapted from reference 233. Copyright 2021 American Chemical Society.

promise for MTO catalysis and were steam-stable up to 900 °C.

In this era, Mark's team made another significant discovery employing one of the above-mentioned imidazole-derivative OSDAs: CIT-13 (*CTH), an extra-large-pore germanosilicate with a 2-dimensional 10/14 MR channel system.²²³ This germanosilicate consists of Si-rich *cfi*-type layers, which are pillared with arrays of Ge-rich d4r units. CIT-13 showed a close structural relationship to CIT-5,^{140,224} another extra-large-pore molecular sieve that was first discovered by Mark and his team in the 1990s, showing that CIT-13 can spontaneously transform into CIT-5 at room temperature after sorbing moisture.²²⁵ Mark's team also established a synthetic method for producing CIT-13 without the use of fluoride mineralizer and investigated the influence of fluoride absence on the arrangement of germanium siting within the d4r units.²²⁶ The hydrothermal lability of Ge-rich d4r units further enabled various transformations that led to the discovery of two new frameworks, namely, CIT-14 and CIT-15.

■ THE MULTI-DECADE QUEST FOR AN ENANTIOENRICHED MOLECULAR SIEVE

Recognizing the potential significance of chiral molecular sieves in enantioselective separation and asymmetric heterogeneous catalysis in the very early phase of his career, the synthesis of enantioselective chiral molecular sieves has been one of Mark's lifelong goals. The evolution of his thinking during this 30-year journey toward this objective is evident in the accounts he published in 1992,⁸⁵ 2003,²²⁷ and 2018.²²⁸

Mark's interest in the synthesis of chiral zeolites dates to his time at Virginia Tech, during which he cultivated a profound interest in the enantioselective synthesis of zeolite beta polymorph A, a newfound structure of the late 1980s. Zeolite beta comprises a disordered structure characterized by the intergrowth of both chiral polymorph A domains and achiral polymorph B domains. Mark sought to synthesize pure beta

polymorph A but could only demonstrate a partial enantioselective enrichment of the polymorph A domain in their zeolite beta products using a bulky chiral OSDA. His team provided evidence of symmetry breaking during the ring-opening hydrolysis of *trans*-stilbene oxide, resulting in an enantiomeric excess (e.e.) value of ~5%.^{85,228}

After relocating to Caltech, the group sought to continuously develop chiral OSDAs that might enantioselectively crystallize chiral zeolites. Throughout the 1990s, his team reported several novel frameworks,^{88,130,138,140,224,229} including CIT-1 (CON) and CIT-5 (CFI), using chiral OSDAs, yet regrettably, none of the frameworks were chiral. In his account published in 1992 (and one in 2018),^{85,228} he proposed a set of five essential criteria that chiral OSDAs for chiral zeolite syntheses must satisfy: (1) chirality, (2) rigidity, (3) strong host–guest interaction, (4) thermochemical stability, and (5) the absence of rotational degrees of freedom within the micropores of the as-made zeolite. The team suggested that the chiral *N*-methyl(-)-sparteinium cation's rotational freedom within the pore system of as-made SSZ-24 (AFI) led to the loss of its ability to “transfer” its chirality to the inorganic framework.²³⁰

An important breakthrough in his chiral zeolite research was attained through discussions with two distinguished collaborators around 2010, Prof. Michael Deem and Prof. Osamu Terasaki, who contributed their knowledge in computational chemistry and electron microscopy, respectively.²²⁸ The chiral framework that caught Mark's attention was STW, which is characterized by helical 10 MR channels with distinct handedness.²³¹ Through collaboration with Prof. Deem, his team demonstrated that a highly symmetric pentamethylimidazolium OSDA cation can crystallize pure-silica racemic STW under a wide range of synthetic parameters, resulting in excellent crystallinity,²³² as the OSDA exhibits the most optimal fit within the micropores of the STW framework, with minimal positional degrees of freedom.²³³ Mark then leveraged the knowledge acquired from decades of work to devise an OSDA for the asymmetric synthesis of the two different

enantiomers of the STW framework. The OSDA molecule required sufficient length to ensure spatial memory, which, in turn, promoted the growth of crystals with a specific handedness. To achieve this, Davis and Deem employed a diquatery structure capable of templating two sequential STW cages (Figure 9). Based on the calculated host–guest interaction energies, his team selected and synthesized a pair of chiral diquats with a *trans*-cyclopropane linker. The crystallization of STW was accomplished in the germanosilicate system.²³⁴ The enantioenrichment of the resulting product was unambiguously confirmed using high-resolution transmission electron microscopy (HR-TEM) through a collaborative effort with Terasaki. Initially, the enantioenriched STW exhibited a Si/Ge ratio of ~ 1 ; later, the team successfully developed improved syntheses that led to higher Si/Ge ratios to enhance hydrothermal stability. The chiral diquat effectively structure-directed the formation of two sequential STW cages, resulting in a material that demonstrated enantioselectivity in both adsorption and catalysis.²³⁴ While further research is needed to expand the array of chiral molecular sieves and improve performance in catalysis and molecular recognition, Mark's 30 year journey demonstrated that creation of significantly enantioenriched structures is possible.

In the final years of the Davis laboratory at Caltech, with growing global concerns about CO₂ emissions, Mark turned his attention to identifying zeolites that could efficiently remove CO₂ from ultradilute mixtures like ambient air.²³⁵ Mark's group systematically evaluated a large number of zeolites for CO₂ adsorption from ultra dilute, 400 ppm of CO₂ streams. His work identified mordenite (MOR) as a commercially available highly advantaged structure, and Mark's team proposed a hypothetical process for CO₂ sorption from air, or "direct air capture" (DAC).^{236,237} The group's patent filings ultimately formed the basis for his sixth start-up company, ZeoDAC Inc. In his role as Emeritus Professor at Caltech, Mark continues to pursue the development of materials and chemical processes in his two newest start-up ventures, HGenium, pursuing hydrogen production from water, and ZeoDAC, working on DAC.

SUMMARY

Over a 43-year period, Mark E. Davis built a research program that ascended to global prominence in catalysis, zeolite science and technology, and drug delivery. This Account details the development of the former two programs, beginning at Virginia Tech in 1981 and spanning through his retirement from Caltech in 2023. The Davis laboratory included over 100 individual researchers, producing over 460 research publications, 2 textbooks, 130 patents, and 6 spin-out companies to date. For over three decades, the Davis group worked at the forefront of zeolite science and technology, creating >20 new zeolites or molecular sieves, the first extra-large-pore molecular sieves, and the first enantiomerically enriched polycrystalline molecular sieves, among other advances. In a long-standing collaboration with Stacey Zones at Chevron, the Davis lab contributed to synthesis and characterization of dozens of additional zeolites first synthesized at Chevron. Significant advances in oxide-supported molecular catalysts, zeolite-catalyzed sugar isomerization, MTO, and oxidation catalysis emanated from the research laboratory. All these advances occurred alongside a parallel program on materials and methods for drug delivery, a description of which is beyond the scope of this paper. The MED research program was thus

extraordinarily impactful in the scientific advances it made, in the scientists and engineers it produced that have contributed to science, technology, business, and humanity, and in the relationships that were built among the various members of the group.

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