

# Contents

Preface .....	V
<b>1 Setting the Scene .....</b>	<b>1</b>
1.1 Introduction .....	1
1.1.1 The Selectivity of Catalysts .....	2
1.2 Perspectives in Catalysis: Past, Present, Future .....	4
1.2.1 Applied Catalysis since the 1940s .....	6
1.2.2 Current Trends in Applied Catalysis .....	10
1.2.2.1 Auto-Exhaust Catalysts .....	10
1.2.2.2 Catalysts in Electrochemistry and Photoelectrochemistry .....	12
1.2.2.3 Asymmetric Sites on Heterogeneous Catalysts .....	13
1.2.2.4 Immobilized Transition Metals .....	15
1.2.2.5 Immobilized Enzymes and Cells: Present and Future .....	16
1.2.2.6 Catalytic Antibodies .....	20
1.2.2.7 Ribozymes .....	23
1.2.2.8 Catalytic Oxidation of Methane: the Centrepiece of Future Power Sources .....	24
1.3 Definition of Catalytic Activity .....	26
1.3.1 Magnitude of Turnover Frequencies and Active Site Concentrations .....	27
1.3.2 Volcano Plots .....	29
1.3.3 The Evolution of Important Concepts and Techniques in Heterogeneous Catalysis .....	30
1.3.3.1 Mechanistic Insights from Isotopic Labelling .....	42
1.3.3.2 Concepts from Organometallic Chemistry .....	44
1.3.3.3 Contributions from Theoretical and Computational Chemistry .....	48
1.4 Some Intellectual and Practical Challenges for Catalysis in the 21st Century .....	49
1.5 Problems .....	57
1.6 Further Reading .....	60
1.6.1 General Background .....	60
<b>2 The Fundamentals of Adsorption: Structural and Dynamical Considerations, Isotherms, and Energetics .....</b>	<b>65</b>
2.1 Catalysis Must Always be Preceded by Adsorption .....	65
2.1.1 Physical Adsorption, Chemisorption and Precursor States .....	65

X	<i>Contents</i>	
2.2	The Surfaces of Clean Solids are Sometimes Reconstructed . . . . .	69
2.3	There are Many Well-Defined Kinds of Ordered Adlayers. . . . .	72
2.4	Adsorption Isotherms and Isobars . . . . .	79
2.4.1	The Empirical Facts. . . . .	81
2.4.2	Information that can be Gleaned from Isotherms. . . . .	81
2.4.3	Adsorption is Almost Invariably Exothermic . . . . .	82
2.5	Dynamical Considerations . . . . .	85
2.5.1	Residence Times . . . . .	85
2.5.2	Rates of Adsorption. . . . .	87
2.5.3	Applying Statistical Mechanics to Adsorption. . . . .	89
2.5.4	Adsorption Kinetics Can Often be Represented by the Elovich Equation . . . . .	91
2.5.5	Rates of Desorption. . . . .	94
2.5.6	Applying Statistical Mechanics to Desorption. . . . .	96
2.5.7	The Influence of a Precursor State on the Kinetics of Desorption . . . . .	98
2.6	Deriving Adsorption Isotherms from Kinetic Principles . . . . .	99
2.6.1	Using the Langmuir Isotherm to Estimate the Proportions of Non-dissociative and Associative Adsorption . . . . .	101
2.6.2	Other Adsorption Isotherms . . . . .	104
2.6.2.1	Henry's Adsorption Isotherm . . . . .	104
2.6.2.2	The Freundlich Isotherm . . . . .	104
2.6.2.3	The Temkin Isotherm. . . . .	104
2.6.2.4	The Brunauer–Emmett–Teller Isotherm . . . . .	105
2.6.2.5	Developments from Polanyi's Adsorption Theory . . . . .	105
2.6.2.6	Kaganer's Isotherm and the DKR Equation. . . . .	107
2.6.2.7	The Virial Equation of State . . . . .	107
2.7	Energetics of Adsorption . . . . .	108
2.7.1	Estimating the Binding Energies of Physically Adsorbed Species. . . . .	108
2.7.2	The Binding Energies of Chemisorbed Species. . . . .	112
2.7.3	Estimating Heats of Adsorption From Thermodynamic Data . . . . .	116
2.7.4	Decline of the Heat of Adsorption with Increasing Coverage . . . . .	117
2.8	Mobility at Surfaces. . . . .	119
2.9	Kinetics of Surface Reactions . . . . .	120
2.9.1	The Influences of Precursor States on the Kinetics and Energy Distribution of Catalysed Reactions . . . . .	122
2.9.2	Comparing the Rates of Heterogeneous and Homogeneous Reactions. . . . .	123
2.10	Autocatalytic, Oscillatory, and Complex Heterogeneous Reactions. . . . .	124
2.10.1	An Outline of Autocatalysis . . . . .	125
2.10.2	Background to Oscillating Reactions. . . . .	125
2.10.3	Instabilities and Transient Phenomena in Heterogeneous Catalysis . . . . .	127
2.10.4	Multiple Steady States . . . . .	127
2.10.5	Transient Phenomena. . . . .	130
2.11	Problems . . . . .	135
2.12	Further Reading . . . . .	142

	<i>Contents</i>	XI
<b>3</b>	<b>Characterizing Catalysts and their Surfaces . . . . .</b>	<b>145</b>
3.1	Model Systems and Real-Life Catalysts . . . . .	145
3.2	A Portfolio of Modern Methods: Introducing the Acronyms . . . . .	146
3.3	Which Elements and Which Phases are Present? . . . . .	149
3.3.1	X-Ray Fluorescence (XRF), X-Ray Emission (XRE) and Proton-Induced X-Ray Emission (PIXE) . . . . .	149
3.3.2	Developing Techniques: ICPMS. . . . .	151
3.3.3	X-Ray Diffraction (XRD) and Electron Diffraction (ED) . . . . .	151
3.3.3.1	Mean Size, Surface Area and Particle-Size Distribution from SAXS . . . . .	153
3.3.3.2	In-Situ Studies by X-Ray Diffraction. . . . .	154
3.4	Detecting, Identifying, and Counting the Atoms at Solid Surfaces: Sub-monolayer Amounts can be Measured. . . . .	157
3.4.1	Ion-Scattering Spectroscopy (ISS): A Detection Limit of $10^{-4}$ Monolayers . . . . .	157
3.4.2	Nuclear Microanalysis (NMI): A Sensitive Means of Detecting Specific Elements, Including Hydrogen, at Surfaces . . . . .	158
3.4.3	Rutherford Back-Scattering (RBS) . . . . .	158
3.5	Identifying the Atoms at a Surface and Probing their Immediate Environment: SIMS, IR, HREELS, AES and XPS . . . . .	159
3.5.1	Secondary-Ion Mass Spectroscopy (SIMS): A Detection Limit of $10^{-5}$ Monolayers. . . . .	159
3.5.2	Infrared Spectroscopy (IR): A Non-destructive Technique Usable on Catalysts Exposed to High Pressure . . . . .	161
3.5.3	High-Resolution Electron-Energy-Loss Spectroscopy (HREELS): The Most Sensitive Tool for Identifying Surface Vibrational Modes. . . . .	164
3.5.4	Electron Spectroscopy: The Ability to Probe Composition and Bonding at Surfaces . . . . .	166
3.5.4.1	The Realization that Electron Spectroscopy is Sufficiently Sensitive to Detect Fractions of a Monolayer . . . . .	169
3.5.4.2	Auger Electron Spectroscopy (AES) and Scanning Auger Microscopy (SAM) . . . . .	170
3.5.4.3	X-Ray Photoelectron Spectroscopy (XPS) . . . . .	171
3.5.4.4	UV-Induced Photoelectron Spectroscopy (UPS) . . . . .	175
3.5.4.5	Inverse Photoemission: A Means of Probing Unoccupied States . . . . .	177
3.6	The Structure and Crystallography of Surfaces: Measuring the Symmetries, Order and Disorder, and Deducing Bond Lengths and Bond Angles in the Adsorbed State . . . . .	179
3.6.1	Two- and Three-Dimensional Surface Crystallography. . . . .	179
3.6.2	Notations for Describing Ordered Structures at Surfaces. . . . .	183
3.6.3	How do Bond Distances at Surfaces Compare with Those of Bulk Solids? What of Displacive Reconstructions? . . . . .	185
3.6.4	Atomic Scattering and Diffraction . . . . .	185
3.6.5	EXAFS, SEXAFS, XANES and NEXAFS: Probing Bond	

	Distances and Site Environments even when There is no Long-Range Order . . . . .	185
3.6.5.1	The Origin of EXAFS and How it is Used . . . . .	187
3.6.5.2	Applications of EXAFS to the Study of Catalysts . . . . .	191
3.6.5.3	SEXAFS . . . . .	193
3.6.5.4	XANES and Pre-edge Structure: Deducing Site Symmetry and Oxidation States . . . . .	194
3.6.5.5	NEXAFS. . . . .	196
3.7	Other Structural Techniques for Characterizing Bulk and Surfaces of Catalysts . . . . .	198
3.7.1	Electron Spin Resonance (ESR): Probing the Nature of Catalytically Active Sites and the Concentration of Paramagnetic Intermediates on Surfaces and in the Gas Phase . . . . .	198
3.7.1.1	Examples of the Use of ESR in Heterogeneous Catalysis. . . . .	199
3.7.2	Electron Spin-Echo Modulation Spectroscopy (ESEMS): Probing the Environment of Paramagnetic Species . . . . .	200
3.7.3	Nuclear Magnetic Resonance (NMR): A Technique Applicable, at High Resolution, to Solids and their Surfaces . . . . .	201
3.7.3.1	Basic Principles . . . . .	201
3.7.3.2	NMR Spectra of Solids. . . . .	204
3.7.3.3	Applications of NMR to the Study of Catalysts, Adsorbents and Adsorbates. . . . .	205
3.7.3.4	Future Prospects for the Study of Catalysts by Solid-State NMR . . . . .	208
3.7.4	Mössbauer Spectroscopy: A Means of Determining Valence, Spin States, and Site Environments of Ions . . . . .	210
3.7.4.1	Specific Applications . . . . .	210
3.7.4.2	Conversion-Electron Mössbauer Spectroscopy (CEMS): A Double-Resonance Technique of an Unusual Kind . . . . .	212
3.7.5	Electron Microscopy . . . . .	213
3.7.5.1	Scanning Probe Microscopy: STM and AFM . . . . .	215
3.7.5.2	Optical Microscopy . . . . .	218
3.7.5.3	Ellipsometry: A Non-invasive Technique . . . . .	219
3.7.6	Neutron Scattering: A Technique of Growing Importance in the Study of Catalysts . . . . .	219
3.7.6.1	Determining the Atomic Structure and Texture of Microcrystalline Catalysts, the Nature of the Active Sites and the Disposition of Bound Reactants. . . . .	221
3.7.6.2	Determining the Structure of, and Identifying Functional Groups in, Chemisorbed Layers at Catalyst Surfaces. . . . .	222
3.8	A Miscellany of Other Procedures . . . . .	224
3.9	Determining the Strength of Surface Bonds: Thermal and Other Temperature-Programmed Methods . . . . .	226
3.9.1	Temperature-Programmed Desorption (TPD) or Flash Desorption Spectroscopy (FDS). . . . .	226
3.9.2	Temperature-Programmed Reaction Spectroscopy (TPRS) . . . . .	229
3.9.3	Magnitude of the Heat and Entropy of Adsorption . . . . .	229

3.10	In-Situ Methods of Studying Catalysts: The Current Scene and Future Prospects . . . . .	232
3.10.1	Isotopic Labelling and Transient Response. . . . .	233
3.10.2	Infrared, Raman, NMR, Mössbauer and X-Ray Absorption Spectroscopy for In-Situ Studies . . . . .	238
3.10.3	In-Situ X-Ray and Neutron Diffraction Studies. . . . .	241
3.10.4	Combined X-Ray Absorption and X-Ray Diffraction for In-Situ Studies of Catalysts . . . . .	243
3.11	Problems . . . . .	247
3.12	Further Reading . . . . .	254
<b>4</b>	<b>The Significance of Pore Structure and Surface Area in Heterogeneous Catalysis . . . . .</b>	<b>257</b>
4.1	The Importance of Pore Structure and Surface Area . . . . .	257
4.2	Experimental Methods of Estimating Surface Areas . . . . .	258
4.2.1	The Volumetric Method . . . . .	259
4.2.2	The Gravimetric Method . . . . .	264
4.2.3	The Dynamic Method . . . . .	265
4.3	Experimental Methods of Estimating Pore Volume and Diameter. . . . .	267
4.3.1	Gas Adsorption Method of Estimating Pore Volume and Diameter . . . . .	268
4.3.2	Mercury Porosimeter Method of Estimating Pore Volume and Diameter . . . . .	272
4.4	Models of the Pore Structure of Catalyst Materials . . . . .	275
4.4.1	Hysteresis and the Shapes of Capillaries. . . . .	276
4.4.1.1	Type A Hysteresis Loops . . . . .	277
4.4.1.2	Type B Hysteresis Loops. . . . .	279
4.4.1.3	Type C Hysteresis Loops . . . . .	280
4.4.1.4	Type D Hysteresis Loops . . . . .	281
4.4.1.5	Type E Hysteresis Loops. . . . .	282
4.4.1.6	Other Adsorption-Desorption Characteristics . . . . .	282
4.4.2	Geometric Models of Pores . . . . .	283
4.4.3	Wheeler's Semi-empirical Pore Model . . . . .	285
4.4.4	Mathematical Models of Porous Structures . . . . .	286
4.4.4.1	The Dusty Gas Model . . . . .	286
4.4.4.2	The Random Pore Model . . . . .	287
4.4.4.3	Stochastic Pore Networks and Fractals . . . . .	288
4.5	Diffusion in Porous Catalysts. . . . .	290
4.5.1	The Effective Diffusivity . . . . .	290
4.5.1.1	Molecular (Maxwellian) Diffusion or Bulk Diffusion . . . . .	292
4.5.1.2	Knudsen Diffusion. . . . .	294
4.5.1.3	The Transition Region of Diffusion. . . . .	294
4.5.1.4	Forced Flow in Pores . . . . .	295
4.6	Chemical Reaction in Porous Catalyst Pellets . . . . .	295
4.6.1	Effect of Intraparticle Diffusion on Experimental Parameters. . . . .	303

4.6.2	Non-isothermal Reactions in Porous Catalyst Pellets . . . . .	305
4.6.3	Criteria for Diffusion Control . . . . .	308
4.6.4	Experimental Methods of Assessing the Effect of Diffusion on Reaction . . . . .	313
4.7	Problems . . . . .	314
4.8	Further Reading . . . . .	317
<b>5</b>	<b>The Solid-State and Surface Chemistry of Catalysts . . . . .</b>	<b>319</b>
5.1	Classification of Heterogeneous Catalysts. . . . .	319
5.2	Structures . . . . .	320
5.2.1	Metals and Alloys . . . . .	320
5.2.1.1	Miller Indices and Miller-Bravais Indices . . . . .	321
5.2.1.2	Transition-Metal Alloys and Bimetallic Clusters . . . . .	324
5.2.1.3	Highly-Dispersed Metals . . . . .	325
5.1.3	Interstitial Phases . . . . .	327
5.1.4	Simple Metallic Oxides and their Non-stoichiometric Variants . . . . .	328
5.2.4	Shear and Block Structures Based on $\text{ReO}_3$ . . . . .	335
5.2.5	More Complicated Metallic Oxides. . . . .	339
5.2.6	Even More Complicated Oxides . . . . .	340
5.2.6.1	Perovskites and their Defective Variants . . . . .	340
5.2.6.2	Perovskites as the Prototypes of New Homologous Series . . . . .	341
5.2.6.3	Spinel, Scheelites and the Bismuth Molybdates . . . . .	344
5.2.6.4	Heteropolyions (Keggin Structures) as Catalytically Significant Entities . . . . .	346
5.2.7	Clays, Zeolites and Related Structures. . . . .	347
5.2.7.1	Pillared Clays are Effectively Two-Dimensional Zeolites . . . . .	352
5.2.7.2	A Synoptic Guide to the Structure of Zeolitic and Related Solid Catalysts . . . . .	353
5.3	Computational Approaches. . . . .	364
5.3.1	A Resumé of Available Methodologies . . . . .	364
5.3.1.1	Selected Applications . . . . .	369
5.4	A Chemist's Guide to the Electronic Structure of Solids and Their Surfaces. . . . .	377
5.4.1	Energy Bands . . . . .	378
5.4.1.1	Bands in 1D and 3D Crystals. . . . .	381
5.4.1.2	Energy Bands in Ionic Solids . . . . .	384
5.4.1.3	Energy Bands in Transition-Metal Oxides: Understanding the Electronic Structure of the Monoxides of Titanium, Vanadium, Manganese and Nickel . . . . .	386
5.4.1.4	Energy Bands in Structures Related to $\text{ReO}_3$ . . . . .	387
5.4.2	Fermi Levels in Insulators and Semiconductors. . . . .	389
5.4.3	Surface Electronic States and the Occurrence of Energy Levels Within the Band Gap . . . . .	391
5.4.4	Band Bending and Metal-Semiconductor Junctions: Schottky Barriers . . . . .	392

5.4.4.1	Depletive Chemisorption on Semiconductors . . . . .	394
5.4.4.2	The Bending of Bands when Semiconductors are Immersed in Electrolytes . . . . .	395
5.4.5	Quantum Chemical Approaches to the Electronic Properties of Solids . . . . .	397
5.4.5.1	The Cluster and Thin-Slab Approach . . . . .	398
5.4.6	Hückel and Extended Hückel Calculations . . . . .	398
5.4.6.1	'Ab-Initio' Methods . . . . .	400
5.4.7	A Brief Selection of Quantum Chemical Studies . . . . .	402
5.4.7.1	Band Widths, DOS and Fermi Levels of the Transition Metals. . . . .	403
5.4.7.2	Heats of Chemisorption from EHT Calculations . . . . .	404
5.4.7.3	The Adsorption of CO on Nickel . . . . .	406
5.4.7.4	Dissociative Chemisorption of CO . . . . .	407
5.4.7.5	Insight from Ab-Initio Computations: Methanol Synthesis and Olefin Metathesis. . . . .	408
5.5	Epilogue . . . . .	410
5.6	Problems . . . . .	411
5.7	Further Reading . . . . .	414
<b>6</b>	<b>Poisoning, Promotion, Deactivation and Selectivity of Catalysts . . . . .</b>	<b>417</b>
6.1	Background . . . . .	417
6.1.1	Effect of Mass Transfer on Catalytic Selectivity . . . . .	418
6.1.1.1	Effect of Intraparticle Diffusion . . . . .	418
6.1.1.2	Non-isothermal Conditions . . . . .	423
6.1.1.3	Effect of Interparticle Mass and Heat Transfer . . . . .	425
6.1.2	Bifunctional Catalysts . . . . .	427
6.2	Catalyst Deactivation. . . . .	429
6.2.1	Deactivation Processes . . . . .	430
6.2.2	Deactivation Models . . . . .	432
6.2.2.1	Steady-State Model . . . . .	432
6.2.2.2	A Dynamic Model. . . . .	437
6.2.3	Operational Consequences of Poisoning. . . . .	440
6.3	Modern Theories of Poisoning and Promotion . . . . .	440
6.3.1	General Theoretical Considerations . . . . .	440
6.3.2	Theoretical Interpretation of Poisoning and Promotion. . . . .	445
6.3.2.1	The Electronegativity of a Poison Seems to be of Secondary Importance . . . . .	448
6.3.2.2	Other Factors Responsible for Promotion and Poisoning . . . . .	449
6.4	Problems . . . . .	450
6.5	Further Reading . . . . .	453
<b>7</b>	<b>Catalytic Process Engineering . . . . .</b>	<b>455</b>
7.1	Statement of the Problem . . . . .	455
7.2	Kinetics of Heterogeneous Catalytic Reactions . . . . .	455

7.2.1	The Overall Rate of Reaction	455
7.2.2	The Rate of Chemical Reaction	460
7.2.3	Fundamental Kinetic Models	460
7.2.4	The Effect of Intraparticle Diffusion	465
7.2.5	The Effect of Interparticle (Fluid-to-Solid) Transport	466
7.2.6	The Effect of Catalyst Deactivation	468
7.3	Catalytic Reactors	472
7.3.1	Experimental Laboratory Reactors	472
7.3.1.1	Batch Reactors	473
7.3.1.2	Tubular Reactors	474
7.3.1.3	Continuous Stirred-Tank Reactor	477
7.3.1.4	Recycle Reactor	480
7.3.1.5	Flowing-Solids Reactors	481
7.3.1.6	Slurry Reactors	483
7.3.2	Industrial Chemical Reactors	486
7.3.2.1	Batch Reactors	487
7.3.2.2	Continuous Tubular Reactors	489
7.3.2.3	Fluidised-Bed Reactor	499
7.3.2.4	The Trickle-Bed Reactor	502
7.3.2.5	Metal Gauze Reactors	503
7.3.3	Thermal Characteristics of a Catalytic Reactor	504
7.4	Problems	509
7.5	Further Reading	513
<b>8</b>	<b>Heterogeneous Catalysis: Examples and Case Histories</b>	<b>515</b>
8.1	The Synthesis of Methanol	515
8.1.1	Proof that CO is not Dissociated During Methanol Synthesis	516
8.1.2	The Role of CO <sub>2</sub> : Evidence that it is the Main Source of CH <sub>3</sub> OH	517
8.1.3	The State of Copper in the Working Catalyst	517
8.1.4	The Role of Oxide Supports: Is There Anything Special About ZnO?	519
8.1.5	Views on the Mechanism of the Reaction	519
8.1.6	Process Conditions, Reaction Configurations and Kinetics	521
8.2	Fischer-Tropsch Catalysis	524
8.2.1	Mechanistic Considerations	526
8.2.1.1	Does Synthesis Proceed via Hydroxymethylene Intermediates?	527
8.2.1.2	What of the CO Insertion Mechanism?	528
8.2.1.3	Synthesis by the Fischer-Tropsch Process First Requires Dissociation of CO	528
8.2.1.4	Schultz-Flory Statistics	531
8.2.1.5	Other Possible Mechanisms	532
8.2.2	Fine-Tuning the Fischer-Tropsch Process	533
8.2.3	Practical Fischer-Tropsch Catalysts and Process Conditions	536
8.2.4	Reductive Coupling of Two CO Ligands Forming Acetylene from Syn-Gas	538

8.2.5	Methanation, Steam Reforming and Water-Gas Shift Reactions	540
8.2.5.1	Methanation	540
8.2.5.2	Steam Reforming	541
8.2.5.3	Water-Gas Shift Reaction	545
8.3	The Synthesis of Ammonia	548
8.3.1	Catalyst Promoters are of Two Kinds	549
8.3.2	Kinetics of the Overall Reaction: The Temkin-Pyzhev Description	549
8.3.3	The Surface of Iron Catalysts for Ammonia Synthesis Contain Several Other Elements: But is the Iron Crystalline?	551
8.3.3.1	Does Ammonia Synthesis Proceed via Atomically or Molecularly Adsorbed Nitrogen?	553
8.3.3.2	How and Where are the Reactant Gases Adsorbed at the Catalyst Surface?	554
8.3.3.3	A Potential-Energy Diagram Illustrating How the Overall Reaction Leading to Ammonia Synthesis can be Constructed	557
8.3.3.4	How Potassium Serves as an Electronic Promoter	558
8.3.4	The Technology of Ammonia Synthesis	559
8.3.4.1	Reactor Configurations are Important Industrially	561
8.4	Oxidation of Ammonia: Stepping Towards the Fertilizer Industry	564
8.5	In-Situ Catalytic Reaction and Separation	567
8.5.1	Catalytic Distillation	567
8.5.2	Pressure Swing Reaction	571
8.5.3	Catalytic Membrane Processes	572
8.6	Automobile Exhaust Catalysts and the Catalytic Monolith	576
8.6.1	The Three-Way Catalyst (TWC)	577
8.6.2	Why is Rhodium in the Auto-Exhaust Catalyst?	578
8.6.3	The Catalytic Monolith	580
8.6.4	Catalytic Monoliths may be Used in Several Applications	581
8.6.5	Rate Characteristics of Catalytic Combustion Processes	582
8.6.6	Combustion Reactions in a Catalytic Monolith Differ from Those Occurring in a Homogeneously Operated Combustor	583
8.6.7	Simulation of the Behaviour of a Catalytic Monolith is Important for Design Purposes	585
8.7	Photocatalytic Breakdown of Water and the Harnessing of Solar Energy	590
8.7.1	Oxygen Generation by Photo-induced Oxidation of Water	591
8.7.2	Hydrogen Generation by Photo-induced Reduction of Water	593
8.7.3	Simultaneous Generation of Hydrogen and Oxygen by Catalysed Photolysis of Water	594
8.7.4	Other Photochemical Methods of Harnessing Solar Energy	596
8.7.5	Catalysis and Photoelectrochemistry: Photocatalysis and Photoelectrosynthesis	597
8.7.5.1	The Principles	598
8.7.5.2	Practical Examples	602
8.7.5.3	The Prospects	604

## XVIII *Contents*

8.8	Catalysis Using Microporous or Mesoporous Solids and Modified Clays: Its Growing Role in the Petroleum Industry and Clean Technology . . . . .	608
8.8.1	Activity of Zeolitic Catalysts . . . . .	612
8.8.2	Shape-Selective Zeolitic Catalysts . . . . .	614
8.8.3	New Microporous Crystalline Catalysts . . . . .	616
8.8.4	Some Case Studies of In-Situ Monitoring of Catalysis with ZSM-5 . .	619
8.8.5	A Rationally Chosen Zeolitic Catalyst . . . . .	621
8.8.6	New Mesoporous Catalysts . . . . .	622
8.8.7	Clays and Other Solid Acid Catalysts . . . . .	624
8.8.7.1	Clays and their Possible Role in Replication, Evolution and the Origin of Life . . . . .	626
8.9	Catalytic Processes in the Petroleum Industry . . . . .	627
8.9.1	Catalytic Reforming . . . . .	627
8.9.2	Catalytic Cracking . . . . .	631
8.9.2.1	Cracking Reactions . . . . .	632
8.9.2.2	Cracking Catalysts . . . . .	633
8.9.2.3	The Catalytic Cracking Reactor . . . . .	634
8.9.3	Hydrotreating . . . . .	636
8.10	The Role of Catalysis in Energy-Related Environmental Technology . . . . .	641
8.11	Problems . . . . .	643
8.12	Further Reading . . . . .	650
<b>Index</b>	. . . . .	<b>659</b>