

BOOK REVIEWS

An Investigation on Promoted Iron Catalysts for the Synthesis of Ammonia. By ANDERS NIELSEN. Jul. Gjellerups Forlag, Copenhagen, 1968. Third Edition, 263 pp. Price: Da.Cr. 28, paperbound; Da.Cr. 36, clothbound (excl. Danish sales tax).

This book, written by Dr. Anders Nielsen in collaboration with colleagues at the Haldor Topsøe Research Laboratory (Chemical Engineers, Vedbaek, Denmark) and the Department of Chemistry of the Royal Veterinary and Agricultural College, Copenhagen, is meant in the first place for those who are engaged in the development and construction of new ammonia plants, or who are employed on the staff of such plants. However, the book is distinctly dual in character, so that also anybody who wants to learn about the present state of fundamental research on ammonia synthesis will find in it a rich source of information and a reliable and complete survey of everything that has so far been done in the field. At the same time, the research worker can inform himself about the way in which the chemical engineer manages to apply the knowledge gained.

The general plan of the second edition has been retained, but a new chapter has been added dealing with the examination of ammonia catalysts by normal and electron microscopy. In addition, many of the other chapters have been extended and improved. The literature, which in the previous edition was taken into account up to 1955, has now been covered up to the end of 1967.

After a brief introduction (Chapter I), the book gives, in Chapter II, a comprehensive treatise on the thermodynamic data needed in calculating the maximum possible ammonia yield. Very interesting aspects are brought out here, e.g., as regards the nitrogen-to-hydrogen ratio, the influence of inert gases, and the deviation from the ideal gas laws.

The complicated problems arising if, starting from laboratory experiments, one wants to predict the behavior of industrial-scale reactors are presented clearly in Chapters II, IV, and V. A courageous attempt is made here to arrive at an optimum technical result on the basis of the numerous and often contradictory literature data

and of appropriate technological research on a laboratory scale.

The next chapter, VI, deals adequately with the technical factors that are determinative of an economic application of ammonia catalysts in industrial practice. It is clearly shown here that in the choice of a catalytic material the size of the plant, the pressures and temperatures to be applied, and the purity of the gases to be used, are the decisive factors. In some cases it is even desirable to use several layers consisting of different types of catalyst, in view of the temperature gradient in the reactor.

Chapters VII to X discuss the more fundamental aspects, but in such a way as to bring out clearly the points of importance in practical applications. For those who have to carry out laboratory examinations of fresh and used ammonia catalysts, these chapters make an indispensable guide. It is in particular the combination of different techniques, such as X-ray analysis, microscopic examination, surface area determination, and the establishment of pore distributions, which should be paid attention to if a reliable judgment is to be formed about the usefulness of new catalysts or the decrease in activity in used materials.

In summing up, it may be said that the book excellently meets the object its authors had in mind. In a following edition, however, the referee would like to see included a chapter providing some insight into the design and construction of modern ammonia production plant. He would also welcome a better picture of the economic aspects. One might ask, for instance, what economic advantage is gained in applying improvements which are fully justified from a scientific and technical point of view. A further useful addition would be a description of the large-scale production of ammonia catalysts.

In general, the author does not arrive at any distinct pronouncements about his own views and conclusions in those cases where literature data are contradictory. This is indicative of a large measure of scientific prudence. On the other hand, making hypothetical pronouncements is a condition of stimulating others to renewed investigation, to prove the hypotheses true or untrue. About the effect of the promoters Al_2O_3 and KOH only hesitant remarks are made. Neverthe-

less, it may be stated that at present almost all investigators agree that Al_2O_3 only serves to enlarge the surface area and maintain the thermal stability. It is not clearly brought out that KOH is a promoter which is needed only in high-pressure experiments. The reason why this should be so has not yet been clarified. It is not impossible that at high pressure virtually the whole iron surface is occupied by chemically adsorbed nitrogen, so that the dissociative adsorption of hydrogen is hampered. It might be that at high temperature the KOH is slightly reduced (see Gmelin, Vol. 22, p. 201). From the work done by Gomer (field ion microscopy) it has appeared that a surface layer of potassium on tungsten is capable of dissociative hydrogen splitting, but does not cause dissociative nitrogen adsorption. This would imply that KOH creates new centers enabling the dissociative splitting of hydrogen (dissociation energy approx. 100 kcal/mole!) to take place also if the entire iron surface is occupied by nitrogen.

A following point for criticism is that the book does not sufficiently stress the great influence which the degree of reduction of the catalyst has on the eventual catalyst activity. It is especially by prolonged reduction of the catalyst with extremely pure hydrogen that a considerable rise of the activity can be brought about. The fact that type and concentration of the promoters greatly influence the rate of the reduction process renders a comparison of the activities of different samples extremely difficult.

All in all, it must be said that this is an excellent book; it is to be hoped that many young investigators may be induced to take up again research in the field of ammonia synthesis, using the newer techniques now available, which are aimed more directly at the study of the catalyst *surface*. In this way the often unfruitful method of trying to find correlations between bulk properties and catalytic properties might be abandoned.

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Experimental Magnetochemistry—Nonmetallic Magnetic Materials. By MICHAEL M. SCHIEBER. North-Holland Publishing Co., Amsterdam, and John Wiley and Sons, New York, 1967. 572 pp., 253 fig. price \$28.00.

Those elements and compounds useful in heterogeneous catalysis exhibit, not infrequently,

magnetic properties of such a nature and variety as to arouse speculation concerning a possible basic relationship between catalysis and magnetism—a relationship of the kind often discussed between catalysis and semiconductivity. But, except for the magnetic ortho-parahydrogen conversion, no such relationship has been verified for any reaction. The applications of magnetism to catalysis (and they are not unimportant) have thus far been concerned with analytical and structural parameters, like the presence and particle size of a ferromagnetic such as nickel metal, or to the changes in magnetization caused by a chemisorbed molecule, or to the particle size of a typical antiferromagnetic such as chromium sesquioxide. These applications are sufficient for any book on the subject to gain review in the *Journal of Catalysis*, but the reader will not find the word "catalysis" mentioned in the index of this book. The book is reviewed here because it gives a wealth of information about many compounds of actual or potential interest in catalysis. Here are our old standbys— CoO , Cr_2O_3 , CuO , Fe_2O_3 , MnO_2 , MoO_3 , VO_2 , ZnCr_2O_4 , and ZnO —together with nearly a thousand others. Who would today dare deny that the magneto-electric polarization of Cr_2O_3 , or the spin-flop transition in V_2O_5 , may someday give a clue to those fugitive activated surface complexes that lie at the heart of our problem?

To this reviewer's knowledge there have been five previous books in which the word "magnetochemistry" could be found in the title. The most difficult of these could be read with ease, if not profit, by anyone with an undergraduate major in chemistry. Not so with this book—it requires a preknowledge of elementary solid state physics (and precious little else). Topics covered include an outline of magnetic principles; the preparation of solids, most of which are metal oxides; experimental methods for magnetic measurements; nearly 300 pages dealing with the magnetic properties of specific substances ranging in complexity from CdO to $\text{Gd}_2\text{CaMn}_2\text{Ge}_2\text{O}_{12}$; and finally some review problems for the serious reader. In brief, the book is not a book about magnetochemistry, it is a thorough and effective introduction to the magnetic properties of non-metallic solids, and this is exactly what is implied by the subtitle. The book can be recommended to anyone with an interest in knowing all he can about the inorganic solids with which heterogeneous catalysis is concerned.

No professional chemist can read this book without reflecting on the state and future of chemistry as a science. Inorganic chemistry has seen a phenomenal rebirth and growth in the past