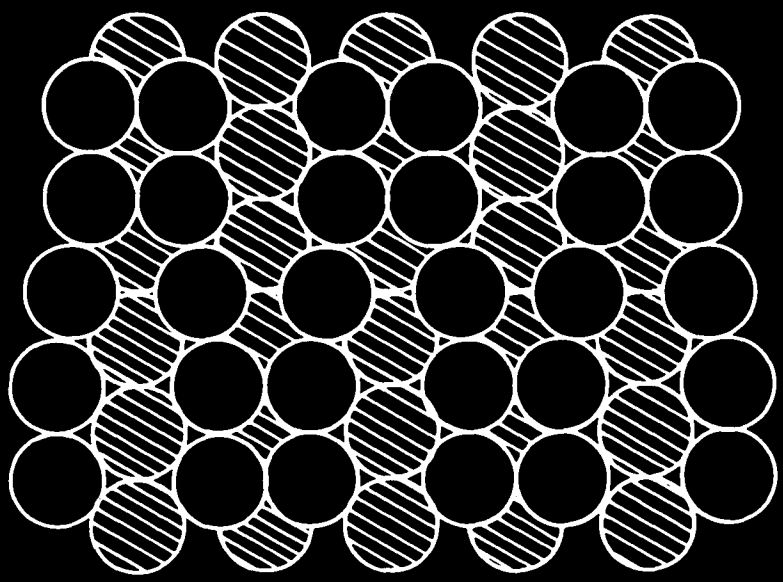
# HYDROGEN EFFECTS IN CATALYSIS

## Fundamentals and Practical Applications



edited by
Zoltán Paál
P. G. Menon

# Hydrogen Effects in Catalysis

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Zoltán Paál

Institute of Isotopes of the
Hungarian Academy of Sciences
Budapest, Hungary

P. G. Menon

Dow Chemical (Nederland) B.V.
Terneuzen, The Netherlands
Chalmers University of Technology
Gothenburg, Sweden

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# Preface

It is now being increasingly recognized that catalytically active surface sites may (or should) contain atoms different from that of the catalyst material. Several attempts have been made to define working catalysts as "catalytic systems" rather than clean substances. Boudart wrote as early as 1975 that "the definition of a working catalyst must include all the surface species of the catalyst in its working state": the catalyst itself, added promoters, chance impurities, and components arising from the reactant(s). However, the exact information on this working state still "remains an elusive goal of research in catalysis" (M. Boudart, *J. Vac. Sci. Technol., 12*, 329 [1975]).

One should not think that the additives responsible for catalytic action are necessarily present in minute amounts. G. K. Chesterton in one of his Father Brown stories describes a case when four reliable and observant persons testify that nobody entered a house where and when a murder was committed. Father Brown's simple wisdom is necessary to realize that a "mentally invisible man" must be held responsible—a man who in a "striking and showy costume" entered the house "under eight human eyes"—namely a postman. "Nobody ever notices postmen, somehow," he concludes, "yet they have passions like other men" (G. K. Chesterton, The Invisible Man. In *The Innocence of Father Brown*, Penguin, Harmondsworth [1950], p. 92).

Hydrogen, especially in metal catalysis, can be compared to this "mentally invisible" postman. Its presence (usually in ample amounts) has been taken for granted and, so far, most studies have not tried to dig deep and look at whether it participates in creating catalytically active surfaces, and if so, how. Unlike postmen, hydrogen does not wear a "striking and showy costume": on the contrary, it is a rather difficult species to detect by most of the regular techniques of surface science. So we may conclude that nobody ever notices hydrogen; yet it has an influence on catalytic systems as other additives. Not that this influence would be murderous to catalysis; experience shows just the contrary—but alas! "mentally invisible" benefactors escape notice much easier than villains.

The interest in hydrogen increases in various fields of science and technology, especially its prospective use as an absolutely "clean" energy source (see also Chapter 23). Several changes in the chemisorptive and catalytic properties of metals brought about by hydrogen have been reviewed recently by us elsewhere (Z. Paál and P. G. Menon, *Catal. Rev.-Sci. Eng., 25*, 229 [1983]). The time and context now are considered proper for an attempt to

devote a full book to hydrogen effects in catalysis. Such a book should necessarily cover a very wide range of subjects. Throughout the present compilation, a vertical treatment has been attempted which covers hydrogen effects in catalysis in the broadest sense, from surface science to industrial applications. This is reflected by the five main parts of this work.

Part I deals with phenomena observed with well-defined catalyst surfaces—the typical surface science approach. Most of the methods applied here are indirect ones. These are summarized in Chapter 1. Chapter 2 deals with vibrational spectroscopy, representing a rare family of techniques suitable for gaining direct information from surface hydrogen. The results can be summarized in terms of postulating a "hydrogen fog" *on* metal surfaces which can be almost as much delocalized as the "electron cloud" *in* metals.

Physico-chemical methods suitable for characterizing practical catalysts have been collected in Part II. Traditional techniques supplying indirect information such as adsorption heat measurements, surface titrations, and temperature-programmed studies are presented first. The description and results of less common techniques such as magnetic measurements, infrared spectroscopy, and neutron diffraction follow, the last two being able to supply direct information on hydrogen. Their vast possibilities are still dormant. Also included is a chapter on electrochemical methods, which are able to give exclusive results on what happens on the surface proper.

Perhaps the climax of the book is Part III, dealing with the role of hydrogen to produce active working catalyst surfaces. The complex nature of catalysis science is truly reflected in its five chapters. One or more of the phenomena treated here (e.g., sintering, dissolution of hydrogen, and eventual hydride formation—all solid-state transformations) or the two particular aspects related to catalysis, namely hydrogen spillover and strong metal-support interactions, may often take place in the lifetime of any catalyst, be it the few grams in a laboratory test or the several tons in an industrial reactor. In Chapter 12 it is correctly remarked that hydrogen spillover may not be tremendously significant by itself, but as a first crucial step in a sequence it may be very important. The same is more or less true for other effects treated in Part III and, perhaps, in the whole book.

Real catalytic chemistry comes in Part IV, where hydrogen effects on various reactions are treated. These include those when hydrogen is an "astoichiometric" component, i.e., when it does not participate in the stoichiometric equation of the reaction. Most typical examples of reactions are hydrocarbon transformations on metals. That is the reason that these reactions were selected to illustrate the general kinetics of hydrogen effects. In Chapter 15, rather uncommon effects of hydrogen are revealed. Such delicacies as comparing low- and high-pressure reactions on single crystals follow: hydrogen effects may help construct that long-awaited bridge between single-crystal work and real catalysts. Both hydrogenation and skeletal reactions of hydrocarbons offer a number of examples of hydrogen effects. Still, attention has to be drawn to Chapter 19, where a largely unexplored field has been opened up: the catalytic transformations of oxygenated organic compounds. Although a host of phenomena are highlighted here, these compounds still represent a minority of organic compounds. The present trends toward striving at producing special chemicals in increasing numbers certainly will benefit from hydrogen effects in selectivity regulation. The last two chapters of this part illustrate that hydrogen effects are not confined to metal catalysts; oxide and sulfide catalysts—though less explored at present—also exhibit some of them.

The last part (Part V, Technological Implications) can necessarily give only an incomplete excerpt on what hydrogen can do in industrial catalysis.

Again, metal catalysts and hydrocarbon reactants represent most widely studied systems, as indicated by the three chapters dealing with this subject. Apart from industrial hydrogenations, such important processes as those in catalytic reforming and such novelties as hydrogen diffusion through metal catalysts are dealt with. There are indications that even an important process like ammonia synthesis can also exhibit typical hydrogen effects; these have, however, not been explored to an extent that a separate chapter could be devoted to them. The last two chapters also divert attention from metallic systems: hydrogen transfer reactions, so important in up-to-date industrial processes using zeolite catalysts, have been treated adequately. The last chapter calls attention to hydrogen effects in Ziegler-Natta and other olefin polymerization, an area with which most people in (heterogeneous) catalysis research and development are usually not very familiar. Just as with metallic and oxide catalysts, here, too, hydrogen plays a double role: on the one hand, it is part of the catalyst system itself; on the other hand, it is a powerful probe to investigate the nature of active sites in olefin polymerization catalysts (because it can respond so selectively and specifically to the different polymerization centers).

The book contains altogether 28 chapters, written by 38 authors from 10 different countries. A beautiful example, indeed, of international cooperation, typical for catalysis as for any other specialized field of science. The editors want to thank here all the other 36 authors—colleagues and friends, whose whole-hearted cooperation has made this venture possible and successful. We also thank Dr. Heinz Heinemann, Consulting Editor of the Chemical Industries series, for his advice and helpful comments at various stages in the compilation of this work.

Compiling this book was undertaken with a double goal in mind: to obtain state-of-the-art reviews on the phenomena collectively called "hydrogen effects" and to draw the attention of the catalysis community to the importance of these phenomena both in the science and technology of catalysis. Hence this book does not close or summarize the subject; instead, it is meant to introduce the various facets of this subject and stimulate further studies in this field.

Zoltán Paál
P. G. Menon

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PART V TECHNOLOGICAL IMPLICATIONS