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BOOK REVIEWS

Fluid Catalytic Cracking: Science and Technology. Edited by J. S. Magee and M. M. Mitchell, Jr. Studies in Surface Science and Catalysis, Vol. 76, Elsevier, Amsterdam, 1993. 605 pp.

Fluid Catalytic Cracking: Science and Technology, edited by J. S. Magee and M. M. Mitchell, Jr., is an excellent up-to-date assessment of the continually evolving and multifaceted FCC field. Its 15 chapters by well qualified authors with diverse backgrounds cover a complex technology with uniformly high quality and minimal redundancy.

A. A. Avidan provides a road map for the volume as a whole with a review of the evolution of the cracking process from the earliest prototypes through the most modern resid FCC with catalyst coolers. The chapter addresses hardware schemes and process dynamics and is tightly integrated with catalyst advances and changing feed and product demands. It discusses future potentials for improvement (ultimate yields in catalytic cracking still have not been reached), including resid upgrading and integration with petrochemical production.

The chapter by A. Humphries, D. H. Harris, and P. O'Conner focuses on the zeolite, with a detailed description of the structure and function of the active sites in zeolite cracking catalysts such as Y and ZSM-5. A comprehensive review of methods for determining the number, strength, and type of acid sites is provided, including both direct and indirect methods. Also included is a discussion on the carbenium ion mechanism of catalytic cracking and its relationship to product distribution. D. E. W. Vaughan describes the complexities of structure of the primary (e.g., zeolite Y) and secondary (e.g., ZSM-5, small pore zeolites, or even large pore materials) promoters utilized in a modern cracking catalyst. The emphasis is on characteristics of zeolite catalysts controllable via synthesis, including morphology, as documented by numerous electron photomicrographs. Postsynthetic modification and critical needs in characterization are also highlighted. G. M. Woltermann, J. S. Magee, and S. D. Griffith describe the continually evolving and increasingly complex area of commercial FCC catalyst preparation. Synthesis and modification of the zeolite component (Y is still the major zeolite), criticalities of FCC matrix technology, and formation of the composite FCC catalyst by mixing, spray-drying, and (sometimes) ion exchange are discussed. Characterization by chemical analysis, physical property testing, spectroscopy, etc., and quality assurance by statistical process control (SPC) are also described. J. Scherzer analyzes the relationships between structural features of FCC catalysts and activity/selectivity patterns in cracking. Structural characteristics of the zeolite (e.g., type, acidity, elemental analysis, Si/Al ratio, crystallite size), the matrix, and additives (both cracking and noncracking) are related to product distributions and fuel quality (e.g., MON, RON), catalyst deactivation/coke formation, catalyst design, and changing product demands for the future.

A. W. Peters provides an extensively documented review of instrumental methods for characterizing the complex dimensionalities of FCC catalysts, both fresh and after exposure to process conditions. Diffractive techniques (e.g., XRD, SAXS, neutron diffraction), analysis of pore structure by adsorption and absorption, surface analysis and imaging to assess catalyst topology and elemental analysis (e.g., SEM, TEM, EDX, Auger, STM), spectroscopy (e.g., MASNMR, IR, Mössbauer), and thermal analysis (e.g., TPD, TGA, DSC, TPR) are comprehensively covered. A thorough analysis of the microreactivity test (MAT), one of the most widely used tests for laboratory evaluation of FCC catalysts, is provided by E. L. Moorehead, J. B. McLean, and W. A. Cronkright. In addition to giving the history and descriptions of the various versions of this fixed bed test for catalyst activity and product selectivity, the chapter addresses important issues relevant to simulation of equilibrium catalyst behaviour by hydrothermal deactivation. It also discusses analytical options and relevance of the MAT to yield prediction in commercial riser FCC units. G. W. Young focuses on the dilemmas and test limitations encountered in assessing the significance of various FCC catalysts in the laboratory. After discussion of pretreatment practices (e.g., presteaming, cyclic aging if metals contaminants are present), a detailed description of catalyst testing using the Davison Circulating Reactor (DCR) follows. The DCR is a small-scale computer-controlled dilute phase riser reactor with fluidized bed regenerator that can operate in isothermal or adiabatic mode, or fully heat balanced operation. Comparisons with the MAT are included.

M. M. Mitchell, J. F. Hoffman, and H. F. Moore discuss the characteristics and evaluation of catalysts and additive systems for selective catalytic cracking of feeds containing significant amounts of crude residuum. The challenges imposed by these heavier, "dirtier" feeds, e.g., the needs for balance between zeolite and matrix activity, metals management, bottoms-cracking additives, and careful interpretation of the results, are examined in detail. In a related chapter, R. H. Nielsen and P. K. Doolin focus on the area of metals passivation, a technology which has received increased application as catalytic cracking of resid (which contains high levels of heavy metals such as Ni and V) has expanded in recent years. Techniques to mitigate the deleterious effect of these metals poisons, e.g., antimony passivation agents to manage Ni, and tin and rare earth compounds to counteract V, as described, including a review of metals passivation chemistry and laboratory/commercial experience.

L. L. Upson, C. L. Hemler, and D. A. Lomas discuss evolution of FCCU design and the growth of riser cracking, together with the impact of process changes on FCC operation and products. A detailed description of modern reactor designs and operation is provided, with emphasis on design and operational dynamics of the regenerator. A discussion of FCCU operational control, with an analysis of the effects of process variables on product selectivity and quality, is included. After reviewing basic cracking chemistry, W. S. Letzsch and A. G. Ashton discuss the effect of gas oil composition (both in terms of molecular structure and feed constitutive properties such as API gravity, UOP K, etc.) on the yields and quality of cracking products. They also focus on characterization of residual feeds, emphasizing the impact of asphaltenes, metals contaminants, nitrogen, CCR, etc., on product quality. Following a brief description of the chemistry of shape-selective cracking, F. G. Dwyer and T. F. Degnan focus on the application of ZSM-5 as a co-catalyst in catalytic cracking for octane improvement. The mechanism of ZSM-5's selective upgrading of low octane components to higher octane products is examined, and commercial cracking experience using ZSM-5 additive is reviewed. The metals tolerance of ZSM-5 and properties of other shape-selective materials with potential for increasing octane and light olefins (e.g., for oxygenate manufacture) are also discussed.

The chapter by A. Bhattacharyya and J. S. Yoo is relevant to the rapidly changing feedstocks, product specifications, and environmental regulations encountered today, which dictate limitations on refinery emissions of SO_x, NO_x, and CO. This chapter emphasizes FCC flue

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gas SO_x reduction, including SO_x chemistry, and preparation, characterization, and mechanism of action of SO_x reduction catalysts, e.g., CeO_2–Mg alumiante spinel. Brief discussions on catalytic NO_x reduction and refinery CO control via combustion additives are also included. The final chapter on environmental considerations in FCC by R. E. Evans and G. P. Quinn begins with a brief history of FCCU design. Historical perspectives on FCC regenerator stack emissions (e.g., particulates, CO, SO_x, NO_x) and environmental impact of FCC products (e.g., fuel gas, HFO, LCO, naphtha), as well as disposal of waste FCC catalyst, are provided. The chapter concludes with predictions on what process and catalyst changes will be required to respond to environmental regulations in the late 1990s.

Perhaps a chapter focusing exclusively on mechanistic aspects might also have been helpful, but both the breadth and depth of this volume are outstanding. For anyone working in or planning to enter the FCC field, this book is highly recommended.

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Spectroscopy in Catalysis. By J. W. Niemantsverdriet. VCH, Weinheim, 1993.

This is a truly valuable book that could be used as an introductory text for a graduate course on catalyst characterization. Although the subject has already been addressed in a number of previous books, most of them were meant for more or less experienced researchers. As a consequence, they were not easily adapted as textbooks for introductory courses. By contrast, the style and organization of the book written by Professor Niemantsverdriet make it particularly attractive for students starting their research in catalysis. For the same reason, it will also be very useful for industrial practitioners who need to be aware of the type of information that can be obtained from modern surface spectroscopies. The book covers most of the characterization techniques relevant to catalysis, with the two important exceptions of EPR and NMR.

It starts with a brief introduction in which the author emphasizes the importance of materials characterization in modern catalysis research and the need to identify fundamental relationships between the state of a catalyst and its catalytic properties. At the same time, the reader is warned that spectroscopy is not a simple discipline and that the best way to obtain meaningful and correctly interpreted results is by collaborating with an expert spectroscopist.

In the following chapter, the author describes the temperature-programmed techniques (TPR, TPO, TPD, etc.), giving a brief theoretical background and pointing out the type of information that can be obtained from these technqiues. Unfortunately, transport limitations, particularly important in the case of TPD, have not been discussed here, because the section on thermal desorption is restricted to surface science systems rather than to supported catalysts. However, in most of the other chapters, a good balance is maintained between surface science studies performed on single crystals and those performed on real catalysts.

In the chapter dedicated to photoelectron spectroscopies (XPS, UPS, and Auger), the author explains very well the physics behind these techniques and analyzes important applications, such as the use of XPS to estimate the dispersion of supported particles. Among the different applications of UPS, he presents an interesting description of the principles and uses of PAX (photoemission of adsorbed xenon). This site-selective titration technqiue is highly surface sensitive and allows titration of heterogeneous surfaces. Other highly surface sensitive techniques are described in a separate section that covers all the ion spectroscopies (SIMS, SNMS, RBS, and LEIS).

In another section of the book, the author clearly explains the fundamental principles of Mössbauer spectroscopy and includes some examples of its application to Fe, Ir, and Pt catalysts. He notes that one of the main advantages of this technique is the possibility of conducting *in situ* studies. A separate chapter deals with techniques that use the scattering of radiation to obtain structural information. XRD and LEED are discussed as examples of techniques that require relatively long-range order and, as a consequence, provide information on relatively large parts of the sample. By contrast, EXAFS is presented as a technique that provides information about the local structure. In a separate chapter, the author briefly describes the principles of electron microscopy, as well as the recently developed scanning probe microscopy. He gives a clear picture of the potential uses and limitations of the two new techniques, STM and AFM. The last type of techniques reviewed is the vibrational spectroscopies: infrared, electron energy loss spectroscopy, and Raman spectroscopy. In this chapter, the author offers a very pictorial and easily understandable description of the fundamental principles involved in these techniques and gives interesting examples of applications.

To demonstrate that the best results are obtained when a combination of techniques are employed to study one particular catalytic system, the author has dedicated a chapter to describing three typical case studies. The selected cases are metal–support interactions occurring in supported Rh catalysts, the nature of the active phase in Co–Mo sulfide HDS catalysts, and the effect of alkali promoters on noble metals. Each case demonstrates how different techniques can provide complementary information which, when combined with catalytic activity measurements, may result in a clear representation of the system under reaction conditions.

The book ends with a list of ingredients for a successful research program in catalysis, which has a superb pedagogic value. In those brief remarks, the author emphasizes the need for *in situ* characterization, the combination of several techniques, and the use of realistic model catalysts and suitable references.

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