NEW CONCEPTS AND NEW STRATEGIES IN SELECTIVE OXIDATION

7.1. INTRODUCTION

In the previous chapters it was shown, first, that breakthroughs in the field of selective oxidation have been driven by the need for new, more economical raw materials and the ecological issue, and, second, that progress in the field demands innovative new catalytic materials and reactor options.

Innovation requires the discovery of new catalysts, reactions, and technologies, but another fundamental component is the development of novel concepts that can open new fruitful areas of research. One example is the discovery of Ti-silicalite (TS-1) and its applications,1,2 which stimulated widespread and more general interest in the use of microporous materials containing transition metals for liquid phase heterogeneous conversion of hydrocarbons using H₂O₂ or other peroxo compounds. The discovery of this catalyst and its application for selective oxidation with H₂O₂ is not only an industrial breakthrough, but an important scientific one as well, because it has led to the introduction of new concepts and considerably extended the horizons of selective oxidation: selective oxidation at isolated metal ions using H₂O₂ in a hydrophobic local environment, with the metal ion anchored to a quasi-rigid solid matrix (both these factors are the key parameters that enable the stability, selectivity, and nearly negligible activity in H₂O₂ decomposition of TS-1).

A survey of the literature subsequent to this discovery shows how the successive research activity was initially driven mainly by the "analogy factor," i.e., studying the reactivity of a range of analogous catalysts in which the zeolite structure, the nature of the metal, or the type of substrate to be oxidized was changed. However, the necessary step was identification of the key concept(s)
determining reactivity/stability characteristics of TS-1, which is fundamental in stimulating innovation and at the same time an indicator of the dynamism of a scientific field.

An analysis of the field of selective oxidation at solid surfaces in terms of concepts developed in recent years, however, reveals a general lack of novelty with a consequent dearth of primary directions of research, and scientific activity is confined mainly to consolidating knowledge on existing catalysts and reactions, rather than being focused on exploration of new directions. Throughout this book the necessity for a different scientific approach as the key to opening new perspectives for research and the development of improved catalysts has been emphasized. The literature also shows that there are some peripheral areas under initial development that can open "fresh" new prospects and thus can be stimuli for innovations and the discovery of new applications.

This chapter will describe some examples of these new possibilities and related new concepts and point out possible (sometimes speculative) extensions of these concepts. The examples are certainly not exhaustive of all new possible directions of research in the field of selective oxidation, but will illustrate the challenges and new opportunities offered by less common approaches to the study of selective oxidation reactions.

7.2. SELECTIVE OXIDATION AT NEAR ROOM TEMPERATURE USING MOLECULAR OXYGEN

The selective oxidation processes using gaseous oxygen as the oxidizing agent can be classified as: (i) high-temperature processes usually on mixed oxide catalysts (gas–solid reaction) and based mainly on a Mars–van Krevelen type of mechanism (the active sites are lattice oxygens and gaseous oxygen simply reforms the site to close the catalytic site), and (ii) low-temperature processes in the liquid phase, usually involving a radical-type mechanism with the oxygen activated by a homogeneous catalyst such as a Co^{2+} salt or hydrocarbon autoxidation.\(^3,4\) The latter, however, still requires relatively high temperatures/pressures and cannot be applied to a very wide range of substrates or types of oxidation reactions. A challenge in the field is thus to understand how to oxidize hydrocarbons or other organic molecules selectively under very mild conditions (room temperature, atmospheric pressure) using gaseous oxygen.

At near room temperature, oxygen and hydrocarbons are rather inert in the absence of oxygen activation, e.g., by electron transfer. Two possible approaches to solving this problem of oxygen activation have been proposed: (i) electrochemical activation of O\(_2\), and (ii) activation of O\(_2\) by spontaneous electron transfer from the hydrocarbon to be oxidized due to the combined action of a strong electrostatic field and molecule confinement.