

ADVANCES IN CATALYSIS

VOLUME 27

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ADVANCES IN CATALYSIS

VOLUME 27

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Preface

RAINBOWS AND CATALYSIS

A rainbow is a beautiful and somehow a very systematic and complete phenomenon. It presents colors systematically, according to wavelengths, and it is complete in that it presents to us the colors of the entire visible spectrum. We think that its systematic progression and its completeness are responsible for its beauty.

The science of catalysis covers a large spectrum of phenomena. We observe—with some pride and joy—that this volume presents eight topics which, like the rainbow, form an almost systematic and complete sweep of the major classes of topics in catalysis. It spans from the most classical mechanistic study (P. W. Selwood), to a presentation of a “hard” practical application (M. Shelef *et al.*). As we sweep across, we cover characterization studies of catalyst solids in terms of electronic (G. M. Schwab), surface chemical (H. A. Benesi and B. H. C. Winquist), as well as physicochemical and structural (F. E. Massoth) parameters, chemical reaction mechanisms and pathways (G. W. Keulks *et al.*, and B. Gorewit and M. Tsutsui), and a topic on reactor behavior (V. Hlaváček and J. Votruba), which takes us from the single catalyst particle to the macroscopic total reactor operation.

It strikes us that by way of this display of major topics in catalytic science, this volume will serve doubly; as a record of progress as well as a book of general instruction on catalysis.

P. B. WEISZ

Corrigendum

On page xiv of Volume 26 of this publication, the following correction should be noted:

Humphrey Owen Jones Professor of Colloid Science should read John Humphrey Plummer Professor of Colloid Science at Cambridge.

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Electronics of Supported Catalysts

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I. Introduction

The term *electronics* normally refers to the theory and function of the electronic devices and circuits used so universally for measurement, control, and computation. Conventional electronics is an important tool also in the study of supported catalysts.

In this paper the term *electronics* is used with a different connotation: it stands for the description of electron transitions to and from, as well as within supported catalysts. It will be shown that in many cases such transitions are responsible for the enhanced or reduced catalytic activities of supported catalysis. In this concept, supported catalysts are described as solid state systems in which a catalytically active component (the

catalyst) is in electrical contact with a second solid (the support or carrier) that, by itself, has little or no catalytic activity.

The electronic structure of a solid metal or semiconductor is described by the band theory that considers the possible energy states of delocalized electrons in the crystal lattice. An apparent difficulty for the application of band theory to solid state catalysis is that the theory describes the situation in an infinitely extended lattice whereas the catalytic process is located on an external crystal surface where the lattice ends. In attempting to develop a correlation between catalytic surface processes and the bulk electronic properties of catalysts as described by the band theory, the approach taken in the following pages will be to assume a correlation between bulk and surface electronic properties. For example, it is assumed that lack of electrons in the bulk results in empty orbitals in the surface; conversely, excess electrons in the bulk should result in occupied orbitals in the surface (1). This principle gains strong support from the consistency of the description thus achieved. In the following, the principle will be applied to supported catalysts.

New experimental methods such as AES, ESCA, FEM, FIMS, LEED, SEM, and SIMS (2) allow for the first time to dispense with the above assumption since they permit direct study of surface processes. Stimulated by these developments, the theoretical treatment tends to turn more toward consideration of single surface atoms and their orbitals or bonds. However, it is clear that this direction of research is still in its beginning and therefore restricted to very special cases. The treatment of the more complex problems presented by supported catalysts by such methods—in experiment and in theory—is still ahead. Thus for the moment the use of band theory is much more promising as it can be based on a large amount of existing data.

A. TEST REACTIONS

During the last two decades it has been found that there is a special group of chemical reactions, essentially redox reactions, for which the catalytic influence of solids can be interpreted in terms of the catalyst's electronic structure and the controlled variations of that structure. The study of single-phase catalysts and the relationship between function and electronic structure of solid state catalysts show that redox reactions may be divided into two classes. *Donor reactions* are reactions in which the rate-determining step involves an electron transition from the reactant molecule to the catalyst; *acceptor reactions* are those where the reactant must accept electrons from the catalyst in order to form the activated state. Broadly speaking, donor reactions mobilize reducing agents like

hydrogen or carbon monoxide and thus are involved in reactions such as hydrogenation, dehydrogenation, parahydrogen conversion, deuterium exchange, and so forth. Acceptor reactions mobilize oxygen or other oxidants such as H_2O_2 (3). Following this concept, certain reactions have come to be used as tests for the ability of catalysts to accept or donate electrons. For example, the dehydrogenation of formic acid vapor is a typical donor reaction while the decomposition of hydrogen peroxide is a typical acceptor reaction; the oxidation of carbon monoxide can be of one or the other type, depending on the electronic character of the catalyst.

With metallic catalysts as well as with semiconductors,* it has been found experimentally that donor reactions are best catalyzed by metals with many empty electron states (*d* metals or univalent *B* metals) and by p-type semiconductors, whereas acceptor reactions require electron-rich alloys or n-type semiconductors.

These general considerations, which may be summarized as "the electronic factor in catalysis," describe a broad group of catalytic reactions satisfactorily, although not all kinds (4). Thus, it appears hopeful to extend these considerations from single catalysts to mixed catalysts—and especially supported catalysts—with their often striking effects. The technical significance of these catalyst systems provides added incentive for applying the electronic viewpoint, in an attempt to gain a better understanding of their function and effectiveness.

B. GENERAL CONSIDERATIONS

Two kinds of influence of a carrier on the activity of a catalyst have been known since many years (5):

1. *Structural promotion*: A highly dispersed support can provide and (or) stabilize a high surface area of the catalyst supported by it. A typical example is ammonia synthesis where the thermal sintering of the iron catalyst is inhibited by alumina (although the phase configuration is different).

2. *Synergetic promotion*: Here the support interacts energetically with the catalyst and produces a new kind of active entity.

Phenomenologically, synergetic promotion is characterized by an increased reaction rate, accompanied by a decreased activation energy, compared with the catalyst alone. Structural promotion, on the other

* Insulators are not amenable to treatment of catalytic activity in terms of electronic band theory.

hand, does not alter the activation energy.* Since nearly all industrially important catalytic reactions use supported catalysts of the synergetic type, development of a correlation between these effects and other solid state properties is not only a challenging scientific problem but, if successful, promises to yield rational guidelines for the design and preparation of better industrial catalysts.

The task of tackling this problem from the electronics viewpoint must start from the experience with single catalysts, which indicates that correlations exist between catalytic and bulk electronic properties. In going from single-phase to supported catalysts, the working hypothesis may be stated as follows: is it not possible (or even probable) that the electronic and hence the catalytic properties of a catalyst are influenced by the electronic properties of an inert support with which the catalyst is in intimate, electrically conducting contact? For example, a small amount of a metal, dispersed on the surface of a large amount of a semiconducting carrier, must necessarily adjust its Fermi level to the Fermi level of the semiconductor. The position of the Fermi border of the metal within its Brillouin zone in turn influences not only the conductivity in the well-known manner, but also according to the findings cited earlier, catalytic activity. Cases where metallic catalysts are supported by semiconducting carriers (e.g., Al_2O_3) are very frequently encountered in industrial processes (2, 13). The technical success of such catalyst systems thus appears to become accessible to a new understanding, at least in certain cases.

The hypothesis can be tested if the catalytic activity of a metal can be modified by a controlled shift of the Fermi level of the support. With semiconducting supports such a shift is readily achieved by doping: additions of cations of higher charge than that of the matrix cations produces quasi-free electrons and/or removes defect electrons and raises the Fermi level; addition of lower charged cations has the opposite effect. This calls for investigation of metal catalysts on doped semiconductors as supports.

The inverse case, a semiconducting catalyst supported by a metal, termed *inverse supported catalyst*, has been studied systematically only in the last few years. Here, even more drastic effects can be expected because normally the number of free electrons in a metal is several orders of magnitude higher than in semiconductors. The effects are indeed considerably larger as will be shown below. However, the principles and the theory involved are more complex (6-8).

* It should be mentioned here that there are also some cases of "anomalous promotion" in which both reaction rate and activation energy are increased. In these special cases, the frequency factor is increased sufficiently to more than compensate for the increased activation energy.

In a metal, the Fermi level is located within the conduction band. In a semiconductor, this level usually is found in the forbidden gap between the valence band and the conductivity band; by doping it can be shifted up or down relative to the band edges. The activation energy of a catalyzed reaction depends on the distance of the Fermi level from the band edges: for acceptor reactions it is related to the distance from the conduction band, for donor reactions to the distance from the valence band. The exact theory will not be presented here; it has been given by Hauffe (6) and by Steinbach (9).

An important consideration for the electronics of semiconductor/metal supported catalysts is that the work function of metals as a rule is smaller than that of semiconductors. As a consequence, before contact the Fermi level in the metal is higher than that in the semiconductor. After contact electrons pass from the metal to the semiconductor, and the semiconductor's bands are bent downward in a thin boundary layer, the space charge region. In this region the conduction band approaches the Fermi level; this situation tends to favor acceptor reactions and slow down donor reactions. This concept can be tested by two methods. One is the variation of the thickness of a catalyst layer. Since the bands are bent only within a boundary layer of perhaps 10^{-5} to 10^{-6} cm in width, a variation of the catalyst layer thickness or particle size should result in variations of the activation energy and the rate of the catalyzed reaction. A second test consists in a variation of the work function of the metallic support, which is easily possible by preparing homogeneous alloys with additive metals that are either electron-rich or electron-poor relative to the main support metal.

In a few cases (10) catalysts have been studied that consist of mixtures of two semiconductors of the same chemical composition but with different levels of doping. The considerations here are analogous to those presented above. Of course, the ultimate proof as to whether electronic factors are indeed responsible for the catalytic effects discussed above will have to come through physical measurements of the electronic properties of catalyst/support systems.

In this section, we have alternatively mentioned catalytic activity and catalytic activation energy as the characteristics influenced by support effects. In the following examples, we will concentrate on changes of the true or apparent activation energy* as prime indicator. This simplifying procedure is justified by the empirical fact that for a group of closely comparable reactions (here, identical reactions on identical catalysts having variable supports or promoters) there is generally a linear relationship

* The term *true activation energy* refers to the activation energy for the rate-determining step, free of adsorption energy terms.