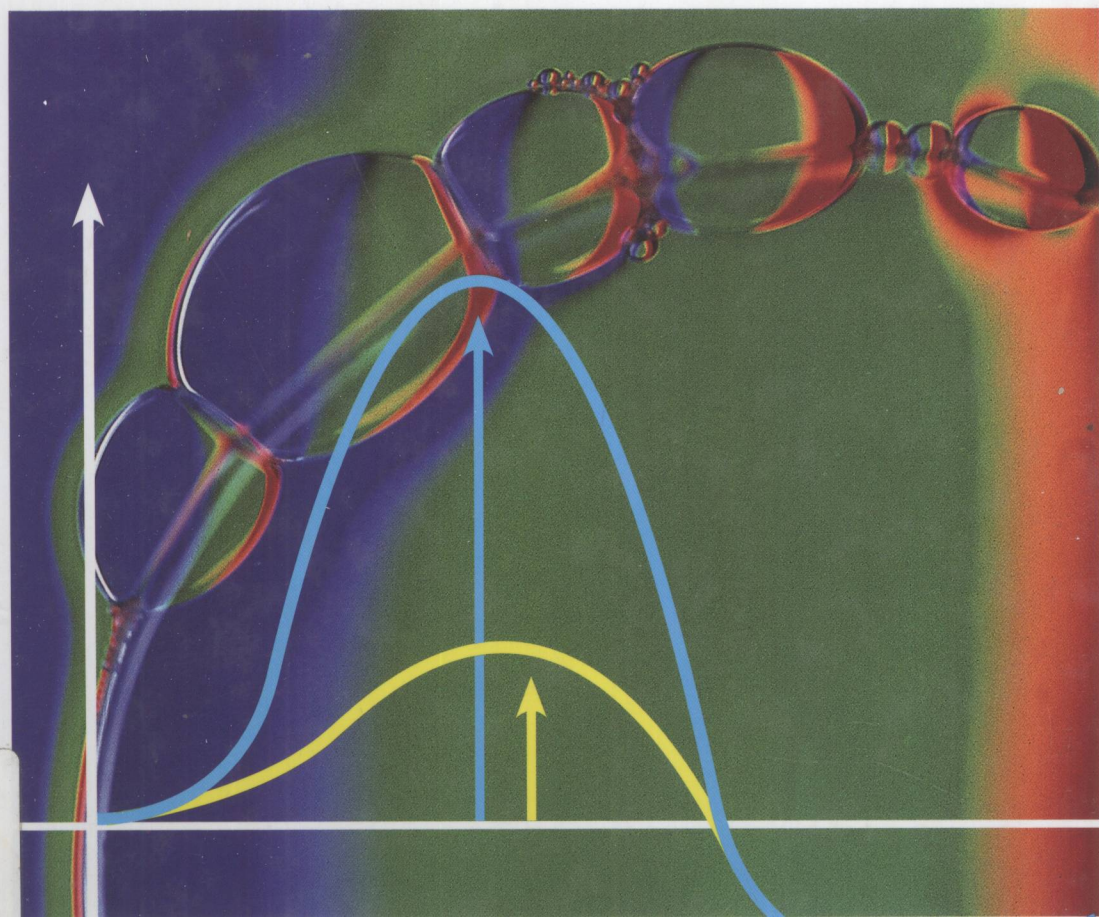


Edited by Noritaka Mizuno

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# Modern Heterogeneous Oxidation Catalysis

Design, Reactions and Characterization



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Design, Reactions and Characterization

*Edited by*  
Noritaka Mizuno



WILEY-VCH Verlag GmbH & Co. KGaA

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Oxidation Catalysis**

*Edited by*  
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## Preface

The range of chemical products is enormous and these products contribute greatly to the quality of our lives. The manufacturing processes of chemicals also lead to vast amounts of wastes, and the reduction or elimination of these wastes is now our central issue. To minimize wastes in chemical manufacturing, the catalytic method is a reliable solution, replacing synthetic processes of low atom efficiency using hazardous stoichiometric reagents. Especially for fine chemicals production, antiquated methodologies with stoichiometric oxidations such as permanganate or dichromate reagents are still widely used. But, times are changing! In the manufacture of large-scale petrochemicals as well as laboratory-scale syntheses, the environmentally-unfriendly processes should be replaced with cleaner and greener oxidants such as  $O_2$ ,  $H_2O_2$  and  $N_2O$  in combination with heterogeneous catalysts. In the last few decades, many efficient heterogeneous oxidation catalysts and methods have been developed and the editor feels that it is necessary to survey the recent developments in heterogeneous oxidation catalysis. This book will discuss mainly the case studies of recent developments in heterogeneous oxidation catalysis and will be directed towards chemists engaged in catalyst preparation and design, catalysis and catalytic organic synthesis, both in academia as well as industry.

In this book, both gas- and liquid-phase oxidations are included although the latter are more numerous. Chapter 1 deals with the concepts in selective oxidation of small alkane molecules. Chapters 2–6 then review the strategies of catalysts design with metal oxides, metal nanoparticles, zeolites, hydroxyapatites, hydrotalcites, montmorillonites and polyoxometalates. The chemistry and application of  $N_2O$  as an oxidant are discussed in Chapter 7. Chapters 8 and 9 deal with recent developments in the direct synthesis of  $H_2O_2$  and greener industrial processes, respectively. Each chapter contains extensive references covering the very important and principal literature through to the beginning of 2000.

Finally, the editor would like to express sincere thanks to colleagues and friends who have contributed such fine chapters. He also thanks Dr Kazuya Yamaguchi (The University of Tokyo) and Dr Stefanie Volk (Wiley-VCH) for their help in preparing this book.

March 2009

Noritaka Mizuno

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## 1

## Concepts in Selective Oxidation of Small Alkane Molecules

Robert Schlögl

## 1.1

### Introduction

The subject of heterogeneously catalyzed selective oxidation has been reviewed many times. Under the keyword combination “selective catalytic oxidation” the ISI database reports about 5400 papers. Over 100 reviews on the topic have been published. In the present discussion, the subjects of methane activation and model studies of unselective CO oxidation, which represent large fields, are excluded. Homogeneously or biologically catalyzed selective oxidation, a combined field that is about 10-fold larger in scientific coverage, is also excluded from this chapter.

Instead, the present chapter deals mainly with the activation of C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> hydrocarbons focussing on oxidative dehydrogenation and oxo-functionalization as target reactions. This seemingly limited field of research encompasses a central entry port to commodity molecules used in chemical industry. The issues of selectivity and energy conversion are of enormous practical relevance as the potential is great for making the chemical industry more sustainable in this small area of catalytic chemistry. However, the still limited success in performing these reactions effectively sheds light on the level of our scientific understanding of these reactions. The science is based upon a set of phenomenological concepts referred as “principles” in the literature, enabling the discovery and optimization of the present catalytic materials.

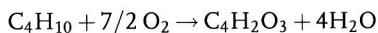
By far the most influential principle is that of “lattice oxygen” [1–3]. It states at its core that atomic oxygen that can selectively oxidize a hydrocarbon has to come from a lattice position of the catalyst. The reduction of the metal centers is thought to arise from oxygen anion transport from deeper layers of the catalyst to its surface. Gas-phase oxygen, being detrimental as reagent with organics, re-oxidizes the catalytic material in a spatio-temporal separation between the hydrocarbon redox chemistry and the catalyst redox chemistry. This separation is widely referred to as the “Mars–van Krevelen type (MvK)” reaction “mechanism” [4, 5]. The original derivation by the authors Mars and van Krevelen [6] did, however, not contain any interpretation of their finding in SO<sub>2</sub> oxidation over vanadium oxides. In their

kinetic work a second term had to be added to the conventional Langmuir equation to explain the experimental finding. Only much later was it realized that this term should describe the “slow re-oxidation of the catalyst,” for which there is little experimental evidence [7]. The postulated general validity of the principle is questioned by the operation of monolayer oxide catalysts [8], which have little ability to deliver lattice oxygen, and by numerous findings in homogeneous catalytic oxidation where molecular oxides such as  $\text{RuO}_4$  afford excellent [9] selective oxidation.

Another strongly prevailing principle is that of “phase cooperation” [10–13]. This states that high-performance oxidation catalysts must be of the multi-phase type, as the different functions required in performing the selective oxidation of a hydrocarbon are only adequately optimized when independent functionally optimized phases cooperate in the catalytic cycle. This intuitively appealing concept renders it almost impossible applying the tools of functional analysis to selective oxidation as the chemical and structural complexity arising from a multi-element-multi-phase oxide (MMO) overwhelms all analytical possibilities of today’s experimentation and theory. Recent developments in catalyst synthesis have shown on the model level [14–16], as well as with high-performance systems [17–21], that substantial catalytic action can be obtained from proven single-phase systems.

At present, the field is still without an unchallenged scientific base despite the enormous effort invested into the issue and the many papers written. This situation is unsatisfactory with respect to the enormous relevance of selectivity in large-scale industrial processes. In the opinion of the author this is not due to a lack of excellent ideas – almost all possible ideas about the function of these catalysts have been proposed. It is a rational experimental approach beyond the principles described in the literature that is needed to unify the concepts into a scientific foundation for better catalyst developments. A parallel search for such catalysts has been advocated and performed [22] with great effort but apparently no success in solving the challenges of the field. This statement is not negative against high-throughput experimentation as such but shows that this technique also requires a scientifically sound basis for its useful application [23].

The above critical remarks do not diminish the enormous success in the development of oxidation reactions that seem close to impossible within the framework of homogeneous chemistry. The most successful process is the one-step reaction of butane to maleic anhydride (MA):



The process solves the problem of activating the poorly reactive butane and then abstracting eight protons without cleaving a carbon–carbon bond. In addition, three oxygen atoms are attached without forming any carbon oxides. This is only possible as the product MA is kinetically stable against further oxidation at the remaining protons, as the locations of further attack are strongly bound to the cyclic carbon skeleton. The reaction occurs in many intermediate steps that are all stabilized against oxidative attack due to chemisorption at an active site that has to become progressively less active during the whole transformation. We assume that the active



site stores electrons from the substrate in its structure and becomes progressively reduced, which in turn reduces its ability to activate C–H bonds. With release of the product we expect concomitant release of water from stored OH groups and re-oxidation by oxygen from the feed. As there are no split oxygen molecules at hand (excluding special oxidants) the active site has to accommodate one extra oxygen atom for every two-center bond being made. The fact that per turnover 14 electrons have to be stored at the active site and that the highly suitable vanadium cation changes its oxidation states between 5 and 3 would call for an active site consisting of seven vanadium centers and a suitable combination of terminal and bridging oxygen atoms. A minimum size of an active site of vanadium species would be two centers as they can store the four electrons required to activate one molecule of oxygen. Such a cluster is hardly a “lattice.” It also can not be a section of an oxide lattice, as then the reacting site would not be isolated electronically, as through oxygen ion diffusion and electronic conductivity the oxidation state of the active site would be kept as constant as possible so as to minimize the free energy of the system. The active site is thus seen as a cluster supported on a matrix of a foreign material (supported catalyst) or of a compound from which the cluster originates by segregation (self-supported). The cluster exhibits a structure capable of adsorbing activated oxygen and of holding protons as intermediate hydroxyl groups. The adsorbed oxygen, being part of the coordination geometry of the cluster in its regenerated state, has been called “surface lattice oxygen” [8, 24, 25], a term for which the author sees no need as this oxygen is an adsorbate situated at a high energy position of the structure.

The general principle of site isolation [26] is the consequence of many observations in selective catalysis that are not confined to selective oxidation. High performing catalysts exhibit isolated sites, minimizing the influx of electrons and activated reactants (oxygen, hydrogen) during conversion of a substrate molecule. This principle of site isolation [1, 2, 26–32] is the most powerful rule for finding selective oxidation catalysts. It is, however, mostly applied in a crystallographic manner, meaning that structures are sought that exhibit strong variations in atom density in their motifs by combining locally dense building blocks with linking polyhedra, leaving substantial empty space in the unit cell “channels.” A particular, instructive example of site isolation is the idealized crystal structure of salts of heteropolyacids (HPA), a family of compounds [18, 33–35] capable of performing many selective oxidation reactions.

It is apparent that logical clashes occur when in the literature the principle of site isolation is applied in conjunction with phase cooperation and lattice oxygen dynamics. Both concepts require for their operation a close contact of the active site with its environment and suggest a continuing exchange of reactants and electrons during the conversion of a substrate molecule. Elaborate sets of assumptions are made to remedy these clashes. The purpose of this review is to suggest a reconciliation of these conflicting concepts as all of them are based on undeniable observations. Table 1.1 gives a (incomplete) list of reviews that highlight the complexity of the arguments that arose from the applications of empirical principles. The list is split into two groups: articles covering reactions and those dealing with the structure and function of catalysts. There is no ordering within the groups.