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Book Review

The Use of Tracers to Study Heterogeneous Catalysis. Edited by JOHN HAPPEL AND MIGUEL A. HNATOW. *Ann. N. Y. Acad. Sci.* **213**, 1–246 (1973).

An international conference on the Use of Tracers to Study Heterogeneous Catalysis was held on August 28 and 29, 1972 in New York City under the auspices of the New York Academy of Sciences. The catalytic science community will be grateful to the editors of the proceedings of the conference for preparing this valuable book containing not only the text of the papers but also a lively transcript of the extensive discussions that followed the papers.

Most readers are familiar with the many studies of equilibration and exchange reactions involving the isotopes of hydrogen and oxygen, that have been so invaluable during the past 40 years in providing information on the nature of adsorbed intermediates during catalytic reactions. The continuing vitality of this mechanistic tool is attested by a penetrating review by Kemball of exchange reactions of organic molecules with deuterium or heavy water on oxide catalysts. As noted by Haller in the Discussion: "When you read the full paper of Dr. Kemball, you will see he's made several classifications . . . that allow one to understand or appreciate reactions on oxides. It allows you to recall a great deal of chemistry on a large number of systems . . . ." Other papers dealing with exchange reactions include one by Boreskov and Muzykantov on oxygen exchange on oxide catalysts, one by Tamaru on deuterated exchange products with localization of the deuterium in the product by means of microwave spectroscopy and one by Guczi and Tétényi on exchange of hydrocarbons with hydrogen isotopes on metallic catalysts. Another classical approach to reaction mechanism by way of tracers is illustrated by Haag's paper on dehydrocyclization of ^{14}C-tagged molecules.

If the volume contained only these excellent papers on traditional topics, it would already be a valuable addition to the personal library of catalytic chemists and chemical engineers. But it contains in addition a number of papers on the less known methods developed by C. Wagner, Horiuti, Temkin and their disciples. Wagner's school is represented by Grabke's summary on oxygen transfer from water and carbon dioxide to metals and oxides. Wagner's phenomenological approach requires no molecular model and no assumption on surface behavior. It deserves much more attention than it has received in the past. Horiuti's concept of the stoichiometric number is discussed in theory and in its application by Horiuti, Temkin, Ratner and Happel and Hnatow. The concept is very straightforward but has not been presented in the past with too much clarity, largely as a result of unfamiliar terminology and excessive generality. The papers under review are, alas, in the obscure style of many of their predecessors but put together as they are in this volume, they appear to this reviewer to be a Rosetta stone waiting for its Champollion. Professor Happel has kindly brought my attention to an incorrect statement in his paper p. 206. It is said that more than one level of marking by tracers can be used advantageously for the study of reactions of the type $A \rightleftarrows A_{ads} \rightleftarrows B_{ads} \rightleftarrows B$. In fact, it is possible to use only one level of tracing to obtain new information in this case and the information obtained is not sufficient by itself to calculate the step velocities. Perhaps the method of the stoichiometric number will find a wider acceptance if it can be shown to be applicable to nonuniform catalytic surfaces. In other words, is the concept of a rate determining step valid in the case of catalysis on a nonuniform surface? Some say no, some say maybe but, unfortunately the question was not raised at this conference.

Finally, the volume contains a paper on Neiman's Kinetic Isotope Method by Gál *et al.* The method is also discussed in the paper of Guczi and Tétényi mentioned above. In this case, all these authors warn against the danger of applying this powerful tool in mechanistic studies unless it has been established that adsorption–desorption equilibria prevail. In this respect, I wish to note that perhaps the only application of tracers to the study of heterogeneous catalysis which is not mentioned in this remarkable international collection of papers, is the work of Dwyer *et al.* on the deviation of the distribution of deuterium exchanged products from the binomial distribution when one deuterium is exchanged at a time in a molecule containing a number of equivalent hydrogen atoms. According to the workers at Mobil and the University of Pennsylvania, this deviation can be ascribed to either pore diffusional limitations or lack of adsorption-desorption equilibria [Dwyer *et al.*, *Proc. Roy. Soc., Ser. A* **302**, 253 (1968)].

M. Boudart

Stanford University
Stanford, California 94305