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BOOK REVIEWS

Catalysis by Ceria and Related Materials. Edited by Alessandro Trovarelli (Università di Udine, Italy). Catalytic Science Series. Volume 2. Series Edited by Graham J. Hutchings. Imperial College Press: London. 2002. vviii + 508 pp. $78.00. ISBN: 1-86094-299-7.

Catalysts based on cerium oxide are well established in many large-volume applications, most notably three-way catalysts in automotive catalytic converters, fluid-cracking catalysts in refineries, and ethylbenzene dehydrogenation catalysts used during the production of styrene. Ceria-based catalysts are also being evaluated for a range of emerging applications, including oxidation catalysts (e.g., soot removal from diesel engine exhausts, low-temperature CO and VOC oxidation catalysts, wet-oxidation of organic pollutants in water, etc.), hydrocarbon-reforming catalysts (e.g., partial oxidation, steam reforming, and water-gas-shift, etc.), and as components in electrodes for solid oxide fuel cells. Ceria-based oxides usually are not "stand-alone" catalysts; rather, ceria serves as an "active" support for catalytic metals, such as nickel, platinum, rhodium, etc.

The remarkable enhancement of catalytic activity by ceria is attributed to its so-called "oxygen storage capacity", that is, the ability to temporarily donate oxygen to reactions that are catalyzed by the metal and to accept oxygen after the reaction is completed. This phenomenon can be understood generically as oxygen being liberated by reduction of Ce^{4+} to Ce^{3+} and oxygen being reabsorbed during reoxidation of Ce^{3+} to Ce^{4+}. However, the mechanisms involved are extremely complicated, and a considerable body of literature has been devoted to research aimed at clarifying various compositional and structural aspects of ceria-based catalysts and demonstrating their utility for a wide variety of reactions. This book does an excellent job of summarizing this previous work and provides a solid foundation for students and researchers involved in catalyst applications where ceria-based catalysts are candidates. The book has 16 chapters, each providing a review on specific topics, with an average of 113 references per chapter. The list of authors includes some of the more prominent scientists in the field of catalysis.

The first three chapters provide broad overviews of cerium oxide from the perspective of sources of raw materials, structural properties, and synthesis. The first chapter, by Schermanz, reviews the production and applications of ceria-based materials. It begins with a discussion of ceria-based minerals and ores, refining of these ores, and production processes for cerium chemicals. Commercial applications of cerium-based materials in catalysts, ceramics, metals, and phosphors are then briefly summarized. The next chapter, by Trovarelli, summarizes structural properties and nonstoichiometric behavior of cerium oxide. The various stoichiometric and substoichiometric oxide phases in the binary cerium−oxygen system are discussed, and the defect structure of cerium oxide is reviewed. Electrical conductivity and oxygen diffusion in cerium oxide are also discussed. Adachi and Masui then provide an excellent summary of past work on the synthesis of cerium oxides and modified ceria compositions, with an emphasis on preparation and characterization of nanoscale materials that are useful as catalysts.

Chapters 4−7 contain summaries of work related to the synthesis and characterization of metal/ceria systems, with a primary emphasis on characterizing ceria-based three-way catalysts used in catalytic converters. Chapter 4, by Bernal et al., provides a very comprehensive review (397 references) of previous work on metal/ceria catalysts and an excellent discussion of analytical techniques for characterizing the oxygen storage capacity of ceria-based catalysts. In the next chapter, Conesa et al. cover the use of magnetic resonance and X-ray spectroscopic studies for characterization of unsupported ceria and ceria-supported precious metal catalysts. The following chapter, by Kaspar and Fornasiero, provides a detailed discussion of structural properties and thermal stability of solid solutions of ceria-zirconia, including a description of various distorted crystalline phases that can be formed during high-temperature annealing in oxidizing and reducing atmospheres. In the concluding chapter of this group, Duprez and Descorme describe measurements of the capacity of ceria-based oxides and ceria-supported precious metal catalysts to store oxygen and discuss the results in the context of applications to catalytic converters.

The next two chapters provide reviews of a more fundamental nature. The first of these, by Islam and Balducci, addresses the use of computational methods, for example, atomistic, molecular dynamics, and ab initio quantum mechanical methods, in the investigation of defect structures, transport properties, surface chemistry, and redox behavior of cerium oxide and related materials. In the second, Overbury and Mullins review the use of methods of surface analysis using ultrahigh vacuum techniques for characterizing "model" thin-film ceria-based catalysts. These methods, when applied to precisely controlled surfaces, can provide a considerable amount of useful information on the effects of composition, structure, and metal−ceria interactions. An especially useful summary of previous studies on the chemisorption of various gaseous species onto ceria surfaces is presented.

Chapters 10−12 are focused primarily on application-specific issues associated with using ceria-based catalysts in applications to emissions control. In Chapter 10, Shelef et al. describe the evolution of ceria-based "three-way" catalysts and discuss mechanisms for deactivation of these catalysts as well as approaches that have been developed to address issues of deactivation. In the next chapter, Gorte and Luo address the issue of sulfur poisoning of ceria-supported precious metal catalysts. The authors conclude that the degradation of catalysts in the presence of sulfur is related to the ceria and not the precious metal component of the catalysts and attribute this to the negative effect of sulfur on the capacity of ceria to store oxygen. The final chapter of this group, by Makkee et al., describes the use of cerium and platinum fuel additives in

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conjunction with particulate filters for soot abatement systems in diesel engines.

Additional (nonautomotive) applications of ceria-based catalysts are addressed in Chapters 13−16. The first of these chapters, by Primet and Garbowski, covers the use of ceria-based catalysts in applications to catalytic combustion. The importance of maintaining thermal stability through either addition of zirconia to ceria or by supporting the ceria-based catalysts on thermally stable materials such as alumina or barium hexaaluminate is discussed. Previous results obtained on ceria-based combustion catalysts with transition metals (Mn, Co, Cr, Fe) and precious metals (Ag, Pt, Pd, Rh) are reviewed. In the next chapter, Imamura describes the use of ceria as a component in wet oxidation catalysts. Most of these formulations include precious metals (mainly Pt, Pd, or Ru) supported on ceria, mixed oxides of CeO_2 and MnO_2, and Mn/Ce oxides promoted by precious metals. Mogensen, in Chapter 15, covers the use of ceria as a component of anode electrocatalysts in solid oxide fuel cells. Issues related to thermal and chemical compatibility of ceria are addressed, and the potential of using ceria-based anodes in solid oxide fuel cells operating on hydrocarbon fuels is discussed. Boaro et al. then review additional applications of ceria-based catalysts, including fluid cracking catalysts used in refineries, catalysts used in desulfurization processes and NO_X abatement processes, and ethylbenzene dehydrogenation catalysts used during the production of styrene.

In summary, this book is an excellent compendium on the science, technology, and applications of ceria-based catalysts. It provides useful overviews, both to graduate students beginning their scientific careers in the field of catalysis and to industrial researchers working in the fields of industrial, environmental, and automotive catalysts. Although the majority of chapters in this book address fundamental science and issues associated with automotive applications, this focus is probably warranted on the basis of the importance of this application to our society at large. Furthermore, this science can be easily translated to other catalytic applications of interest.

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