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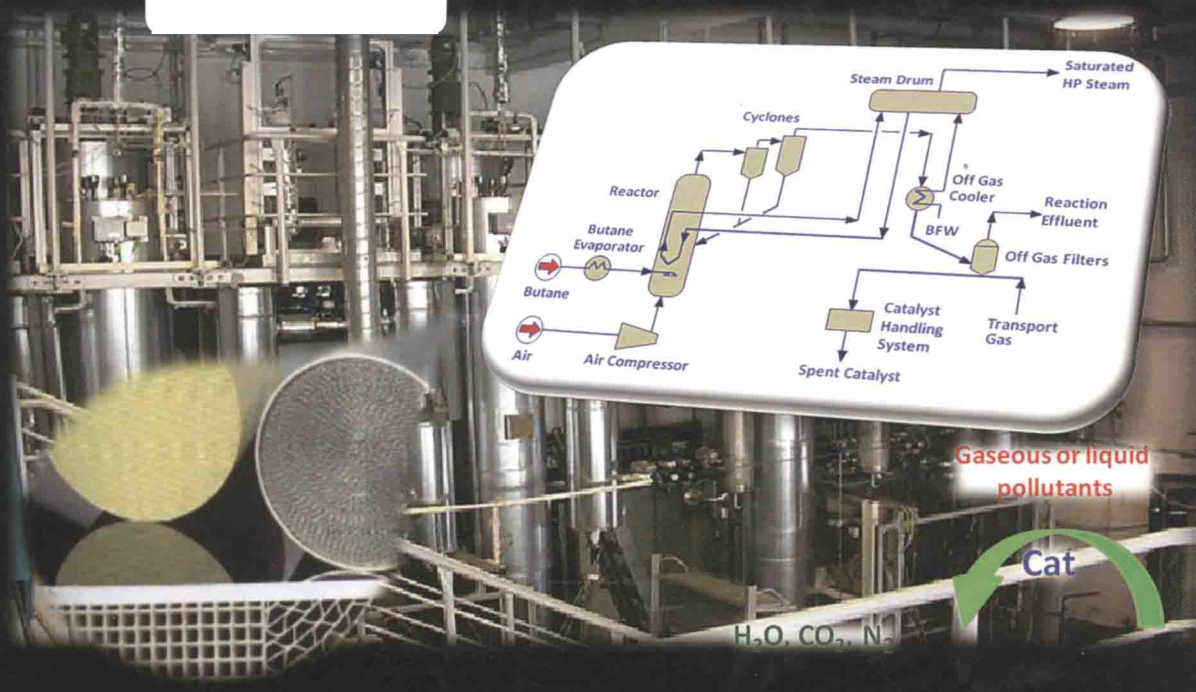

From Laboratory to Industry

Editors

Daniel Duprez • Fabrizio Cavani

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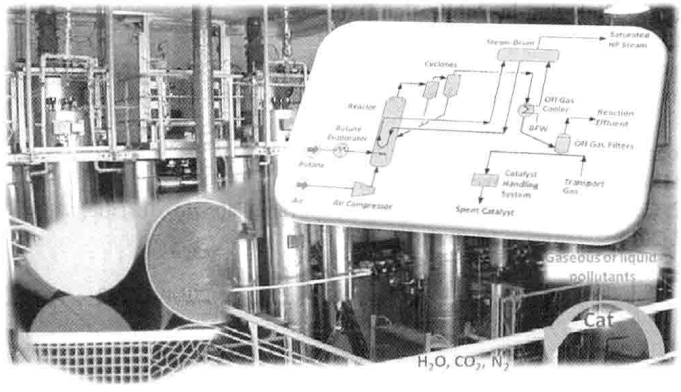

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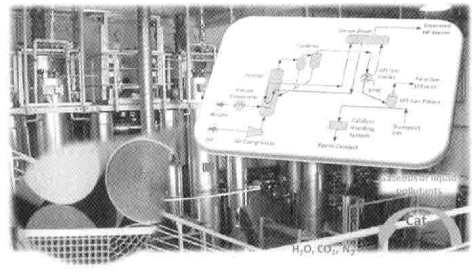

From Laboratory to Industry

Preface

Advanced Methods and Processes in Oxidation Catalysis From Laboratory to Industry

edited by **Daniel Duprez** *(University of Poitiers, France)* &
Fabrizio Cavani *(Università di Bologna, Italy)*

Since the discovery by Humphry Davy in 1817 of the flameless combustion of coal gas over Pt wires, tremendous progress has been made in the understanding of complex phenomena occurring in oxidation catalysis. In parallel, advanced technologies were developed to make these processes more efficient and safer. In the nineteenth century, researchers observed that hydrocarbon oxidation could lead to organic intermediates on noble metals. The huge demand from the chemical industry for new compounds prompted them to take advantage of the selective oxidation to synthesize oxygenated chemicals. Synthesis of new compounds required specific oxide catalysts much more selective than noble metals. Considerable progress was made during the twentieth century while the development of cleaner, greener and safer catalytic processes remains a permanent objective of the chemical industry today.

This book offers a comprehensive overview of the most recent developments in both total oxidation and combustion and also in selective oxidation. For each topic, fundamental aspects are paralleled with industrial applications. The book covers oxidation catalysis, one of the major areas of industrial chemistry, outlining recent achievements, current challenges and future opportunities. One distinguishing feature of the book is the selection of arguments which are emblematic of current trends in the chemical industry, such as miniaturization, use of alternative, greener oxidants, and innovative systems for pollutant abatement. Topics outlined are described in terms of both catalyst and reaction chemistry, and also reactor and process technology.

The book is presented in two volumes. The first ten chapters are devoted to total oxidation while the next eighteen chapters deal with selective oxidation.

Different aspects of total oxidation processes are reviewed in the first part of the book: hydrocarbon oxidation (Chapter 1) and soot oxidation (Chapter 2) for mobile applications while oxidation of volatile organic compounds (VOC) is treated in the next five chapters. Chapter 3 provides a general overview of VOC oxidation while chlorinated VOCs are specifically discussed in Chapter 4 and persistent VOC in Chapter 5. Plasma catalysis processes for VOC abatement are reviewed in Chapter 6. Finally, Chapter 7 gives the point of view of industry for the development and applications of catalysis for air depollution technologies. Total oxidation is also used for energy production by combustion processes exemplified in Chapter 8. The last two chapters are devoted to oxidation processes in liquid media by electrochemical techniques (Chapter 9) or more generally as "advanced oxidation processes" for water depollution (Chapter 10).

The part devoted to selective oxidation includes chapters aimed at providing an overview of oxidation technologies from an industrial perspective, with contributions from chemical companies such as eni SpA, Radici Chimica, Polynt, Sabic, DSM, and Clariant (Chapters 11–16). Then, Chapters 17–19 gives an updated view of experimental tools and techniques aimed at the understanding of catalyst features and interactions between catalysts and reactants/products. Chapters 20–23 are focussed on specific classes of homogenous and heterogeneous catalysts, such as vanadyl pyrophosphate, polyoxometalates, supported metals and metal complexes. Finally, Chapters 24–28 deal with classes of reactions, reactor configurations and process technologies used in selective oxidation, again offering a perspective on recent developments and new trends, such as oxidation of alkanes, oxidations under supercritical conditions, use of non-conventional oxidants, membrane and structured reactors.

Daniel Duprez and Fabrizio Cavani

Contents

Chapter 1

Oxidation of CO and Hydrocarbons in Exhaust Gas Treatments

Jacques BARBIER Jr and Daniel DUPREZ*

The present chapter aims to describe the kinetics and mechanisms of CO and HC oxidation in exhaust gas treatments. Attention will be paid to reactions carried out on noble metal catalysts (Pt, Pd, Rh) usually employed in three-way catalysts (spark ignition engines) around stoichiometry. The effect of ceria, usually employed as an oxygen storage material, will also be reviewed.

1.1. Introduction

Since 1972 in the United States and 1989 in Europe, regulations have been imposed on the automobile industry to limit air pollution emitted by vehicles. Since these dates, legislation has been regularly reinforced with more and more severe regulations concerning four categories of pollutants: carbon monoxide, hydrocarbons (and other organics), nitrogen oxides (NO and NO_2) and soot particulates.[1–3] To achieve abatement of these pollutants, automotive catalytic converters were implemented on new cars to eliminate CO, HC and NOx, while particulate filters are intended to be mounted in the exhaust gas pipe of diesel engines. Oxidation of CO and hydrocarbons is an important process occurring over three-way catalysts. These catalysts are currently employed in the catalytic converters of gasoline engines (close-looped engines) while similar formulations are used in diesel oxidation converters. Three-way (TW) catalysts contain Pt, Pd and Rh deposited on a mixed oxide made typically of doped alumina (La, Ca, ...) and an oxygen storage capacity component ($Ce_xZr_{1-x}O_2$ binary oxides or CeZrXOy ternary oxides, X being another rare earth element).[4–7] The term "oxygen storage capacity" was introduced by Yao and Yu Yao to qualify the ability of the catalyst to work in cycling conditions: the solid stores oxygen during the lean phases and releases it during the rich ones.[8] With this method, the noble metals continue to be fed with O species when the O_2 concentration significantly decreases in the gas phase.

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Oxidation of CO and hydrocarbons in conditions of exhaust gas conversion (concentrations around 1% for CO and less for HCs) has been widely studied since the implementation of catalytic converters. Yu Yao was one of the first authors to publish a systematic study of these reactions over Pt, Pd and Rh catalysts in O_2 excess.[9,10] Moreover, the effect of ceria was also investigated, making Yao and Yu Yao's reports a source of important information. Their results will be analyzed and summarized in the first part of this chapter. In the second part, more recent studies will be reviewed with special attention paid to investigation under cycling conditions.

1.2. The Pioneer Works (1970–1990)

In TW catalysis, an optimal conversion of all the pollutants (reducers like CO and HC, and oxidants like NO and NO_2) is achieved for an S ratio (defined by Schlatter)[11] close to unity. The S ratio is given in Eq. 1.1, in which chemical formulae represent the volume percentages of the gases.

$$S = \frac{2O_2 + NO + 2NO_2}{CO + H_2 + 3nC_nH_{2n} + (3n+1)C_nH_{2n+1}} \tag{1.1}$$

The numerator represents the number of O atoms available in the oxidants (O_2 and NOx) while the denominator represents the number of O atoms required for a total oxidation of the reducers: CO, HC (alkenes and alkanes) and H_2. The Schlatter equation may easily be extended to other HC (aromatics for instance) or oxygenated compounds. However, other gases such as H_2O and CO_2 are not supposed to react with pollutants, which is not always observed (see Section 1.4). Yu Yao investigated CO and HC oxidation in O_2 excess (S = 2). Oxidation reactions were carried out over Pd, Pt and Rh catalysts of different metal loading and dispersions and at different temperatures. In the publications of Yu Yao,[9,10] the reactions were carried out over bulk metals (wires), alumina-supported catalysts and finally over metals supported on ceria-alumina. Specific rates (per gram of catalyst) were reported as well as activation energies, metal dispersions of supported catalysts or metal area of bulk catalysts. From this information it was possible to calculate turnover frequencies (TOF) extrapolated at a given temperature (the same for every metal catalyst).[12] Metal catalysts are compared on the basis of their TOF.

1.2.1. *Oxidation of carbon monoxide*

1.2.1.1. *Effect of metal particle size*

Oxidation of carbon monoxide (Eq. 1.2) is a reaction which can be catalyzed by all the noble metals usually employed in TW converters but also by many oxides or