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Book Review

HANDBOOK OF HETEROGENEOUS CATALYSIS

Second, Completely Revised and Enlarged Edition
Volume 6

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The sixth volume of the Handbook of Heterogeneous Catalysis deals with the ***energy-related catalytic processes***. The first Chapter (*Perspectives in Oil Refining)* contains an overview of the present situation in oil refining and analyses the main driving forces for the future evolution in this field. Catalyst improvements are expected to have a major impact on refining. Thus, better catalysts are needed for hydrogen production and reduction of the associated CO_2. Hydrotreating/hydroconversion needs new catalysts with increased activity for heavy cuts and deep desulfurization of diesel oil.

The *hydrotreating* process, representing the third largest catalyst business after exhaust gas catalysts and fluid cracking catalysts, is presented in Chapter 2. After an introduction, the most important hydrotreating reactions, hydrodesulfurization (HDS), hydrodenitrogenation (HDN), hydrodeoxygenation (HDO) and hydrodechlorination (HDCl) are described. The mechanisms employed to explain these reactions are presented. Then, the synthesis of a hydrotreating catalyst, from its oxidic to its sulphidic form, through impragnation, drying, calcination and sulfidation steps, is presented. It is shown how, by using modern physical-chemical characterization methods, it is possible to asses which Mo, Ni (or Co) and P species are present in the impregnating solutions, which species adsorb on the support surface and how these species are converted through calcination and sulfidation in the catalytic active species. The relation between the catalyst structure and the reaction mechanisms is also explored. The structure of Mo and Ni (or Co) sites on the catalyst surface is correlated with the elementary steps in the reaction pathways.

Finally, state-of-the-art processes and possible future processes for the removal of sulfur from fuels (naphta and diesel) are described.
The removal of the metal compounds present in petroleum, via *hydrodemetalation* is reviewed in the next chapter. After a presentation of the main metallic compounds in petroleum, a short description of the residue hydrotreating technology is given. The existing understanding of the reaction kinetics and diffusion, illustrated for model compounds, such as metal porphyrins, Cs, Na, Ni and V, as well as the catalyst deactivation are explored in the second part of this chapter.

Chapter 4 is devoted to *catalytic reforming*, one of the primary process technology in modern refinery. Firstly, the history and the importance on this process are presented in the introduction. Then the chapter is divided into three parts: the chemistry of reforming, reforming catalysts and reforming processes. Feed composition and characteristics, reforming products and selected analysis methods for their identification and quantitative analysis and the reactions involved in the reforming process are the major topics presented in the first part. A general description of the main catalytic systems used in this process is given in the following subchapter, together with some aspect of catalyst poisoning and regeneration. The next part, on the reforming process, deals with the process variables, modeling and optimization of commercial reforming units and describes the available commercial catalysts and the principles of the process flow schemes.

Chapter 5, on *fluid catalytic cracking (*FCC), starts with a historical presentation followed by an overview of FCC today and its position in modern petroleum refinery.

The FCC unit types, heat balance and the modes of operation (regeneration mode – partial burn vs. full burn, resid processing and petrochemical mode) are shortly exposed. Next, the importance of the FCC feed and the effects on FCC unit operation are outlined. The main reactions involved in this complex process are described in the subsequent part. Then, the FCC catalysts, with a focus on the zeolitic component and its activity and selectivity effects, are discussed. The role of the catalyst matrix and the most common characterization methods are also approached. The following part is devoted to environmental issues and the chapter ends with a presentation of laboratory and pilot plant testing methodology of the FCC catalysts and with some remarks on the future trends in catalytic cracking.

Chapter 6, titled *Hydrocracking and Catalytic Dewaxing,* is divided in two parts, corresponding to these two processes. In the first part the authors show that catalysts form an essential part of the hydrocracking process, inasmuch as they have a strong influence in the product distribution. In is also shown that the type of feedstock and the operation conditions influence de performance of the process. An important part of this chapter is focused on the presentation of the main bi-functional catalytic systems, including some recommendations for catalyst design and a review of the new catalyst developments. The catalytic dewaxing and the importance of the shape-selectivity of some catalysts proposed for this process are approached in the second part of the chapter.

The *Isomerization* process is presented in Chapter 7. The discussion is centered mainly on the skeletal isomerization of alkanes. More specifically, acid-catalyzed processes, considered the most important practical route, are discussed while the metal-catalyzed isomerizations are ignored. A special attention is given to the technological aspects of alkane isomerization and to the more recent concepts and data. The *Alkylation of Isobutane with Light alkenes on Solid Catalysts* presents the main lines of developments using solid catalysts in the last decade. The main drawback of the process – the deactivation by carbonaceous deposits – is presented in detail, followed by some aspects on catalyst regeneration. The best regeneration method, which seems to allow the commercial application of solid acid catalyzed isobutene/alkene alkylation is presented as a noteworthy breakthrough for heterogeneous catalysis. Chapter 9 is focused on the *oligomerization* of alkenes. Of particular interest is the oligomerization of cycloalkenes, such as the dimerization of cyclopentene to cyclohydronaphtalene, which usually takes place over liquid acid catalysts but can occur over solid phosphoric acid. Controlled dimerization of styrene using cation-exchange resins and cyclotrimerization of acetylene to benzene using lanthanide – Ti(IV) catalysts are other examples of oligomerization reactions presented herein.

The main focus of Chapter 10 *(Etherification*) is on tertiary ethers, including formation reactions (thermodynamics and kinetics), their properties and the processes for their commercial production. However, the problem of linear ethers is also approached. The *steam reforming* process – a key technology to produce synthesis gas and hydrogen – is described in the following chapter. Of particular interest are the discussions on the catalyst, including the major catalyst problems and the role of the active sites.

Chapter 12 *Water Gas Shift and COS Removal*, presents the three technical processes based on the WGS: the high-temperature shift, the low-temperature shift and the "sour gas" shift. Chapter 13 concentrates on the main themes of industrial relevance for the well-known *methanol synthesis* process. The mechanism and the structure of copper-based catalysts and the progresses made on the low-temperature methanol synthesis catalysts are of specific interest. In the next chapters different processes, such as *methanol-to-hydrocarbons, Fischer-Tropsch synthesis, gas-to-liquids and oxidative coupling of methane,* present the background for the strong industrial interest for these technologies and review the most important catalyst and some relevant mechanistic and kinetic aspects. The leading industrial processes are also described, with remarks on the industrial perspectives. The next two chapters offer a broad view of catalyzed coal liquefaction and coal and carbon gasification processes and the challenges in this field of energy and materials-related catalysis.

The Chapter 20 titled *Fuel Cell Related Catalysis* is the last part of this volume. It is divided in two parts: Fuel processors and Fuel Cells. The first part explains the major aspects of fuel processor developments, from the viewpoint of heterogeneous catalysis, taking into account several engineering tools for constructing fuel processor units for different applications based on a variety of fuels (methane, methanol, ethanol and fossil-based fuels). In the second part, a general description of all fuel cells is given, with a detailed discussion on anodic oxidation (i.e. for hydrogen and methanol) and cathodic reduction (for oxygen) reactions occurring in PEMFCs and DMFCs. The perspectives and the present limitations of these technologies are convincingly presented. Finally, the major applications in transportation, stationary and portable applications are presented.

This volume is authored by an impressive number of experts, in a remarkable cooperative effort. Most of the chapters are illustrated with high quality images, and representative charts and tables. Moreover, the wealth of information offered here is easily accessible, with the aid of a detailed subject index.

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