

BASE METAL OXIDE CATALYSTS

for the Petrochemical, Petroleum,
and Chemical Industries

A Special Report by

JOHN HAPPEL MIGUEL HNATOW

and

LAIMONIS BAJARS

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*Catalysis Research Corporation
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PREFACE

Complex oxide catalysts are finding increasing application in oxidation, hydrogenation, and dehydrogenation reactions. These materials are often superior to mere mixtures of their component binary oxides. Thus, magnesium ferrites used in oxidative dehydrogenation to produce butadiene cannot be considered simply as iron oxide on a magnesia support. Many such ternary and quaternary oxides have become available because of their use in electroceramics, but their use as catalysts is still far from completely exploited.

Though no simple rules can be presented for catalyst selection, crystal structure plays an important role in determining the performance of such catalysts and thus furnishes a unifying thread for their development. In the survey of catalytic applications of complex oxides presented in this book, a classification based largely on the several types of crystal structures available has been employed. This furnishes a convenient point of departure from the voluminous literature on polycrystalline materials and their physical properties. Separate chapters are devoted to such structures as the perovskites and spinels. A number of other complex oxide catalysts are discussed which owe an important element in their behavior to their structures.

PREFACE

Special attention is devoted to the patent literature, which is an important source of available information in catalysis in many cases. A considerable body of Russian literature in this field is also reviewed.

It is hoped that this book will be of interest to those faced with problems of development and improvement of industrial catalysts. Formulations based on complex oxides may prove more effective and economical than the precious metals for a variety of applications in such fields as energy and environmental control.

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Chapter 1

INTRODUCTION

Complex oxides containing two or three cations have attracted increased attention for application in heterogeneous catalysis in recent years. Such ternary and quaternary oxides possess a variety of properties which are not possible with the simple binary oxides that are more commonly employed as industrial catalyst components. Many of these properties have been exploited by the demands of electronics technology, which have led to a fast-growing synthetic ceramics industry. Starting with the production of special oxide refractories, this new branch of industry expanded into the development of ceramic insulators, capacitor dielectrics, and most recently, ceramic semiconductors and magnetic ceramics. A vast amount of information on the physical properties of electronic interest has become available in the literature. Many of the compounds developed have potential application as catalysts.

The purpose of this book is to examine the properties of various electroceramics and related materials from the viewpoint of applications to catalysis. General principles and rules for catalyst selection will be briefly reviewed in this chapter with special attention devoted to those which may serve as guides to selection of appropriate complex oxides from the wide variety of possibilities. New ideas for experimental development of

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catalysis will also be briefly discussed since development on purely theoretical grounds is still not possible. The following chapter will deal specifically with properties of the complex oxides which are useful for catalytic applications and how these can be varied by catalyst preparation procedures. Later chapters will survey the structure and applications of specific crystal types: spinels, perovskites, and others.

At the outset, it should be appreciated that the complex oxides will not find application in all branches of catalysis. Thus, a useful classification of catalytic reactions divides them into two types: oxidation-reduction (electronic) and acid-base (ionic). Reactions of the first type include those of oxidation, reduction, hydrogenation, dehydrogenation, and hydrogenolysis. These reactions are catalyzed by solids possessing free or easily excited electrons, i. e., metals and semiconductors. Reactions of the second type include polymerization, isomerization, cracking, dehydration, alkylation, halogenation, and dehalogenation. These reactions are catalyzed by acidic or basic properties of the catalyst, often accelerated by carbonium ion mechanisms in the case of hydrocarbon reactions. The complex oxides which we consider in this book belong to the oxidation-reduction type and their effectiveness is related to electronic properties.

Of the electronic catalysts, the metals possess characteristics which distinguish them from semiconductors. They are in general suitable for hydrogenation and dehydrogenation but not as suitable for oxidation. The semiconductors include largely oxides and, to a smaller extent, sulfides. These

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materials are generally suitable for oxidation-reduction processes but are not as good as metals for hydrogenation reactions. Some success has been achieved in the case of metals in relating catalytic activity to position in the periodic table, metals of Groups VIII and I-B being most useful. In the case of binary compounds (mostly oxides), the number of possibilities increases, especially when different valence states and crystal modifications are considered. Periodic table position for these and the mixed oxides which we will consider is not as useful as in the case of metals.

One of the chief uses of mixed oxide catalysts has been in hydrocarbon oxidation. The binary oxides tend to catalyze deep oxidation to carbon dioxide and water and thus have potential use instead of the metal catalysts for atmospheric pollution abatement by treatment of industrial fumes and automotive exhausts. Partial oxidation to selectively produce various petrochemicals represents a field in which the mixed oxide formulations have shown great versatility.

Table 1.1 illustrates the formation of some of these products and furnishes a basis for catalyst solution using a descriptive chemistry classification for these reactions. Materials catalyzing one reaction in any of the three classes will often be useful for catalyzing other reactions in the same class.

A recent book by Hucknall (1974) presents a critical review of the selective oxidation of olefins and alkanes. Special emphasis is given to reactions of commercial interest, including:

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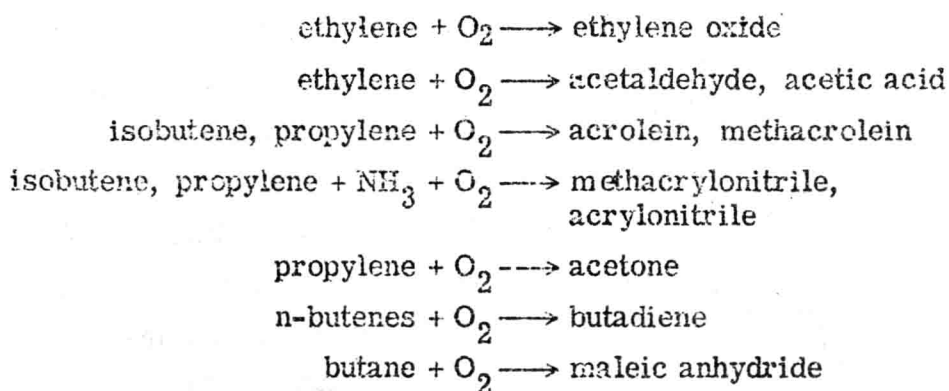


TABLE 1. 1

Classification of Hydrocarbon Oxidation Reactions

-
- I. Reactions without carbon-carbon bond fission
 - A. Without oxygen incorporation
 - Oxidative dehydrogenation (butene to butadiene)^a
 - Oxidative dehydrocyclization (hexane to cyclohexane)
 - Oxidative dimerization (propylene to hexadiene and benzene)
 - B. With oxygen incorporation
 - Formation of aldehydes and ketones (propylene to acrolein and acetone)
 - Formation of alcohols (propylene to allyl alcohol)
 - Formation of unsaturated acids (propylene to acrylic acid)
 - Formation of esters (ethylene and acetic acid to vinyl acetate)
 - II. Reaction with carbon-carbon bond fission
 - Formation of saturated aldehydes and acids (propylene to acetaldehyde and acetic acid)
 - Reaction of alkyl aromatics without ring fission (toluene to benzene)

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TABLE 1.1 (continued)

Reaction of aromatics with ring fission (benzene to maleic anhydride, naphthalene to phthalic anhydride)

III. Deep oxidation

Formation of CO and CO₂

^aExamples are given in parentheses.

Source: After Bond (1974).

Catalysis by metals and binary oxides as well as mixed oxides is discussed. As this author notes, surprisingly few facts of general applicability have emerged. Experimental evidence indicates that all selective oxidation catalysts are composed of at least two oxide components, one responsible for activity and the other for selectivity, but it is still not known whether both cationic centers participate in surface processes or whether the role of activating component consists only in modifying the oxygen-metal bond in the base catalyst.

In addition to reactions involving hydrocarbons, mixed oxides have some application in oxidation-reduction reactions involving simpler molecules. Included in this category are the oxidation of CO and the reduction of NO_x and SO₂.

To proceed past the classification stage and arrive at the selection of a catalyst for a specific reaction is not a straightforward process but requires interplay of theory and experiment. A heterogeneous overall chemical reaction will be

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characterized by intermediate steps like its homogeneous analog, but it is because of the steps involving the catalyst that the velocity of the reaction is increased. This is accomplished by the formation of intermediates which are formed and decomposed on the catalyst surface. The unique function of the catalyst lies in the so-called activated processes involving reactant chemisorption, surface reaction, and product desorption. Diffusional controlled processes whereby reactants are transferred from the bulk phase of a reactant gas mixture to the catalyst surface and through catalyst pores to active sites and the reverse process in which products are returned to the bulk phase are important in catalyst performance. The presence of such effects must be taken into account in catalyst preparation and in design of equipment for its use but will usually not be the major factor in catalyst selection.

A systematic approach to the problem of developing a catalyst for a new reaction consists in establishing first a plausible mechanism for the desired reaction. Based upon the chemistry involved, a network of simple reactions can be written which will satisfy the required stoichiometry. Following ideas of surface chemistry as exemplified by the Langmuir-Hinshelwood approach to heterogeneous kinetics, mechanistic steps involving chemisorption and desorption can be included. At this point, either by analogy to similar reactions which have been studied or by obtaining experimental data for the system involved on a potential (not necessarily optimum) catalyst, one attempts to assess which step or steps are critical or rate-controlling in the chosen mechanism.

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The method for developing the appropriate rate equations using the Langmuir-Hinshelwood procedure has been well documented (Hougen and Watson, 1947; Boudart, 1968; Thomas and Thomas, 1967; Smith, 1970). Although some of the basic postulates used in arriving at rate expressions using this procedure have been questioned, it appears to lead to useful and reasonable interpretation of experimental data.

A simple illustration (Happel, 1968) of the use of this procedure to obtain information on reaction mechanism is arrived at by considering the overall reaction



with the following assumed mechanism for a heterogeneous catalyzed system:



Here l represents catalyst sites and Al and Bl are chemisorbed intermediates. The reaction velocities at steady-state for the three mechanistic steps are given by $v_{\pm i}$, $i = 1, 2$, or 3 .

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The Langmuir hypothesis amounts to assuming that the velocities of individual reaction steps may be expressed as

$$\begin{aligned} v_{+1} &= k_{+1} p_A C_\ell & v_{-1} &= k_{-1} C_{A\ell} \\ v_{+2} &= k_{+2} C_{A\ell} & v_{-2} &= k_{-2} C_{B\ell} \\ v_{+3} &= k_{+3} C_{B\ell} & v_{-3} &= k_{-3} C_\ell p_B \end{aligned} \quad (1.3)$$

where reaction velocity constants are denoted by k_i , and C_i refers to the surface concentrations of appropriate species. By making use of the relationships for steady-state,

$$V = v_{+1} - v_{-1} = v_{+2} - v_{-2} = v_{+3} - v_{-3} \quad (1.4)$$

we can express $C_{A\ell}$ and $C_{B\ell}$ in terms of C_ℓ , the concentration of unoccupied sites. To obtain C_ℓ , we then use the equation

$$C_\ell + C_{B\ell} + C_{A\ell} = C_t = 1 \quad (1.5)$$

Taking the total area C_t as unity does not result in loss of generality of the final expression, since the units of reaction velocity constants are arbitrary. The final expression for reaction velocity is then

$$V = \frac{k_{+1} k_{+2} k_{+3} C_\ell p_A}{k_{+2} k_{+3} + k_{+3} k_{-1} + k_{-1} k_{-2}} \left(1 - \frac{p_B}{p_A K_P} \right) \quad (1.6)$$