ELSEVIER

www.elsevier.nl/locate/jorganchem

Journal of Organometallic Chemistry 584 (1999) 217–218

Journal of Organometallic Chemistry

Book Review

Transition Metal Sulfides: Chemistry and Catalysis; T. Weber, R. Prins and R.A. van Santen (Eds.); Kluwer Academic Publishers, Dordrecht, Netherlands, 1998, pp. vii–355, ISBN 0-792-35255-6, GBP 99.00 (US$ 159)

Hydrodesulfurization (HDS), the removal of sulfur from organosulfur compounds in petroleum distillates and other feedstocks by treatment with hydrogen gas at high pressure and elevated temperatures, is desirable not only on ecological grounds, but also to reduce sulfur poisoning of precious-metal-based reforming catalysts used in the production of high-octane gasoline. This book contains 12 review-type chapters based on lectures presented at a NATO Advanced Research Workshop on Challenges for Sulfides in Material Sciences and Catalysis, and its title, perhaps because of an attempt to make it as general as possible, is rather misleading. With the sole exception of Chapter 1, devoted specifically to solid-state transition-metal sulfides, and maybe Chapter 2, which considers charge-transfer phenomena in transition-metal sulfur chemistry, all the other chapters deal with the chemistry of hydrodesulfurization processes considered from different points of view. Other important processes, such as the removal of nitrogen (hydrodenitrogenation), oxygen (hydrodeoxygenation) and heavy metals (hydrodemetallation) from crude oil, are also treated throughout the book.

Chapter 1 describes some aspects of the structures and physical properties of transition-metal sulfides, with particular emphasis on those of Mo and Co, given their relevance to HDS reactions. The general properties of sulfides are compared with those of oxides and of other chalcogenides. The main part of this solid-state chemistry review is a discussion of binary and some ternary transition-metal sulfide structures, and it ends by considering some possible geometries for catalytically active sites in MoS_2.

Undoubtedly, the chapters that will attract most attention from the coordination/organometallic chemistry community are Chapters 2–6. Chapter 2 deals with structural and electronic aspects of transition-metal complexes containing tetrathiometallate (MS_4^{n-}) ligands. One particularly interesting section within this chapter describes the spectroelectrochemistry of these compounds, either as intermediates or as transient species.

In Chapter 3, the chemistry of the dihydrogen ligand in transition-metal complexes with *S*-donor ligands is reviewed. Dihydrogen is proposed to be activated at metal sites with ligand vacancies on sulfides such as MoS_2 and RuS_2 that are active in HDS reactions, and transition-metal hydride species have been implicated in the mechanism of action of the industrial catalysts used in such processes. Among several general aspects of the chemistry of transition-metal dihydrogen complexes, the preparation and reactions of compounds containing sulfur donors are discussed. This sort of compound is still rare, although some of their properties have been revealed.

Of the organosulfur compounds present in petroleum feedstocks, the thiophenes require the more extreme conditions employed in hydrotreating. 4,6-Disubstituted dibenzothiophenes are particularly unreactive towards ordinary HDS catalysts. One approach to understanding the adsorption and reactions of these species is to examine their modes of bonding and reactivity in transition-metal complexes, and these are described in Chapter 4. This comprehensive review discusses all the observed coordination modes of thiophene, benzothiophene, and dibenzothiophene. For some coordination modes, the ligands are highly activated to further reactions that often lead to C–S bond cleavage and even to complete desulfurization. This particular topic forms the main part of Chapter 5, entitled Hydrogenation, Hydrogenolysis and Desulfurization of Thiophenes by Soluble Metal Complexes. All the known reactions belonging to any of these three categories are presented and discussed in this chapter in a clear and interesting way. Although no transition-metal catalyst capable of selectively and efficiently hydrodesulfurizing thiophenes in the homogeneous phase has yet been found, the results obtained have contributed to answering some questions of relevance for elucidating the mechanism of HDS catalysis promoted by late transition metals.

The remaining chapters of the book deal with various topics related to HDS processes, from the viewpoints of theoretical chemistry (Chapter 6, Sulfur Bonding in Transition Metal Sulfides and MoS_2 Based Structures);

PII: S0022-328X(99)00144-8

physical chemistry (Chapter 7, Chemistry and Reactivity of Transition Metal Sulfides in Relation to Their Catalytic Performance); heterogeneous catalysis (Chapter 8, Characterisation of Unsupported and Alumina-Supported Molybdenum Sulfides); surface science (Chapter 9, Preparation, Structure and Surface Chemical Properties of Hydrotreating Model Catalysts: A Surface Science Approach); reaction mechanisms (Chapter 10, Reaction Dynamics During C–S Bond Breaking in Sulfur Containing Molecules: Isotope Studies); catalyst properties (Chapter 11, Effects of Catalyst Composition and Pre-treatment on the Product Distribution in Hydrodesulfurization, Hydrodenitrogenation and Hydrodechlorination); and chemical engineering (Chapter 12, Metal Sulfides and Refinery Processes). I am not able to comment in an informed manner on these, but all the reviews seem quite complete, with reference citations appropriate to the content and coverage of each chapter.

Overall, this book gives an up-to-date account of the nature of HDS processes viewed from different areas of chemistry. It will be of great value as a work of reference for the increasing number of organometallic chemists who are developing homogeneous organometallic catalysts for HDS reactions, a research field that is yet to be thoroughly explored.

Manuel Jimenez Tenorio
Departamento de Ciencia de Materiales e
Ingenieria Metalurgica y Quimica Inorganica
Universidad de Cadiz
Apartado 40
E-11510 Puerto Real
Cadiz
Spain