ADVANCES IN CATALYSIS

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Edited by

D. D. ELEY
The University
Nottingham, England

HERMAN PINES
Northwestern University
Evanston, Illinois

PAUL B. WEISZ
University of Pennsylvania
Philadelphia, Pennsylvania

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Advisory Board

Contributors

Numbers in parentheses indicate the pages on which the authors' contributions begin.

M. BÜLOW, *The BOC Group, Murray Hill, New Jersey 07974* (351)

J. CARO, *Zentrum für Heterogene Katalyse, D-1199 Berlin-Adlershof, Germany* (351)

B. E. HENRY, *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455* (51)

ENRIQUE IGLESIA, *Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801* (221)

H. JOBIC, *Institut de Recherches sur la Catalyse, 69626 Villeurbanne, France* (351)

J. KÄRGER, *Fachbereich Physik der Universität Leipzig, D-7010 Leipzig, Germany* (351)

ROSTAM J. MADON, *Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801* (221)

L. E. MANZER, *Corporate Catalysis Center, Central Research and Development, Du Pont Company, Experimental Station, Wilmington, Delaware 19880* (329)

YUTAKA MORIKAWA, *Research Laboratory of Resources Utilization, Tokyo Institute of Technology, Yokohama 227, Japan* (303)

V. N. M. RAO, *Corporate Catalysis Center, Central Research and Development, Du Pont Company, Experimental Station, Wilmington, Delaware 19880* (329)

SEBASTIAN C. REYES, *Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801* (221)

WOLFGANG M. H. SACHTLER, *Ipatieff Laboratory, Department of Chemistry, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208* (129)

L. D. SCHMIDT, *Department of Chemical Engineering and Materials Science, University of Minnesota, Minneapolis, Minnesota 55455* (51)

F. SCHÜTH, *Institut für Anorganische and Analytische Chemie, Universität Mainz, D-6500 Mainz, Germany* (51)

STUART L. SOLED, *Corporate Research Laboratories, Exxon Research and Engineering Company, Annandale, New Jersey 08801* (221)

ZONGCHAO ZHANG, *Ipatieff Laboratory, Department of Chemistry, Center for Catalysis and Surface Science, Northwestern University, Evanston, Illinois 60208* (129)

V. P. ZHDANOV, *Institute of Catalysis, Novosibirsk 630090, Russia* (1)

B. ZIBROWIUS, *Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M601QD, England* (351)

Preface

The diverse efforts of authors and the wide scope of coverage undertaken in *Advances in Catalysis*—indeed, the breadth of catalysis itself—are well characterized by the seven chapters of this volume. These chapters were written by authors from departments of chemistry, chemical engineering, inorganic and analytical chemistry, materials science, and physics; from several universities; from two major industrial laboratories; and from at least three institutes dedicated specifically to catalysis!

Similarly, the breadth of subjects covered is rather remarkable. The subjects covered in the present volume include

Principles of the physical structure of solid catalysts: V. P. Zhdanov reviews modern concepts concerning pore structures that go beyond the old, lumped parameters of pore size and tortuosity.

Catalytic phenomena: F. Schüth *et al.* have collected many observations, theories, and ideas concerning oscillatory rate behavior.

Structure–rate relationships: W. M. H. Sachtler and Z. Zhang present a view of many aspects of catalysis and catalysts utilizing transition metals in zeolites; E. Iglesia *et al.* discuss catalysts, mechanisms, and performance in the Fischer–Tropsch reaction; and Y. Morikawa makes us aware of a class of intracrystalline catalysts other than zeolites.

Specific product orientation: L. E. Manzer and V. N. M. Rao describe catalytic pathways to the modern product challenge of alternatives to chlorofluorocarbons.

New analytical techniques for internal catalyst properties: The unique collaborative team of J. Caro *et al.* describes developments of NMR techniques for the study of the motions of guest molecules in zeolites.

Altogether, one must marvel at the many "disciplinary" aspects that interplay to generate the knowledge and applications of catalytic science.

PAUL B. WEISZ

Mikhail I. Temkin

Mikhail I. Temkin, 1908–1991

Mikhail I. Temkin, born in Bielostock, graduated in 1926 from the Lepeshinsky School in Moscow. At that time, the law prescribed two years of work prior to admission to a university. According to Temkin, these years spent at chemical plants shaped his future interests in linking theory to practice. He graduated in 1932 from Moscow State University and joined the Karpov Institute of Physical Chemistry, where he began studies on thermodynamics and kinetics, with applications to catalysis. After a visit in 1935 to the laboratory of Michael Polanyi in Manchester, Temkin returned to the Karpov Institute, where he started the Laboratory of Chemical Kinetics that he headed for 50 years.

All his life, Temkin contributed to science in many areas, such as diffusion of heavy water into ordinary water, fugacity of gas mixtures, theory of mixtures of molten salts, and mass transfer in chemical engineering. But he left his indelible mark in the fundamentals of catalytic kinetics, on a par with C. J. Christiansen and J. Horiuti.

It all started in 1938 when Temkin first applied transition state theory to heterogeneous catalysis. Soon after, he published with V. Pyzhev one of the most frequently cited papers in catalytic ammonia synthesis. Since both Mikhail Temkin and Paul Emmett had a profound influence on the theory and practice of this famous reaction, it seems proper to quote here Emmett's assessment of the 1939–1940 paper of Temkin and Pyazhev.*

Numerous studies of the kinetics of ammonia synthesis and decomposition have been made. With a few exceptions, work has tended to show that the slow step in the synthesis of ammonia is the chemisorption of nitrogen and the slow step for the decomposition is the desorption of nitrogen. Furthermore, it turns out that the decomposition and synthesis of ammonia usually involve in the rate expression a term $P_{NH_3}^x/P_{H_2}^y$, where y/x is close to 1.5. In 1940, Temkin and Pyzhev derived an equation consistent with both of these observations [M. I. Temkin and V. Pyzhev, *Acta Physiochim. U.R.S.S.* **12,** 327 (1940)]. It has formed the basis for most of the kinetic treatments of ammonia synthesis and decomposition in recent years.

Temkin assumed a heterogeneous surface and set up equations for the adsorption equilibrium of nitrogen on iron, for the rate of adsorption, and for the rate of de-

sorption. Specifically his three pertinent equations are:

$$\theta = \frac{1}{f}\ln a_0 P' \tag{4}$$

$$v = k_a P e^{-g\theta} \tag{5}$$

$$w = k_d e^{h\theta} \tag{6}$$

where θ is the fraction of the surface covered, P' is the equilibrium pressure or the "virtual pressure" of nitrogen, v is the rate of adsorption, w is the rate of desorption, and f, a_0, k_a, k_d, g, and h are constants. These equations are constructed to conform to the idea that the rates of adsorption and desorption of nitrogen depend exponentially on the fraction of the surface covered with nitrogen. At high coverage, adsorption is slow and desorption fast. Incidentally, it may be noted that measurements by Emmett and Brunauer [P. H. Emmett and S. Brunauer, *J. Am. Chem. Soc.* **56**, 35 (1934)] showed that up to 50 atm partial pressure, the adsorption of nitrogen increased as $(P_{N_2})^{1/6}$ regardless of whether the nitrogen was by itself or equilibrated with a 3:1 H_2:N_2 mixture.

In applying these equations, the authors assumed that the adsorption of nitrogen on the iron catalyst in the presence of an ammonia–hydrogen mixture is the same as it would be when at a nitrogen pressure equivalent to the existing partial pressure of ammonia and hydrogen in the gas mixture. Thus, since the equilibrium constant for ammonia synthesis is

$$K = (P_{NH_3})^2 / (P_{H_2})^3 (P_{N_2}) \tag{7}$$

the value of P' can be represented by $(P_{NH_3})^2 / K (P_{H_2})^3$, and the first of the Temkin equations becomes

$$\theta = (1/f)\ln \frac{a_0 (P_{NH_3})^2}{(P_{H_2})^3 K}. \tag{8}$$

As an illustration, the application of these equations to the decomposition of ammonia would take the form

$$W = k_d \exp\left[(h/f)\ln a_0 \frac{(P_{NH_3})^2}{(P_{H_2})^3 K}\right] = k_d \left[\frac{(P_{NH_3})^2 a_0}{(P_{H_2})^3 K}\right]^{h/f} = k_2 \left[\frac{(P_{NH_3})^2}{(P_{H_2})^3}\right]^{\beta}. \tag{9}$$

Love and Emmett [K. S. Love and P. H. Emmett, *J. Am. Chem. Soc.* **63**, 3297 (1991)] found experimentally that over a doubly promoted catalyst the rate of decomposition is proportional to $(P_{NH_3})^{0.6}/(P_{H_2})^{0.9}$. This would correspond to β having a value of 0.3.

The three seminal ideas in this early work of Temkin are quite general. The first is that adsorption of nitrogen is rate determining. The second is the virtual pressure or fugacity of adsorbed nitrogen, a concept of great importance to the understanding of catalytic cycles at the steady state. The third idea is the kinetic description of the catalytic surface as a nonuniform one. The last was systematized later by Temkin's school, both in theory and in application, to a

large number of important catalytic reactions. The importance of Temkin's theory of kinetics on nonuniform surfaces is not so much in its formation but in the deeper kinetic understanding of how any catalyst works and how to select the catalyst with the fastest turnover rate.

Like the kinetic concepts of Christiansen and Horiuti, those of Temkin were far ahead of their common acceptance by the catalytic community. Even today, more than 50 years after the Temkin–Pyzhev paper, the idea of virtual fugacity is not well understood by the majority of workers in catalytic kinetics. It is safe to predict that many of the other ideas of Temkin, like that of average stoichiometric number or reaction routes, will influence younger catalytic kineticists who now have access to powerful computers.

The legacy of Temkin is a rich one. While strong on theory, Temkin was also a gifted and exacting experimentalist. He and his co-workers proposed and built in 1950 a continuous flow reactor that operates in a "gradientless" manner to measure directly the rate of reactions catalyzed by solids.

Jean-Paul Sartre is reported to have said "I shall die twice: the first time physically, and the second time when no one shall read my works." Mikhail Temkin will live a long, long second life, as his name will remain known by new generations of kineticists who will not even need to read the original writings, since the main ideas of Temkin are already in all textbooks and monographs on heterogeneous catalysis.

MICHEL BOUDART

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Application of Percolation Theory to Describing Kinetic Processes in Porous Solids

V. P. ZHDANOV

Institute of Catalysis
Novosibirsk 630090, Russia

I.   Introduction

Porous solids are widely encountered in industry and everyday life, and their importance has long been recognized by scientists and engineers (*1*). A considerable amount of work on porous solids has been undertaken in both academic and industrial laboratories (*1,2*).

The properties of porous solids, e.g., adsorptive capacity, chemical reactivity, and catalytic activity, are dependent on their pore structure. In general, porous materials may have extremely complex pore structures, which are difficult to represent by simple geometrical models. As a rule, however, the actual pore structures belong to either corpuscular or spongy classes (*3,4*). Corpuscular systems are formed by particles of various shapes connected to one another. In this case, the pores represent interstices between particles (see, e.g., Fig. 1). In spongy structures, the pore space can be treated as a lattice of voids interconnected by necks in a three-dimensional network (Figs. 2 and 3). In turn, the latter class of porous solids can be divided into two groups: (1) structures with the pore volume concentrated primarily in voids, whereas the necks possess no volume of their own (Fig. 2), and (2) structures with the pore volume concentrated in necks, whereas the void volume is negligible (Fig. 3). There exist, of course, mixed structures wherein, for example, particles of a corpuscular system may have inner spongy porosity.

A feature of special interest for many purposes is the width of pores, e.g., the diameter of a cylindrical pore, or the distance between the sides of a slit-shaped pore. A convenient classification of pores according to their
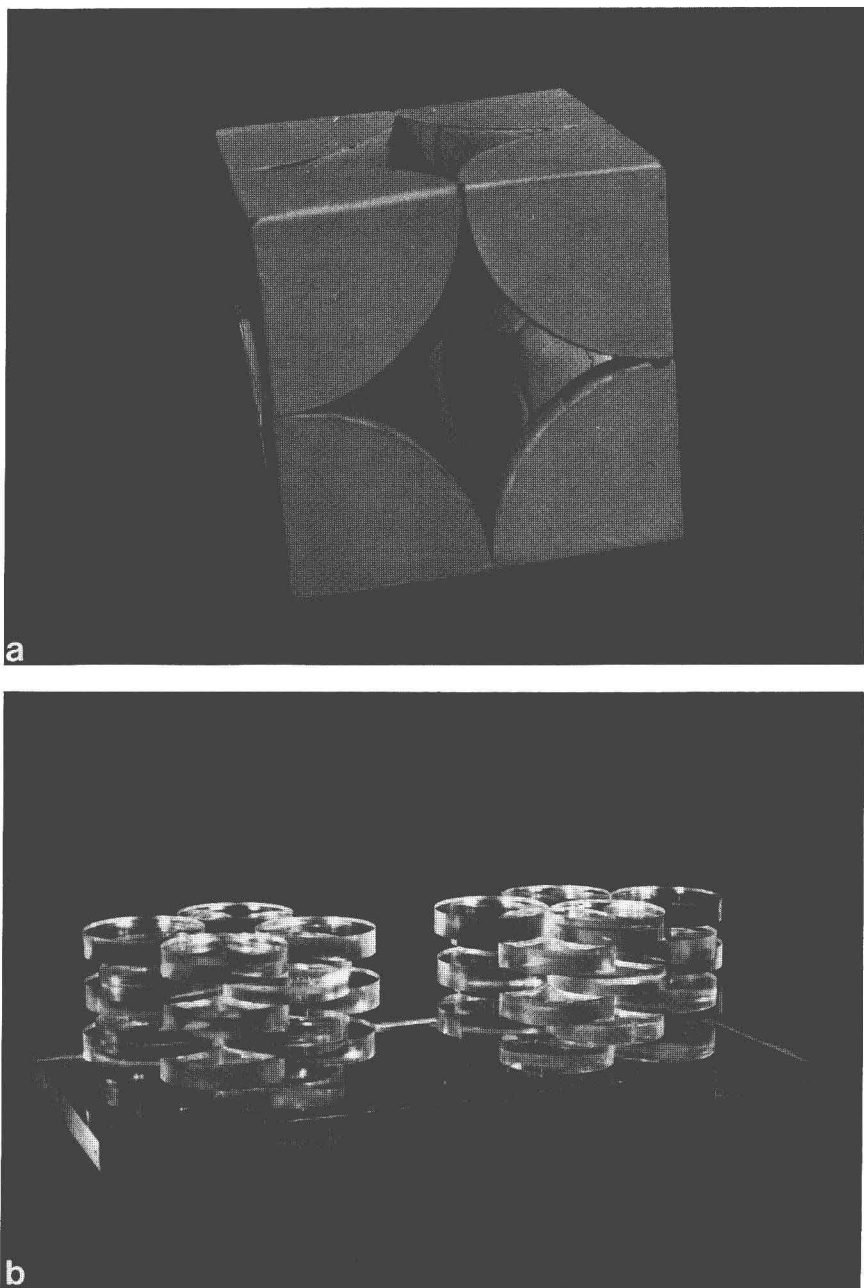
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FIG. 1. Corpuscular porous structures. (a) The element of the packing of spheres; (b) the model of round disk packings; (c,d) models of the packing of round rods.