

Contents

Chapter 1	Catalysis by Single-crystal Surfaces <i>By R. W. Joyner</i>	1
1	Introduction	1
2	Hydrogen Reactions	2
	Synthesis	2
	Hydrocarbon Adsorption and Reaction	10
	Reactions of Oxygen-containing Molecules	19
	Formic Acid Decomposition	19
	Reactions of Alcohols	26
	Ethene Oxidation and Ethylene Oxide Synthesis	29
3	Oxidation	30
	Oxidation of Carbon Monoxide	30
	Oxidation of Nitric Oxide	33
	Oxidation of Hydrogen	35
4	Reactions of Ammonia	35
	Synthesis	35
	Oxidation	42
5	Miscellaneous	44
	Alloy Studies	44
	Oxide Studies	45
	MoS ₂ Hydrodesulphurization (HDS) Catalysts	46
Chapter 2	Fischer–Tropsch Synthesis and Related Reactions <i>By V. Ponc</i>	48
1	Introduction	48
2	Some Recent Contributions to the Discussion on the Mechanism of Reaction Intermediates	51
3	Adsorption and Dissociation of CO	59
4	Specific Problems with Some Metals	65

5	Why was the Role of 'C_s' and of 'CH_x' in the FTS so long Denied	67
6	Some Contemporary Alternative Views on the Mechanism	69
7	Related Reactions	71
8	Search for New Catalysts and Technologies	75
Chapter 3	Reactions of Hydrocarbons on Metallic Catalysts	80
	<i>By Z. Paál and P. Tétényi</i>	
1	Introduction	80
2	Reactions of Alicyclic Hydrocarbons	81
	Dehydrogenation	81
	Cyclohexane	81
	Degradative Cyclohexane Dehydrogenation	84
	Other Alicyclic Rings	85
	Ring Rearrangement	87
	Ring Opening	88
	The Nature of the Ring	88
	Substituent Effects	90
	Associate Flat Adsorption	91
	Dissociative Flat Adsorption	92
	Associative Edgewise Adsorption	93
	Dissociative Edgewise Adsorption	93
3	Reactions of Open-chain Hydrocarbons	94
	Dehydrogenation	94
	Ring Closure	95
	C ₆ Dehydrocyclization	95
	C ₅ Cyclization	97
	Cyclization with Skeletal Rearrangements	99
	Skeletal Isomerization	100
	Bond-shift Isomerization	100
	C ₅ Cyclic Isomerization	103
4	Degradation Reaction: Hydrogenolysis	106
	Hydrogenolysis of Ethane	106
	Hydrogenolysis of Higher Hydrocarbons	109
	Formal Characteristics	109
	Kinetics and Mechanism	112
5	Build-up Reaction: Homologation	114

6 Interpretation of Catalytic Activity of Metals	117
The Nature of the Metal	118
Geometric Effects	118
Electronic Effects	118
Ensemble Effects	119
Active Surface Species in the Catalytic System	120
Astoicheiometric Surface Components	122
7 An Example – For Concluding Remarks	124
Chapter 4 Catalysis of Reactions Involving the Reduction or Decomposition of Nitrogen Oxides	127
<i>By B. Harrison, M. Wyatt, and K. G. Gough</i>	
1 Introduction	127
Formation of Nitrogen Oxides	127
Sources of Nitrogen Oxides	129
Environmental Effects of Nitrogen Oxides	130
Emission Legislation	131
2 The Chemistry and Adsorption Properties of Nitric Oxide	131
The Physical and Inorganic Chemistry of Nitric Oxide	131
The Adsorption of Nitric Oxide on Transition Metals	133
Chromium, Molybdenum, and Tungsten	133
Manganese, Technetium, and Rhenium	136
Iron, Ruthenium, and Osmium	136
Cobalt, Rhodium, and Iridium	138
Nickel, Palladium, and Platinum	140
Copper	143
Conclusions	143
3 The Kinetics and Mechanism of Reduction and Decomposition Reactions of Nitric Oxide	146
Nitric Oxide Decomposition	146
The Reduction of Nitric Oxide by Carbon Monoxide	147
Base-metal Catalysts	147
Precious-metal Catalysts	150
The Reduction of Nitric Oxide by Hydrocarbons	154
The Reduction of Nitric Oxide by Hydrogen	156
The Reduction of Nitric Oxide by Ammonia	161
4 The Commercial Application of NO_x Removal Catalysts	166
Mobile Sources	166
Stationary Sources	169
Non-catalytic Methods	171

Chapter 5	Characterization of Catalysts by Electron Microscopy	172
	<i>By T. Baird</i>	
1	Introduction	172
2	Instrumentation and Imaging Modes: Contrast	173
	The TEM: Instrumentation	173
	The TEM: Imaging Modes and Contrast	173
	Electron Diffraction	175
	The SEM	175
	The STEM	177
	Microanalysis with the STEM: Microdiffraction:	
	Energy Loss Spectroscopy	177
	Controlled Atmosphere Electron Microscopy (CAEM): <i>In-situ</i> TEM	178
3	Specimen Preparation	179
	Grinding: Extraction Replication	179
	Thin Films: Thin Sections	180
	Thin Substrates for High Resolution Microscopy	180
4	Atoms, Clusters, and Molecules on Surfaces	181
5	Electron Microscopy of Supported Catalysts	185
	Particle Size Determination	185
	The Structure of Small Metallic Particles	188
	Catalyst Support Structures: Pores	191
	TEM Studies	191
	SEM Studies	193
	Metal-Support Interaction	194
6	Sintering and Redispersion	196
7	Electron Microscopy in the Study of Reactions on Wires, Ribbons, Foils, and Single-crystal Spheres	201
8	Oxide Catalysts	202
9	Zeolites	204
10	Intercalation Compounds of Graphite	207
11	Metal-catalysed Hydrogenation and Oxidation of Graphite	210
12	Metal-catalysed Carbon Deposition	213

<i>Contents</i>		xi
	The Nature of the Solid Carbon Product	213
	The Nature of the Catalyst	216
13	Miscellaneous	218
	Polymerization Catalysts	218
	LaPO ₄	218
	Ni(OH) ₂ to NiO Transformation	219
	Electron Microscope Autoradiography	219
Chapter 6	Coal Hydrogenation Catalysis	220
	<i>By D. G. Gavin</i>	
1	Introduction	220
2	Coal Liquefaction and Hydrogenation Processes	223
	Donor Solvent Liquefaction Process	224
	H-Coal	225
	Solvent-refined Coal (SRC)	227
	Zinc Halide Hydrocracking Process	227
	COED	229
	Liquid Solvent Extraction (LSE)	229
	Supercritical Gas Extraction (SGE)	230
3	Disposable Catalysts	230
4	Metal Halide Catalysts	234
5	Homogeneous and Miscellaneous Catalysts	239
	Homogeneous Catalysts	239
	Alkali Metal Catalysts	241
	Hydrogen Permeable Catalysts	241
	Strong Acid Catalysts	241
6	Molybdenum and Tungsten Catalysts	242
7	Pore Size Effects	244
8	Catalyst Deactivation	246
9	Coal Hydrogenation with Syn-Gas	252
10	Fundamentals in Coal Hydrogenation Catalysis	254
	Hydrodenitrogenation	254
	Hydrosulphurization	259
	Hydrodeoxygenation	260

	Hydrogenation and Cracking of Aromatic Hydrocarbons	260
	Kinetics and Mechanisms of Coal Hydrogenation	263
11	Upgrading Coal-derived Liquids	267
Chapter 7	Selective Oxidation of Hydrocarbons <i>By C. F. Cullis and D. J. Hucknall</i>	273
1	Introduction	273
2	Reactions Involving 'Activation' of the Hydrocarbon by the Catalyst	276
	Reactions Occurring During the Formation of an Allylic Species	276
	Reactions Involving the Initial Hydration of the Hydrocarbon	283
	Reactions Involving the Acid-Base Properties of the Catalyst	283
	Reactions Involving the Simultaneous Introduction into the Hydrocarbon of More than One Oxygen Atom	286
3	Interaction of Different Oxygen Species with the Activated Hydrocarbon	288
	Role of Lattice Oxygen	288
	Possible Role of Other Oxygen Species	293
4	Effects of Catalyst Structure	296
5	Conclusions	307
Chapter 8	Heterogeneous Photocatalysis <i>By R. I. Bickley</i>	308
1	Introduction	308
2	The Preparation of Finely Divided Metals on Semiconductor Supports by Heterogeneous Photoreduction	312
3	Heterogeneous Photocatalytic Reactions at Metal-Semiconductor Interfaces	316
	The Oxidative Decarboxylation of Acetic Acid on Pt-TiO ₂	316

	The Oxidative Decarboxylation of other Carboxylic Acids on Pt-TiO ₂	316
	Photocatalytic Oxidation of the Hydrocarbons on Pt-TiO ₂	318
	Heterogeneous Photosynthesis of Amino-acids on Pt-TiO ₂	318
	The Initiation of Free Radical Polymerization at the Pt-TiO ₂ Interface	319
4	The Photocatalytically-induced Splitting of Water	319
5	Photoassisted Heterogeneous Reactions	323
	The Photoassisted Decomposition of Water	323
	The Water-gas Shift Reaction and Related Processes	324
6	Heterogeneous Photocatalytic Reactions at Semiconductor Surfaces	325
	The Photo-oxidation of Alkanes, Alkenes, and Alcohols	325
	The Photosynthesis of Hydrogen Peroxide	328
	The Photocatalytic Oxidation of Carbon Monoxide	329
	Photocatalytic Reactions involving Nitrogen-containing Compounds	330
	Photocatalytic Reactions involving Halogen-containing Compounds	330
	The Photocatalytic Oxidation of Polymeric Materials	331
7	Concluding Remarks	331
Chapter 9	Catalysis by Carbides, Nitrides, and Group VIII Intermetallic Compounds	333
	<i>By S. T. Oyama and G. L. Haller</i>	
1	Introduction	333
2	Carbides and Nitrides	334
	General Properties	334
	Crystallography	336
	Magnetic and Electronic Properties	337
	Preparation of High Surface Area Materials	337
	Bonding Theories	338
3	Surface Reactivity of Carbides and Nitrides	344
	Theoretical Considerations	344
	Surface Cleanliness and Composition	345

4	Catalytic Reactions on Carbides and Nitrides	346
	Oxidation Reactions	347
	Hydrogenation and Dehydrogenation	349
	Isomerization	350
	Hydrogenolysis and Hydrotreating	350
	Methanation and Fischer–Tropsch Synthesis	351
	Ammonia Synthesis and Decomposition	352
	Conclusions	352
5	Intermetallic Compounds of Group VIII Metals	353
	General Properties of Intermetallics	353
	Crystallography and Bonding	354
	Intermetallic Preparation	356
6	Chemisorption and Surface Composition of Intermetallics	356
7	Catalysis over Intermetallics	359
	Hydrogenation and Isomerization of Olefins	359
	NH ₃ Synthesis	362
	Methanation	362
	Conclusions	364
Chapter 10	Homogeneously Catalysed Insertion Reactions	366
	<i>By R. J. Cross</i>	
1	Introduction	366
2	Catalytic Cycles and Carbonylations	367
	The Carbonyl Insertion Step	369
3	Hydroformylation	372
4	Fischer–Tropsch Synthesis	375
5	Polymerization, Oligomerization, and Metathesis of Olefins	381
	Olefin Metathesis	382
	Ziegler–Natta Catalysis	383
	Oligomerization and Cyclo-oligomerization	387
6	Olefin Oxidation	391
	Wacker Oxidation	391