Catal Lett (2012) 142:1262–1263
DOI 10.1007/s10562-012-0874-5

BOOK REVIEW

Christian Hess and Robert Schlögl (eds.): Nanostructured Catalysts: Selective Oxidations

2011, 452 pp., £ 144.99, Hardback, ISBN: 978-85404-186-2

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Received: 28 June 2012 / Accepted: 8 July 2012 / Published online: 25 July 2012

Heterogeneous catalysis by metals has benefited from an increasingly sophisticated suite of tools largely focused upon spectroscopic interrogation of surfaces under reaction (operando) conditions. The catalysis community understands the nature of the metal surface—and hence the active site—under reaction conditions is different than the bulk. Catalysts for selective oxidation of hydrocarbons are typically metal oxides, of which oxides containing vanadium and molybdenum are lords of the realm. In contrast to metals, however, catalysis by these materials has historically been understood based upon models created from our knowledge of the bulk structure; for example, the effort to correlate catalytic performance with the length of the double bond between metal and oxygen; or the concept of cooperation between hydrocarbon-activating acceptor phase, and an activated-oxygen-producing donor phase to produce oxygen spillover to the acceptor phase.

This has begun to change. As such the contribution *Nanostructured Catalysts—Selective Oxidations* edited by Christian Hess and Robert Schlögl is a welcome addition to the field. Its stated goals are two. First, they wish to provide a comprehensive up-to-date summary of the existing information on heterogeneously catalyzed selective oxidations; and second, to do so for an audience of not only specialists but also for graduate students and researchers not familiar with the field. The text is well organized: there is an introductory chapter on the general problem of C–H bond activation; a set of contributions on selective oxidation of small hydrocarbons; a third section on other selective oxidation systems highlighting the techniques necessary to understand these systems. A final section focuses on oxide catalysis by vanadia, here, the penultimate chapter by Schlögl and Hess is a provocative discussion on our poorly-resolved understanding of this field. A theme that emerges is the nature of the surface as revealed by surface resolved spectroscopic techniques is essential for resolving the remaining questions of selective oxidation catalysis.

The first of the stated goals is largely met. For example, specialists in the field will welcome the contribution by Annette Trunschke on propane selective oxidation to acrylic acid, of which the quaternary Mo–V–Te–Nb mixed oxide catalysts developed by Mitsubishi is the main focus of the discussion. The specific structures have been denoted M1 and M2, the former being the active phase for selectivity to acrylic acid. This account notes recent findings of low-energy ion scattering (LEIS) studies demonstrating that the catalyst surface is enriched in tellurium relative to the bulk. Trunschke writes "the M1 system can thus be considered as a support for an active phase … composed of V_xO_y moieties embedded in a matrix of tellurium surface species." She goes on to state that the precise details of the active ensemble remain unknown, and points to the need for in situ spectroscopic investigations with sub-nanometer resolution to ferret out these details. Kondratenko and Baerns' contribution on oxidative methane conversions provide a succinct overview of the subject. They rightly cite increased use of natural gas as a feedstock and the 2007 "Methane Challenge" sponsored by Dow Chemical as motivation for renewed interest in the subject; however, it is then somewhat disappointing that there are few references to work later than 2003. Other contributions by Robert Grasselli on propylene to acrylonitrile, Schunk and Brem on partial oxidation routes to methacrylic acid, and Carreon and Guliants on VPO catalysts for n-butane to

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maleic anhydride support round out that section of the text devoted to metal oxide catalysis of light hydrocarbons. These last three contributions have a character somewhat more relevant to an industrial scientist, as they emphasize development of current industrial technology rather than detail mechanistic discussion of catalytic chemistry.

The four chapters that follow highlight research of a more fundamental nature, involving search for mechanistic understanding using electron microscopy and synchrotron technology. These include a short chapter on selective oxidation by gold nanoparticles from Graham Hutchings. Given the considerable interest in the topic and the status of gold as the poster-child for the unique properties of nanostructured catalysts, this is a necessary contribution. Hutchings highlights the significance of the high-angle annular dark-field (HAADF) techniques coupled with aberration corrected microscopes to reveal size distribution effects in nanostructured gold catalysis. Contributions from Knop-Gericke and Bukhtiyarov describe in-situ XPS studies for elucidating the mechanistic details ethylene epoxidation over silver catalysts. This same theme also emerges from the essay by Kiskinova et al. concerning the oxidation of methanol by ruthenium catalysts. A chapter by Wolfgang Ranke on styrene synthesis over model K-promoted Fe_xOy thin films is primer on the utility of classic UHV techniques (LEED, Auger spectroscopy, XPS); here however, this group couple the UHV system to an in-situ microflow reactor for catalytic studies at ambient pressures. Although all these four chapters have a decidedly fundamental research tone, they are balanced by short introductions and conclusions that put the research into context, and outline directions for future study.

In the book's final section, the first of Hess's two contributions begin with the synthesis and catalytic behavior of supported vanadia oxide, with an emphasis on silica. After a review of various synthesis methods for preparing supported vanadia, Hess notes the unresolved controversy regarding the nature of the dehydrated species. Below monolayer coverage vanadia is widely agreed to be in a tetrahedral configuration. The controversy resides on whether they exist as monomers, dimers or other oligomeric species; this question has considerable implication for the precise nature of reaction mechanisms. Schlögl and Hess pick up this idea in a combined contribution where they discuss propane oxidation on supported vanadia as representative of the general problem of oxide catalysis. They proffer a set of hypothetical mechanistic equations that creates a separate identity for surface versus lattice oxygen, attempts to account for the role of water in mitigating reaction processes, and allows for but does not demand an electron donor/acceptor role for the support. Collectively this makes for a forceful statement about the nature of metal oxide catalysis as supported catalysis, a view Israel Wachs makes more pointedly in a recent review (Wachs IE, Routray K; *ACS Catalysis* (2012) **2** 1235–1246). Schlögl and Hess muster an extensive list of references—over three hundred—for this welcome, provocative discussion that should serve as a basis for future efforts needed to fully unravel the intricacies of partial oxidation.

On the second goal of the text the authors also largely succeed, but with a reservation. The strength of their success here lies in the contribution in Chapter 2 by Lercher and Naraschewski on the basics of C–H bond activation; for those new to the field and especially a graduate student, this will provide an excellent primer on the background needed to enter the field. Similarly the contribution by Schlögl and Hess discussed above provides a valuable framework on how to think about the unresolved questions in selective oxidation catalysis. The one reservation lies in the contribution on propene ammoxidation to acrylonitrile by Robert Grasselli. Here an undiscriminating reader would be lead to believe that our understanding of the active sites and mechanism for this process is a solved problem; perhaps this contribution is better understood as a historical account of catalyst development from one of catalysis science's most creative minds. It is recommended that this account be read immediately after Lercher's primer, or at the very least before Trunschke's more nuanced account of propane to acrylic acid.

This text should be a welcome addition to the library of anyone interested in selective oxidation. The overall organization flows well. Each contribution is well annotated, the list of references at each chapter is extensive, most contributions cite roughly 100 or more primary sources. Though not a textbook, portions could provide supplementary material for graduate courses on catalysis. Its real strength is it a timely and for the most part up-to-date account of a field that is going through a paradigm shift in it understanding of this challenging problem.