

# **Solid State Chemistry in Catalysis**

**EDITED BY**  
**Robert K. Grasselli**  
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*The Standard Oil Company*

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Based on a symposium sponsored by  
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## FOREWORD

The ACS SYMPOSIUM SERIES was founded in 1974 to provide a medium for publishing symposia quickly in book form. The format of the Series parallels that of the continuing ADVANCES IN CHEMISTRY SERIES except that, in order to save time, the papers are not typeset but are reproduced as they are submitted by the authors in camera-ready form. Papers are reviewed under the supervision of the Editors with the assistance of the Series Advisory Board and are selected to maintain the integrity of the symposia; however, verbatim reproductions of previously published papers are not accepted. Both reviews and reports of research are acceptable, because symposia may embrace both types of presentation.

# PREFACE

**H**ETEROGENEOUS CATALYSIS has been synonymous with industrial catalysis and the chemical industry since the time of Berzelius, Sabatier, Ostwald, Haber, Bosch, Mittasch, Fischer, and Hüttig, as well as many others. To this day, virtually all chemical and refining processes are based on the use of solid catalysts that effect selective transformations of hydrocarbon molecules to desired products in the vapor phase. Nonetheless, correlations between structural aspects of solid materials and their behavior as catalysts are relatively recent developments. Probably first to recognize the importance of structure in catalysis were researchers in the field of catalytic cracking who investigated the catalytic activity of natural clays and minerals in the early 1930s. The culmination of that work was the discovery of zeolitic cracking catalysts in the early 1960s and the subsequent development of the concept of shape selective catalysis.

With the advent of highly sophisticated instrumentation for precise structure determination, key catalytic roles are being recognized for many subtle features of solid state materials, such as point and extended defects, surface structure and surface composition, atomic coordination, phase boundaries, and intergrowths. Today, X-ray structure analysis is routine in heterogeneous catalysis research and has become as common and necessary as BET surface area analysis for characterizing solid catalysts. In addition, high resolution electron microscopy; photoelectron, IR, and Raman spectroscopies; solid state NMR; and even neutron diffraction are assuming increasingly important roles in both applied and fundamental catalysis research. Information about solids on the atomic and molecular level, which these techniques provide when combined with traditional catalytic studies (e.g., reaction kinetics, tracer studies, and molecular probes), gives a better fundamental understanding of complex catalytic phenomena. Correlations between the solid state and catalytic properties assessed through the application of sophisticated instrumentation and classical mechanistic approaches are the central theme of this book.

The book comprises 20 chapters that focus on state-of-the-art understanding of solid state mechanisms in heterogeneous catalysis and the relationship between catalytic behavior and solid state structure. The volume contains expanded and updated versions of papers presented on this subject at the ACS symposia in Washington, D.C. (1983) and Las Vegas (1982), and of written contributions from invited participants who could not attend these

meetings. It emphasizes catalysis with oxides, sulfides, and zeolites. Although by no means an exhaustive treatise, we hope that it provides the reader with an understanding of the role the solid state plays in heterogeneous catalysis and gives an appreciation for the contributions solid state chemistry has made to the advancement of catalytic science and technology.

We should like to thank all the contributors for their excellent cooperation and patience during the process of editing this book and to the ACS for making this publication possible.

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## **OXIDES**



# Catalysis by Transition Metal Oxides

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Catalytic oxidation reactions are divided into two groups: electrophilic oxidation proceeding through activation of oxygen and nucleophilic oxidation in which activation of the hydrocarbon molecule is the first step, followed by consecutive hydrogen abstraction and nucleophilic oxygen insertion. Properties of individual cations and their coordination polyhedra determine their behaviour as active centers responsible for activation of hydrocarbon molecules. A facile route for nucleophilic insertion of oxygen into such molecules by group V, VI and VII transition metal oxides is provided by the crystallographic shear mechanism, catalytic properties are thus dependent upon the geometry of the surface. The catalyst surface is in dynamic interaction with the gas phase, and changes of the latter may thus result in surface transformations and appearance of surface phases, which influence the selectivity of catalytic reactions.

The vast majority of catalysts used in modern chemical industry are oxides. Because of their ability to take part in the exchange of electrons, as well as in the exchange of protons or oxide ions, oxides are used as catalysts in both redox and acid-base reactions. They constitute the active phase not only in oxide catalysts but also in the case of many metal catalysts, which in the conditions of catalytic reaction are covered by a surface layer of a reactive oxide. Properties of oxides are also important in the case of preparation of many metal and sulphide catalysts, which are obtained from an oxide precursor. Very often, highly dispersed metals are prepared by reduction of an appropriate oxide phase, and sulphide catalysts are formed from the oxide precursor in the course of the hydrodesulphurization by interaction with the reaction medium. Finally, oxides play an important role in carriers for active metal or oxide phases, very often modifying strongly their catalytic properties. The present paper concerns

only one aspect of the vast field of chemistry of oxides, namely the catalysis by transition metal oxides, which is the basis of the selective oxidation of hydrocarbons.

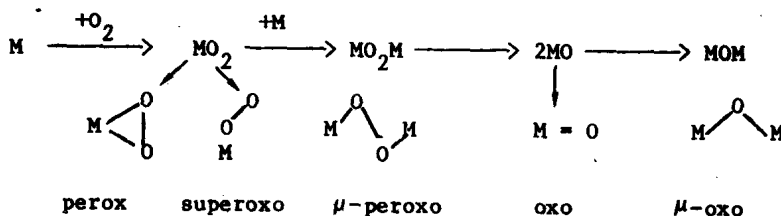
Catalytic oxidation is one of the most important types of processes, both from a theoretical and a practical point of view. As early as 1918, the production of phthalic anhydride by oxidation of naphthalene over  $V_2O_5$  was introduced. The milestone in the development of modern petrochemical industry was the introduction of the gas phase oxidation of propylene to acrolein and ammoxidation to acrylonitrile over bismuth molybdate catalysts, which provided in the early sixties, an abundant supply of new, inexpensive, and useful chemical intermediates(1). Today, catalytic oxidation is the basis of the production of almost all monomers used in the manufacturing of synthetic fibers, plastics, and many other products. With the increasing cost of energy and shrinking supply of cheap hydrocarbons, much effort is now being expended on the development of new oxidation processes of higher selectivity and lower energy consumption. Substitution of the dehydrogenation by oxidative processes, as in the production of styrene from ethylbenzene, may be quoted as an example. Another increasingly important field of catalytic application is the selective oxidation of paraffins.

### Discussion

#### Electrophilic and nucleophilic oxidation

In every oxidation reaction two reactants always take part: oxygen and the molecule to be oxidized. The reaction may thus start either by the activation of the dioxygen or by the activation of the hydrocarbon molecule.

At ambient or moderate temperatures, an oxygen molecule may be activated by bonding into an organometallic complex in the liquid phase. Depending on the type of the central metal atom and on the properties of the ligands, superoxo-, peroxy- or oxo-complexes may be formed:



In the case of the superoxo-complexes, an electrophilic attack of a terminal oxygen atom on the organic reactant occurs resulting in the formation of a  $\mu$ -peroxo-complex, which decomposes into the oxygenated product (lower left part of Figure 1). In the case of perox complexes of group IV, V and VI transition metals, a stoichiometric oxidation takes place if a vacant coordination site exists adjacent to side bonded oxygen and is capable of being occupied by the organic reactant. Its olefin bond is then inserted into the

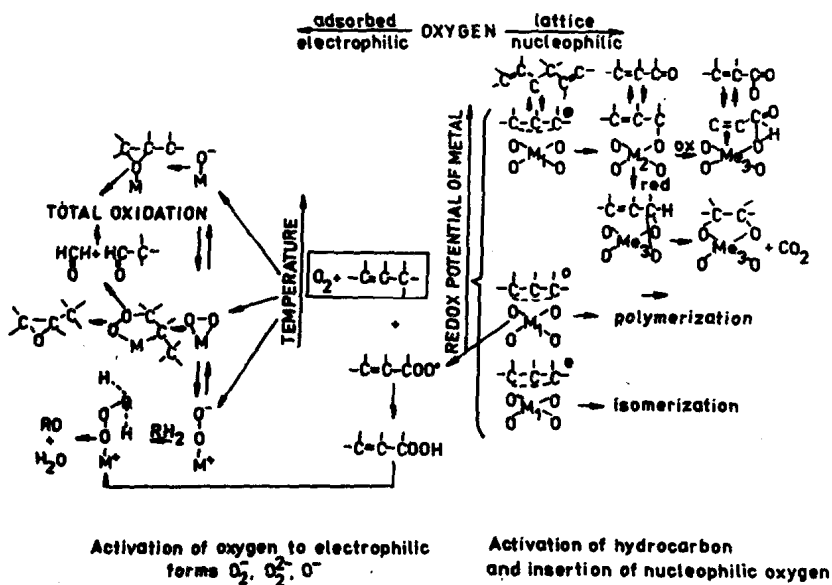


Figure 1. Mechanism of the catalytic oxidation of hydrocarbons. Reproduced with permission from Ref. 31.

metal-oxygen bond forming a peroxometallic cycle which is then decomposed into the oxygenated hydrocarbon molecule and oxo metal complex (2). In order to transform the latter back into the reduced metal which could again form the peroxocomplexes with a new oxygen molecule, a coreducing agent is required, which may be a hydrogen donor or a reactant itself. It should be born in mind that in liquid phase oxidation reactions, the original oxygen complex may be transformed into other reactive species which play the role of active intermediates. A superoxo-complex may be transformed into an alkyl peroxide or peracid complex, which is the oxygen inserting intermediate (3-5).

At higher temperatures the peroxide  $O_2^{2-}$  and superoxide  $O_2^-$  species may appear at the surface of an oxide. Under these conditions, the peroxide ion is unstable and dissociates forming the ion radical  $O_2^-$ . Both  $O_2^-$  and  $O_2^-$  species are strongly electrophilic reactants which attack the organic molecule in the region of its highest electron density. At variance with their behaviour in the liquid phase, the peroxy- and epoxy-complexes formed as the result of an electrophilic attack of  $O_2^-$  or  $O_2^-$  species on the olefin molecule are intermediates which lead to the degradation of the carbon skeleton under heterogeneous catalytic reaction conditions (6). Saturated aldehydes are formed in the first stage (upper left part of Figure 1). These are usually much more reactive than unsaturated aldehydes and at higher temperature undergo rapidly total oxidation. Indeed, experimental data collected in recent years clearly show that electrophilic oxygen species in heterogeneous processes are responsible for total oxidation (7).

When hydrocarbon molecules are activated, a variety of reaction paths may be initiated, consisting of a series of consecutive oxidative steps, each of them requiring a different active center to be present at the catalyst surface (8-10). It should be emphasized at this point that it is the cations of the catalyst which act as oxidizing agents in some of the consecutive steps of the reaction sequence, forming the activated hydrocarbon species. These undergo in subsequent steps a nucleophilic attack by lattice oxygen ions  $O^{2-}$ , which are nucleophilic reagents with no oxidizing properties. They are inserted into the activated hydrocarbon molecule by nucleophilic addition forming an oxygenated product, which after desorption leaves an oxygen vacancy at the surface of the catalyst. Such vacancies are then filled with oxygen from the gas phase, simultaneously reoxidizing the reduced cations. It should be noted that incorporation of oxygen from the gas phase into the oxide surface does not necessarily take place at the same site from where surface oxygen is inserted into the hydrocarbon molecule after being transported through the lattice.

In the case of complex hydrocarbon molecules, the nucleophilic addition of oxygen may take place at different sites of the molecule. It will take place at a site which is made most electropositive by appropriate bonding of the molecule at the active center of the catalyst. When adsorption of the hydrocarbon molecule results in the formation of a radical, interaction between adsorbed molecules is favoured and dimerization or polymerization occurs. When the adsorbed species are negatively charged,

isomerization may be favoured. This type of product obtained depends on the type and proportion of different active centers at the catalyst surface as well as on the ratio of the rate of desorption of the particular intermediate product to the rate of its transformation into the intermediate complex next in the series (upper right part of scheme in Figure 1). These rates may strongly depend on the degree of surface reduction attained in the course of the reaction, as is the case with the carboxylate complex, which is an intermediate in the oxidation of aldehydes to carboxylic acids. On oxidized surfaces, this complex desorbs in the form of an acid, whereas on a reduced surface it undergoes decarboxylation, resulting in the deposition of coke (11).

Reactions of catalytic oxidation may be thus divided into two groups: electrophilic oxidation, proceeding through the activation of oxygen, and nucleophilic oxidation, in which activation of the hydrocarbon molecule is the first step, followed by consecutive steps of nucleophilic oxygen insertion and hydrogen abstraction. They may be conveniently systematized according to the number of elementary structural transformations introduced into the reacting molecule (Table I).

An active and selective catalyst for oxidation of hydrocarbons to oxygenated products with retention of double bonds or aromaticity should thus have the following properties:

- activation of the hydrocarbon molecule by modifying its bonds and generating at appropriate sites the electron distribution favouring the nucleophilic attack of oxygen;
- efficient insertion of the nucleophilic lattice oxygen into the activated hydrocarbon molecule;
- rapid interaction with gas phase oxygen to replenish the lattice oxygen and transport it through the lattice to active sites, where the insertion takes place;
- should not generate electrophilic oxygen species.

The fundamental question arises as to how these properties are related to the solid state chemistry of oxides.

#### Activation of organic molecule

Classical studies of Adams (12, 13), using deuterated propylene and  $C_4-C_8$  olefins, and of Sachtler and de Boer (14), with  $C^{14}$ -labelled propylenes, showed that activation of the olefin molecule consists of the abstraction of  $\alpha$ -hydrogen and the formation of a symmetric allylic intermediate. Conclusions concerning the role of the cationic and anionic sublattices of complex oxide catalysts having an oxysalt character, such as molybdates, tungstates, etc., in the initial  $\alpha$ -hydrogen abstraction and the subsequent steps of the oxidation process, were drawn by comparing the behaviour of  $Bi_2O_3$  and  $MoO_3$  for the reaction of propylene and allyl iodide (15). When allyl iodide was passed over  $MoO_3$ , practically total conversion was observed already at  $310^\circ C$  with 98% selectivity to acrolein. Under the same conditions,  $MoO_3$  was completely inactive with respect to propylene. On contacting allyl iodide with  $Bi_2O_3$ , total conversion at  $310^\circ C$  was also observed. However, in this case 70% of the products formed were 1,5-hexadiene with practically no acrolein being detected. 1,5-hexadiene was also the main product



Table I. Heterogeneous Oxidation of Hydrocarbons

Electrophilic Oxidation		Nucleophilic Oxidation	
Reaction Type	Catalyst	Reaction Type	Catalyst
1. With double bond fission		1. Without introduction of heteroatom	
1.1. oxidation of olefins to oxides	$\text{Ag}_2\text{O}$	1.1. oxidative dehydrogenation of alkanes and alkenes to dienes	$\text{Bi}_2\text{O}_3\text{-MoO}_3\text{-P}_2\text{O}_5$
1.2. oxyhydration of olefins to saturated ketones	$\text{SnO}_2\text{-MoO}_3$	1.2. oxidative dehydrodimerization and dehydrocyclization of alkenes	$\text{MoO}_3\text{-Al}_2\text{O}_3$
2. With C-C bond fission		2. With introduction of heteroatom	
2.1. oxidation of olefins to saturated aldehydes	$\text{V}_2\text{O}_5$	2.1. introduction of heteroatom into hydrocarbon chain	
2.2. oxidation of aromatics to anhydrides and acids with ring rupture	$\text{V}_2\text{O}_5\text{-MoO}_3$	2.1.1. introduction of oxygen a. oxidation of olefins to unsaturated aldehydes and ketones	$\text{Bi}_2\text{O}_3\text{-MoO}_3$
3. Total oxidation to $\text{CO}_2\text{+H}_2\text{O}$	$\text{Co}_3\text{O}_4$ $\text{CuCo}_2\text{O}_4$ $\text{GaCr}_2\text{O}_4$	b. oxidation of alkylaromatics to aldehydes	$\text{Bi}_2\text{O}_3\text{-MoO}_3$
		2.1.2. introduction of nitrogen a. ammoxidation of olefins to nitriles	$\text{UO}_3\text{-Sb}_2\text{O}_4$
		2.2. introduction of heteroatom into acyl group	
		a. oxidation of aldehydes to acids	$\text{NiO-MoO}_3$
		b. oxidation of alkylaromatics to anhydrides	$\text{V}_2\text{O}_5\text{-TiO}_2$