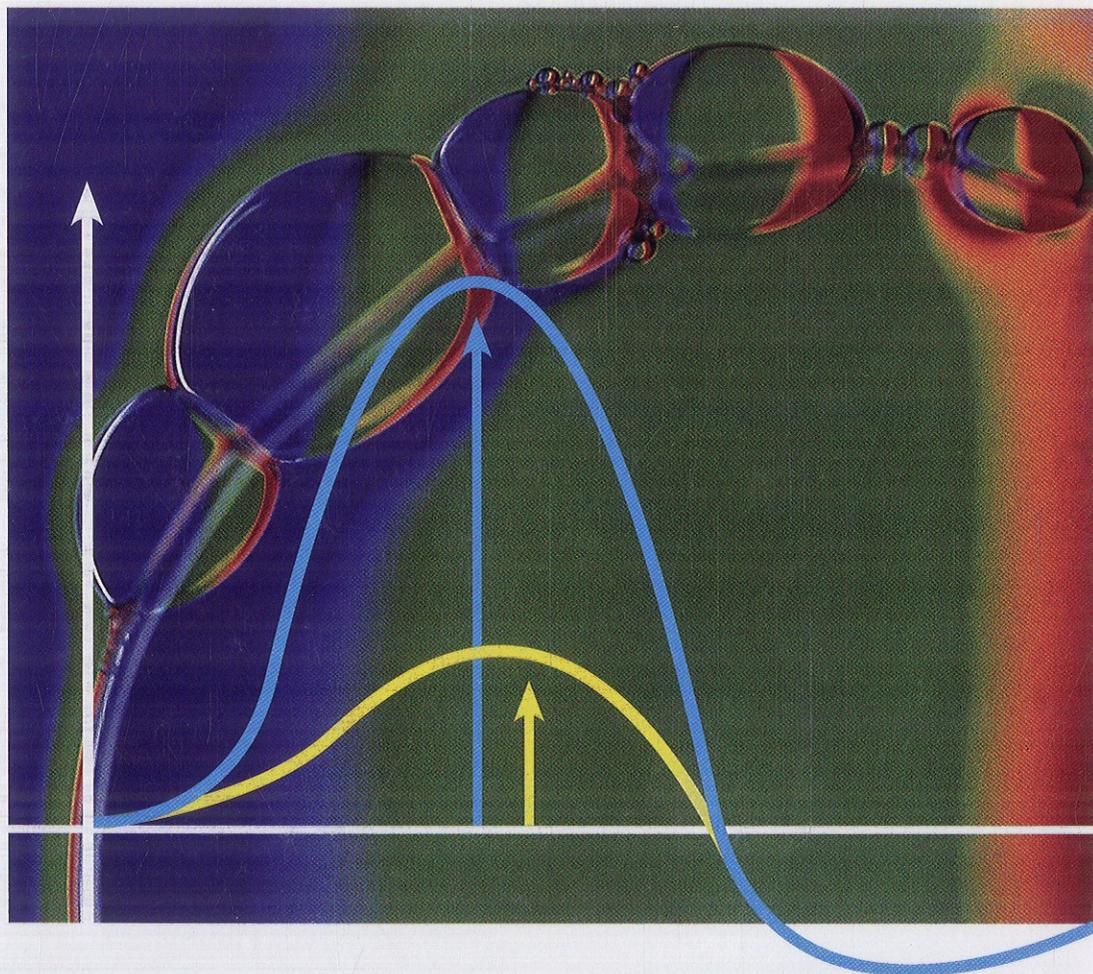


Edited by Noritaka Mizuno

 WILEY-VCH

# Modern Heterogeneous Oxidation Catalysis

Design, Reactions and Characterization



# Contents

Preface XI

List of Contributors XIII

<b>1</b>	<b>Concepts in Selective Oxidation of Small Alkane Molecules</b>	<b>1</b>
	<i>Robert Schlögl</i>	
1.1	Introduction	1
1.2	The Research Field	4
1.3	Substrate Activation	7
1.4	Active Oxygen Species	15
1.5	Catalyst Material Science	22
1.6	Conclusion	34
	References	35
<b>2</b>	<b>Active Ensemble Structures for Selective Oxidation Catalyses at Surfaces</b>	<b>43</b>
	<i>Mizuki Tada and Yasuhiro Iwasawa</i>	
2.1	Introduction	43
2.2	Chiral Self-Dimerization of Vanadium Schiff-Base Complexes on SiO <sub>2</sub> and Their Catalytic Performances for Asymmetric Oxidative Coupling of 2-Naphthol	44
2.2.1	Asymmetric Heterogeneous Catalysis Using Supported Metal Complexes	44
2.2.2	Chiral V-Dimer Structure on a SiO <sub>2</sub> Surface	45
2.2.3	Asymmetric Catalysis for Oxidative Coupling of 2-Naphthol to BINOL	49
2.3	Low-Temperature Preferential Oxidation of CO in Excess H <sub>2</sub> on Cu-Clusters Dispersed on CeO <sub>2</sub>	51
2.3.1	Preferential Oxidation (PROX) of CO in Excess H <sub>2</sub> on Novel Metal Catalysts	51
2.3.2	Characterization and Performance of a Novel Cu Cluster/CeO <sub>2</sub> Catalyst	52

2.4	Direct Phenol Synthesis from Benzene and Molecular Oxygen on a Novel N-Interstitial Re <sub>10</sub> -Cluster/HZSM-5 Catalyst	57
2.4.1	Phenol Production from Benzene with N <sub>2</sub> O, H <sub>2</sub> + O <sub>2</sub> , and O <sub>2</sub>	57
2.4.1.1	Benzene to Phenol with N <sub>2</sub> O	58
2.4.1.2	Benzene to Phenol with H <sub>2</sub> + O <sub>2</sub>	60
2.4.1.3	Benzene to Phenol with O <sub>2</sub>	62
2.4.2	Novel Re/HZSM-5 Catalyst for Direct Benzene-to-Phenol Synthesis with O <sub>2</sub>	64
2.4.3	Active Re Clusters Entrapped in ZSM-5 Pores	66
2.4.4	Structural Dynamics of the Active Re <sub>10</sub> Cluster	68
2.5	Conclusion	71
	References	71

### **3 Unique Catalytic Performance of Supported Gold Nanoparticles in Oxidation**

*Yunbo Yu, Jiahui Huang, Tamao Ishida, and Masatake Haruta*

3.1	Introduction	77
3.2	Low-Temperature CO Oxidation	79
3.2.1	Low-Temperature CO Oxidation in Air	79
3.2.1.1	Junction Perimeter Between Au Particles and the Support	79
3.2.1.2	Selection of Suitable Supports	81
3.2.1.3	Sensitivity to the Size of the Gold Particles	82
3.2.2	Low-Temperature CO Oxidation in H <sub>2</sub>	84
3.2.3	Mechanism for CO Oxidation Over Supported Gold Nanoparticles	87
3.2.3.1	Mechanisms Involving Junction Perimeter Between Gold and the Metal-Oxide Supports	87
3.2.3.2	Mechanisms Involving Specific Size or Thickness of Gold Clusters or Thin Layers	90
3.2.3.3	Mechanisms Involving Cationic Gold	92
3.3	Complete Oxidation of Volatile Organic Compounds	92
3.4	Gas-Phase Selective Oxidation of Organic Compounds	97
3.4.1	Gas-Phase Selective Oxidation of Aliphatic Alkanes	97
3.4.2	Gas-Phase Selective Oxidation of Alcohols	98
3.4.3	Gas-Phase Propylene Epoxidation	100
3.4.3.1	Introduction	100
3.4.3.2	Gas-Phase Propylene Epoxidation with Hydrogen–Oxygen Mixtures on Au/TiO <sub>2</sub>	101
3.4.3.3	Gas-Phase Propylene Epoxidation with Hydrogen–Oxygen Mixtures on Au/Ti-SiO <sub>2</sub>	103
3.5	Liquid-Phase Selective Oxidation of Organic Compounds	106
3.5.1	Oxidation of Mono-Alcohols	107
3.5.2	Oxidation of Diols	112
3.5.3	Oxidation of Glycerol	113
3.5.4	Aerobic Oxidation of Glucose	115
3.5.5	Oxidation of Alkanes and Alkenes	116

3.6	Conclusions	116
	References	118
<b>4</b>	<b>Metal-Substituted Zeolites as Heterogeneous Oxidation Catalysts</b>	<b>125</b>
	<i>Takashi Tatsumi</i>	
4.1	Introduction – Two Ways to Introduce Hetero-Metals into Zeolites	125
4.2	Titanium-Containing Zeolites	126
4.2.1	TS-1	126
4.2.2	Ti-Beta	136
4.2.3	Ti-MWW	137
4.2.4	Other Titanium-Containing Zeolites	145
4.2.5	Solvent Effects and Reaction Intermediate	145
4.3	Other Metal-Containing Zeolites	150
4.4	Conclusion	151
	References	151
<b>5</b>	<b>Design of Well-Defined Active Sites on Crystalline Materials for Liquid-Phase Oxidations</b>	<b>157</b>
	<i>Kiyotomi Kaneda and Takato Mitsudome</i>	
5.1	Introduction	157
5.2	Oxidation of Alcohols	157
5.2.1	Ru Catalyst	158
5.2.2	Pd Catalyst	163
5.2.3	Au Catalyst	164
5.2.4	Au-Pd Catalyst	166
5.3	Epoxidation of Olefins	166
5.3.1	Epoxidation with Hydrogen Peroxide	167
5.3.1.1	Titanium-Based Catalysts	167
5.3.1.2	Tungsten-Based Catalysts	167
5.3.1.3	Base Catalyst	169
5.3.2	Epoxidation with Molecular Oxygen	172
5.4	Cis-Dihydroxylation	173
5.5	Baeyer–Villiger Oxidation	175
5.6	C–H Activation Using Molecular Oxygen	177
5.7	Conclusions	178
	References	178
<b>6</b>	<b>Liquid-Phase Oxidations with Hydrogen Peroxide and Molecular Oxygen Catalyzed by Polyoxometalate-Based Compounds</b>	<b>185</b>
	<i>Noritaka Mizuno, Keigo Kamata, Sayaka Uchida, and Kazuya Yamaguchi</i>	
6.1	Introduction	185
6.2	Molecular Design of Polyoxometalates for H <sub>2</sub> O <sub>2</sub> - and O <sub>2</sub> -Based Oxidations	186
6.2.1	Isopoly- and Heteropolyoxometalates	188

6.2.2	Peroxometalates	189
6.2.3	Lacunary Polyoxometalates	190
6.2.4	Transition-Metal-Substituted Polyoxometalates	192
6.3	Heterogenization of Polyoxometalates	193
6.3.1	Solidification of Polyoxometalates with Appropriate Cations	200
6.3.1.1	Metal and Alkylammonium Cations	200
6.3.1.2	Polycations	201
6.3.1.3	Cationic Organometallic Complexes	203
6.3.2	Immobilization of Polyoxometalate-Based Compounds	205
6.3.2.1	Wet Impregnation	205
6.3.2.2	Solvent-Anchoring and Covalent Linkage	207
6.3.2.3	Anion Exchange	208
6.4	Conclusion	210
	References	211

## **7 Nitrous Oxide as an Oxygen Donor in Oxidation Chemistry and Catalysis** 217

*Gennady I. Panov, Konstantin A. Dubkov, and Alexander S. Kharitonov*

7.1	Introduction	217
7.2	Molecular Structure and Physical Properties of Nitrous Oxide	218
7.3	Catalytic Oxidation by Nitrous Oxide in the Gas Phase	220
7.3.1	Oxidation of Lower Alkanes Over Oxide Catalysts	220
7.3.2	Oxidation Over Zeolites	222
7.3.2.1	Oxidation by Dioxygen	222
7.3.2.2	Oxidation of Benzene to Phenol by N <sub>2</sub> O	223
7.3.2.3	Nature of Zeolite Activity, $\alpha$ -Sites	224
7.3.2.4	N <sub>2</sub> O specificity, $\alpha$ -Oxygen and its Stoichiometric Reactions	227
7.3.2.5	Hydroxylation of Alkanes and Benzene Derivatives	229
7.3.2.6	Other Types of Oxidation Reactions	230
7.4	Catalytic Oxidation by N <sub>2</sub> O in the Liquid Phase	230
7.5	Non-Catalytic Oxidations by N <sub>2</sub> O	231
7.5.1	Liquid-Phase Oxidation of Alkenes	231
7.5.1.1	Linear Alkenes	232
7.5.1.2	Cyclic Alkenes	234
7.5.1.3	Cyclodienes	237
7.5.1.4	Bicyclic Alkenes	238
7.5.1.5	Heterocyclic Alkenes	238
7.5.2	Carboxidation of Polymers	240
7.5.2.1	Carboxidation of Polyethylene	240
7.5.2.2	Carboxidation of Polybutadiene Rubber	241
7.6	Economic Aspects of N <sub>2</sub> O as Oxidant	244
7.6.1	Recovery of N <sub>2</sub> O From Off-Gases	244
7.6.2	Deliberate Preparation of N <sub>2</sub> O	245
7.7	Conclusion	246
	References	247

<b>8</b>	<b>Direct Synthesis of Hydrogen Peroxide: Recent Advances</b>	<b>253</b>
	<i>Gabriele Centi, Siglinda Perathoner, and Salvatore Abate</i>	
8.1	Introduction	253
8.1.1	Industrial Production	253
8.1.2	Outlook for H <sub>2</sub> O <sub>2</sub> Production	254
8.1.3	Uses of Hydrogen Peroxide	255
8.2	Direct Synthesis of H <sub>2</sub> O <sub>2</sub> from an Industrial Perspective	257
8.2.1	Status of Development and Perspectives of Industrial Production	257
8.2.2	Recent Patents on the Direct Synthesis of H <sub>2</sub> O <sub>2</sub>	262
8.3	Fundamental Studies	270
8.3.1	Intrinsically Safe Operations and Microreactors	271
8.3.2	Nature of the Catalyst and Reaction Network	275
8.3.3	Role of the Solvent and of Promoters	281
8.4	Conclusion	282
	References	283
<b>9</b>	<b>Recent Achievements and Challenges for a Greener Chemical Industry</b>	<b>289</b>
	<i>Fabrizio Cavani and Nicola Ballarini</i>	
9.1	Introduction: Old and New Challenges for Oxidation Catalysis in Industry	289
9.2	Recent Successful Examples of Alkanes Oxidation	290
9.2.1	Oxidation of Ethane to Acetic Acid	290
9.2.2	Ammonoxidation of Propane to Acrylonitrile	294
9.3	New Oxidation Technologies: Oxidative Desulfurization (ODS) of Gas Oil	301
9.4	Process Intensification in Catalytic Oxidation	304
9.5	An Alternative Approach: Anaerobic Oxidation with Metal Oxides in a Cycle Process (from an Oxidation Catalyst to a Reusable Stoichiometric Oxidant)	306
9.5.1	Anaerobic Oxidation of Propene to Acrolein in a CFBR Reactor	309
9.5.2	Anaerobic Synthesis of 2-Methyl-1,4-Naphthoquinone (Menadione)	310
9.5.3	Anaerobic Oxidative Dehydrogenation of Propane to Propene	311
9.5.4	Production of Hydrogen from Methane with Oxide Materials and Inherent Segregation of Carbon Dioxide	313
9.6	Current and Developing Processes for the Transformation of Bioplatfom Molecules into Chemicals by Catalytic Oxidation	316
9.6.1	Glycerol: A Versatile Building Block	320
9.7	Conclusion	321
	References	323