



# Contents

Preface XIII

List of Contributors XV

Abbreviations XIX

## Part I Basic Principles and Tools

### 1 General Aspects 3

*Krijn P. de Jong*

- 1.1 Importance of Solid Catalysts 3
- 1.2 Development of Solid Catalysts 4
- 1.3 Development of Solid Catalyst Synthesis 5
- 1.4 About This Book 10
- References 10

### 2 Interfacial Chemistry 13

*Alexis Lycourghiotis*

- 2.1 Introduction 13
- 2.2 Interfacial and Bulk Deposition 14
- 2.3 The Surface of the Oxidic Supports: Surface Ionization Models 15
  - 2.3.1 The Charged Surface of the Oxidic Supports 15
  - 2.3.2 Homogeneous Surface Ionization Models 16
  - 2.3.3 The Music Model 17
- 2.4 The Size and the Structure of the Interface 18
- 2.5 The Arrangement of the Ions Inside the Interface and the Deposition Modes 20
  - 2.5.1 Indifferent Ions 20
  - 2.5.2 Transition-Metal Ionic Species 22
- 2.6 Determining the Mode of Interfacial Deposition and the Surface Speciation/Structure of the Deposited Precursor Species 23
  - 2.6.1 Introductory Remarks 23

2.6.2	Methodologies Based on Macroscopic Adsorption Data and Potentiometric Titrations as well as on Microelectrophoretic Mobility or Streaming Potential Measurements	23
2.6.3	Spectroscopic Investigations	25
2.6.4	Quantum-Mechanical Calculations	26
2.6.5	Electrochemical (Equilibrium) Modeling	26
2.7	A Case Study: The Deposition of $\text{Co}(\text{H}_2\text{O})_6^{2+}$ Aqua Complex on the Titania Surface	27
2.7.1	Experimental Investigation	27
2.7.2	Quantum-Mechanical Calculations	28
2.7.3	Electrochemical (Equilibrium) Modeling	29
	References	30

### **3 Electrostatic Adsorption 33**

*John R. Regalbuto*

3.1	Introduction	33
3.2	Purely Electrostatic Adsorption	37
3.3	Electrostatic Adsorption with Metal Respeciation	38
3.4	Electrostatic Adsorption and Ion Exchange	41
3.5	Electrostatic Adsorption and Deposition-Precipitation	45
3.6	Electrostatic Adsorption and Surface Reaction	46
3.7	Electrostatics and Dissolution, Reaction, and Redeposition	47
3.8	Electrostatics-Based Design	48
3.8.1	Well-Dispersed Single Metals	49
3.8.2	Selective Adsorption onto Promoters	51
3.8.3	Bimetallic Catalysts	54
3.9	Summary	57
	References	57

### **4 Impregnation and Drying 59**

*Eric Marceau, Xavier Carrier, and Michel Che*

4.1	Introduction	59
4.2	Impregnation	61
4.2.1	Methods of Impregnation	61
4.2.2	Physical Models for Impregnation	62
4.3	Drying	64
4.4	The Chemistry	67
4.4.1	Concentrations and pH	67
4.4.2	Precursor-Support Interactions	69
4.4.2.1	Adsorption: From Electrostatic Interactions to Grafting	69
4.4.2.2	The Formation of Mixed Phases	70
4.4.3	Ligands	71
4.4.4	Counterions	73
4.5	Impregnation and Drying of an $\text{MoO}_x/\text{Al}_2\text{O}_3$ Catalyst	74
4.5.1	Molybdenum Speciation and Its Consequences	74

4.5.2	Degrees of Freedom: Drying Parameters and Ligands in Solution	76
4.6	Conclusions	77
	References	78
<b>5</b>	<b>Sol-Gel Processing</b>	<b>83</b>
	<i>Miron V. Landau</i>	
5.1	Introduction	83
5.2	Physicochemical Basis and Principles of Sol-Gel Processing	85
5.2.1	Activation	86
5.2.2	<i>Polycondensation</i>	87
5.2.3	Gelation/Aging/Washing	89
5.2.4	Gel Drying/Desolvation	90
5.2.5	Stabilization of Xero- and Aerogels	90
5.3	Application of Sol-Gel Processing for the Preparation of Solid Catalysts	91
5.3.1	Bulk Catalytic Phase Materials: Xero- and Aerogels	91
5.3.1.1	Monometallic Catalytic Materials	91
5.3.1.2	Multimetallc Composite Catalytic Phases	94
5.3.2	Catalytic Materials and Modifiers Entrapped in Porous Matrices	97
5.3.2.1	Atoms or Molecular Substances Entrapped by Cocondensation at the Colloidization Step	98
5.3.2.2	Molecular Substances Adsorbed or Entrapped at the Gelation Step	103
5.4	Summary	106
	References	106
<b>6</b>	<b>Deposition Precipitation</b>	<b>111</b>
	<i>Krijn P. de Jong</i>	
6.1	Introduction	111
6.2	Theory and Practice	112
6.3	Mechanistic Studies	115
6.3.1	Kinetics	115
6.3.2	Molecular Details	118
6.4	Case Studies	120
6.4.1	pH Increase	120
6.4.2	Reduction Deposition Precipitation	124
6.4.3	Ligand Removal	128
6.4.4	Miscellaneous Methods	129
6.5	Summary, Conclusions, and Outlook	131
	Acknowledgments	131
	References	132
<b>7</b>	<b>Coprecipitation</b>	<b>135</b>
	<i>Martin Lok</i>	
7.1	Introduction	135

7.2	Basic Principles of Precipitation and Nucleation	136
7.3	Raw Materials	139
7.4	Precipitation Conditions	141
7.5	Process Operation	141
7.6	Examples	145
7.6.1	High Metal Nickel/Alumina Catalysts	145
7.6.2	Single-Step Sulfur-Promoted Nickel/Alumina Catalyst	146
7.6.3	Copper/Zinc Methanol Catalysts	147
7.6.4	Iron-Based Fischer–Tropsch Catalysts	148
7.6.5	Unsupported Metal Sulfide Catalysts for Hydrotreating	148
7.7	New Developments in Process Monitoring	148
	Acknowledgments	149
	References	149

## **8 Clusters and Immobilization** 153

*Sophie Hermans*

8.1	Introduction	153
8.2	The Surface of Common Supports	154
8.3	Clusters in Catalysis	157
8.4	Reaction with Unmodified Surface	160
8.5	“Ship-in-a-Bottle” Synthesis	163
8.6	Tethering	167
8.7	Concluding Remarks	168
	References	169

## **9 Shaping of Solid Catalysts** 173

*Bettina Kraushaar-Czarnetzki and Steffen Peter Müller*

9.1	Objectives of Catalyst Shaping	173
9.2	Fixed-Bed Reactors – Particle Beds	177
9.2.1	Pelleting	177
9.2.2	Granulation	179
9.2.3	Extrusion	181
9.2.4	Tailoring of the Pore-Size Distribution	184
9.2.5	Fixed-Bed Egg-Shell Catalysts	186
9.3	Fixed-Bed Reactors – Monoliths	187
9.3.1	Honeycombs	187
9.3.1.1	Ceramic Honeycombs	188
9.3.1.2	Metallic Honeycombs	190
9.3.2	Open-Cell Foams	192
9.3.3	Coating of Monoliths	194
9.4	Catalysts for Moving-Bed Reactors	195
9.5	Catalysts for Fluidized Beds	196
	References	198

<b>10</b>	<b>Space and Time-Resolved Spectroscopy of Catalyst Bodies</b>	<b>201</b>
	<i>Bert M. Weckhuysen</i>	
10.1	Introduction	201
10.2	Space- and Time-Resolved Methods Applied to Catalyst Bodies	201
10.2.1	Invasive Methods	202
10.2.2	Noninvasive Methods	205
10.3	Case Studies	209
10.3.1	Keggin-Type Co-Mo Complexes in Catalyst Bodies	209
10.3.2	Speciation of Co Complexes in Catalyst Bodies	212
10.4	Future Prospects	215
	Acknowledgments	215
	References	216
<b>11</b>	<b>High-Throughput Experimentation</b>	<b>217</b>
	<i>Uwe Rodemerck and David Linke</i>	
11.1	Introduction	217
11.2	Synthesis Strategies	219
11.2.1	Combinatorial Strategies	220
11.2.2	Methods to Reduce Experiments	220
11.3	Catalyst Libraries for Primary Screening	223
11.3.1	Wafer-Based Preparation	223
11.3.2	Single Pellets	224
11.3.3	Single Beads	225
11.4	Catalyst Libraries for Secondary Screening	225
11.4.1	Impregnation Techniques	226
11.4.2	Precipitation	226
11.4.3	Hydrothermal Synthesis	230
11.4.4	Sol-Gel Chemistry	231
11.4.5	Drying, Calcination, and Shaping	231
11.5	Catalyst Libraries for Special Reactor Types	234
11.6	An Industrial Point of View	234
11.7	Conclusions	235
	References	236
<b>Part II</b>	<b>Case Studies</b>	
<b>12</b>	<b>Concepts for Preparation of Zeolite-Based Catalysts</b>	<b>243</b>
	<i>Metin Bulut and Pierre A. Jacobs</i>	
12.1	Introduction and Scope	243
12.2	Zeolite Effects in Catalysis	245
12.2.1	Brønsted Acidity in Metallosilicate Zeolites	245
12.2.2	Zeolite Protonic Superacidity	246
12.2.3	Brønsted Acidity in Substituted Four-Coordinated Aluminophosphates	247
12.2.4	Zeolite Shape Selectivity	250

12.2.5	Concentration Effects by Specific Adsorption	253
12.2.6	Site Isolation or the Role of Zeolites as Solid Solvents	254
12.3	Zeolitization	254
12.3.1	Overall Steps in Zeolite Crystallization	255
12.3.2	Classic Model for Zeolite Growth	257
12.3.3	The Aggregation Model	259
12.3.4	Zeolitization Parameters	260
12.3.5	Nanocrystalline Zeolites	264
12.3.6	Zeolite Synthesis via the Dry Gel Route	265
12.3.7	AlPO <sub>4</sub> -n-Based Molecular Sieve Zeolites	266
12.3.8	Ionothermal Synthesis Method	267
12.3.9	Zeolites with Pores Beyond the 12-MR	267
12.3.10	Upscaling of Zeolite Synthesis	268
	References	268
	Further Reading	276

## **13 Ordered Mesoporous Materials 277**

*Ying Wan and Dongyuan Zhao*

13.1	Introduction	277
13.2	Mesoporous Silica	277
13.2.1	MCM-41	279
13.2.2	SBA-15	280
13.2.3	MCM-48	281
13.2.4	Pore-Size Control	282
13.3	Organic Group Functionalized Mesoporous Silicates	284
13.3.1	Organic Groups Anchored to Mesoporous Silicates	284
13.3.2	Periodic Mesoporous Organosilicas	285
13.3.3	Adsorption and Catalysis	285
13.4	Metal-Substituted Mesoporous Silica Molecular Sieves	287
13.5	Carbon	289
13.5.1	The Hard-Templating Approach	289
13.5.2	The Supramolecular-Templating Approach	290
13.6	Nonsiliceous Oxides	293
13.6.1	The Supramolecular-Templating Approach	293
13.6.2	The Hard-Templating Approach	294
13.7	Nonoxides	294
13.7.1	SiC-Based Materials	294
13.7.2	Metal Sulfides	296
13.8	Summary and Remarks	296
	Acknowledgments	297
	References	297

## **14 Hydrotreating Catalysts 301**

*Sonja Eijssbouts*

14.1	Introduction	301
------	--------------	-----

14.2	Typical Hydrotreating Catalyst	302
14.2.1	Typical Catalyst Composition	302
14.2.2	Literature Describing the Preparation of Hydrotreating Catalysts	302
14.3	Support Preparation	303
14.3.1	Precipitation of $\gamma$ -Alumina	303
14.3.2	Addition of SiO <sub>2</sub>	305
14.3.3	Addition of Other Components (e.g. Zeolites) and Extrusion	305
14.3.4	Drying and Calcination of Al <sub>2</sub> O <sub>3</sub> and SiO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub> Supports	307
14.4	Metal Comixing/Coextrusion and Coprecipitation Routes	307
14.4.1	Addition of Metals to the Al <sub>2</sub> O <sub>3</sub> Dough	307
14.4.2	Bulk Catalysts	308
14.4.3	Drying and Calcination of Catalysts Prepared by Comixing/Coextrusion and Coprecipitation Routes	308
14.5	Impregnation of Metals	309
14.5.1	Typical Additives and Solution Stabilizers	309
14.5.2	Pore-Volume Impregnation versus Dipping/Equilibrium Impregnation of Compacted Support Particles	310
14.5.3	Sequential versus Coimpregnation	314
14.5.4	Drying and Calcination	315
14.6	Presulfiding as the Last Stage in Hydrotreating Catalyst Preparation	318
14.6.1	Presulfiding Goals	318
14.6.2	Gas-Phase versus Liquid-Phase Presulfiding	319
14.6.3	<i>Ex-situ</i> versus <i>In-situ</i> Presulfiding	320
14.7	Industrial Process for the Production of the Oxidic Catalyst	323
14.7.1	Industrial Equipment	323
14.7.2	Health, Safety, and Environmental Issues	323
14.8	Summary	324
	References	324

## 15 Methanol Catalysts 329

*S. Schimpf and M. Muhler*

15.1	Binary Cu/ZnO Catalysts	329
15.2	Coprecipitation	331
15.2.1	Precipitation	333
15.2.2	Aging	334
15.2.3	Washing	337
15.2.4	Drying and Calcination	337
15.2.5	Reduction	339
15.3	The Role of Alumina in Ternary Catalysts	341
15.4	Alternative Preparation Routes	344
15.4.1	Alternative Anions	344
15.4.2	Chemical Vapor Deposition	347
15.4.3	Promising Strategies	347
15.5	Conclusions	348

Acknowledgment 348

References 349

**16 Case Studies of Nobel-Metal Catalysts 353**

*Stuart Soled*

16.1 Introduction 353

16.2 Optimization of Catalyst Preparation 354

16.2.1 Electrostatic Interactions and the Use of Zeta Potential  
Measurements 355

16.2.2 Noble-Metal Impregnation Example onto a Modified  
Silica-Alumina Support 356

16.2.3 A Novel Approach for the Preparation of Dispersed Ru on Silica 358

16.2.4 Other Metals that Form Similar Supported Complexes as Ru 363

16.2.5 Conclusions 365

Acknowledgments 366

References 366

**17 Gold Catalysts 369**

*Catherine Louis*

17.1 Introduction 369

17.2 Preparations Involving Aqueous Solutions 370

17.2.1 Impregnation to Incipient Wetness 370

17.2.2 Anion Adsorption 371

17.2.3 Small Particles from  $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$  371

17.2.4 Deposition-Precipitation with NaOH 373

17.2.5 Gold Complex Interaction with Oxide Supports 375

17.2.6 Deposition-Precipitation with Urea 376

17.2.7 Cation Adsorption 378

17.3 Preparations Involving Organometallic Precursors 379

17.3.1 Impregnation of Phosphine-Based Gold Complexes 379

17.3.2 Impregnation of Other Organogold Complexes 380

17.4 Deposition of Gold Nanoparticles 380

17.4.1 Deposition of Gold Colloids 380

17.4.2 Deposition of Dendrimer-Encapsulated Gold Nanoparticles 384

17.5 One-Step Preparations 384

17.5.1 Coprecipitation 385

17.5.2 Sol-Gel Method 386

17.6 Special Methods 386

17.6.1 Photochemical Deposition 386

17.6.2 Sonochemical Techniques 387

17.7 Conclusion 387

References 388

**Index 393**