

# Design of Heterogeneous Catalysts

New Approaches based on Synthesis,  
Characterization and Modeling

*Edited by*  
*Umit S. Ozkan*



WILEY-VCH Verlag GmbH & Co. KGaA

## Contents

Preface XIII

List of Contributors XV

<b>1</b>	<b>Use of Oxide Ligands in Designing Catalytic Active Sites</b>	<b>1</b>
	<i>Edward L. Lee and Israel E. Wachs</i>	
1.1	Introduction	1
1.2	Molecular Structural Determination of Supported Metal Oxide Catalysts with <i>In Situ</i> Raman Spectroscopy	3
1.3	Characterization of $\text{AlO}_x$ , $\text{TiO}_x$ , and $\text{ZrO}_x$ Surface-Modified $\text{SiO}_2$	3
1.4	Anchoring Site of Surface $\text{M}_1\text{O}_x$ Species on Supported $\text{M}_2\text{O}_x/\text{SiO}_2$	5
1.5	Molecular Structure of Dehydrated Supported $\text{V}_2\text{O}_5/\text{SiO}_2$ and $\text{V}_2\text{O}_5/\text{M}_2\text{O}_x/\text{SiO}_2$ Catalyst Systems	5
1.6	Molecular Structure of Dehydrated Supported $\text{MoO}_3/\text{SiO}_2$ and $\text{MoO}_3/\text{M}_2\text{O}_x/\text{SiO}_2$ Catalyst Systems	8
1.7	Molecular Structure of Dehydrated Supported $\text{Re}_2\text{O}_7/\text{SiO}_2$ and $\text{Re}_2\text{O}_7/\text{M}_2\text{O}_x/\text{SiO}_2$ Catalyst Systems	11
1.8	Electronic Structure of Dehydrated Supported $\text{MO}_x/\text{SiO}_2$ and $\text{M}_1\text{O}_x/\text{M}_2\text{O}_x/\text{SiO}_2$ Catalysts via <i>In Situ</i> UV-Vis Spectroscopy	14
1.9	Determination of Surface Kinetic Parameters	15
1.10	Redox Surface Reactivity of Model Supported $\text{M}_1\text{O}_x/\text{SiO}_2$ Catalysts	16
1.11	Redox Surface Reactivity of Supported $\text{M}_1\text{O}_x/\text{M}_2\text{O}_x/\text{SiO}_2$ Catalysts	16
1.12	Conclusions	18
	References	19
<b>2</b>	<b>Optimal Design of Hierarchically Structured Porous Catalysts</b>	<b>25</b>
	<i>Marc-Olivier Coppens and Gang Wang</i>	
2.1	Introduction	25
2.1.1	Intrinsic Catalytic Activity and Selectivity: the Atomic and the Nanoscale	25
2.1.2	Catalyst Particle Size and Geometry: A Question of Reactor Engineering	26

2.1.3	Porous Catalyst Architecture and Optimization Methods	27
2.1.4	Learning from Nature	28
2.2	Optimizing Mesopore Connectivity and Shape	30
2.2.1	Topology, Order, and Randomness	30
2.2.2	Surface Roughness and Fractal Morphology	32
2.3	Optimizing Catalysts by Macroscopic Distributions in Activity	34
2.4	Optimal Design of the Highway Network	36
2.4.1	Novel Capabilities in Synthesizing Hierarchical Pore Spaces	37
2.4.2	Theoretical Optimization Studies: Opportunities for Optimal Design	39
2.4.3	Application to the Design of a Bimodal Porous Catalyst for NO <sub>x</sub> Abatement	47
2.5	Conclusions	49
	References	50

### **3 Use of Dendrimers in Catalyst Design** 59

*Bert D. Chandler, Jeong-Kyu Lee, Harold H. Kung, and Mayfair C. Kung*

3.1	Introduction	59
3.2	Modified Dendrimer Catalysts	60
3.2.1	Dendrimer Synthesis	60
3.2.2	Dendrimer Properties Important for Catalysis	61
3.2.3	Cooperative Catalysis	61
3.2.4	Site Isolation	64
3.3	Indirect Effects of Dendrimer Architecture	66
3.3.1	Polarity Gradients	66
3.3.2	Steric and Diffusion Effects	67
3.3.3	Comparing Dendrimers with Soluble Polymers	68
3.3.4	Other Novel Dendrimer Effects	70
3.4	Catalysis by Dendrimer Encapsulated Nanoparticles	72
3.4.1	Nanoparticle Synthesis	72
3.4.2	Catalysis by Monometallic DENs	73
3.4.3	Bimetallic Nanoparticles	73
3.4.4	Catalysis by Bimetallic DENs	75
3.5	Dendrimer Templated Nanocages	77
3.6	Conclusion	79
	References	79

### **4 Rational Design Strategies for Industrial Catalysts** 83

*Saeed Alerasool, C.P. Kelkar, and Robert J. Farrauto*

4.1	Introduction	83
4.2	The First Stages Toward Commercialization of a Catalyst	84
4.3	Catalyst Discovery to Commercialization	84
4.3.1	Catalyst Preparation	84
4.3.2	Catalyst Testing	85
4.3.3	Advanced Testing in Accordance to the Duty Cycle	86

4.3.4	Aging Studies	86
4.3.5	Kinetics	87
4.3.6	Catalyst Scale-Up	88
4.3.7	Quality Control	89
4.4	Example 1: Automobile Pollution Abatement Catalyst System	89
4.4.1	The Quality of the Fuel	90
4.4.2	Base Metals Versus Precious Metals	90
4.4.3	Particulate Versus Monolithic Structures	91
4.4.4	The First Generation	91
4.4.5	The Final Test	92
4.5	Example 2: Dehydrogenation of Light Alkanes	93
4.5.1	Understanding Reaction Kinetics, Thermodynamics, and Process Constraints	94
4.5.2	Formulating the Catalyst	95
4.5.3	Pilot Plant Testing	97
4.5.4	Field Testing	98
4.5.5	Commercial Launch	99
4.6	Example 3: Petroleum Refining – Fluid Catalytic Cracking	100
4.6.1	Understanding Deactivation	101
4.6.2	Age Distribution	105
4.6.3	Attrition	105
4.6.4	Feed Effects	107
4.6.5	Scale-Up and Commercialization	109
4.7	Conclusions	109
	References	110
<b>5</b>	<b>Chiral Modification of Catalytic Surfaces</b>	<b>113</b>
	<i>Zhen Ma and Francisco Zaera</i>	
5.1	Introduction	113
5.2	Modification of Metal Surfaces by Cinchona Alkaloid and Related Compounds	115
5.2.1	General Background	115
5.2.2	Ordering Within the Adsorbed Layers	116
5.2.3	Modifier–Substrate Interactions	118
5.2.4	Adsorption Geometry	120
5.2.5	Influence of Reaction Conditions	122
5.2.6	Competitive Adsorption of Modifiers	125
5.3	Modification of Metal Surfaces by Tartaric Acid and Related Compounds	127
5.3.1	General Background	127
5.3.2	Long-Range Order Within the Adsorbed Layers	127
5.3.3	Local Chirality on the Surface	130
5.3.4	Identification of Chiral Sites on Surfaces	132
5.4	Conclusions	134
	References	136

<b>6</b>	<b>Catalytic Nanomotors</b>	<b>141</b>
	<i>John Gibbs and Yiping Zhao</i>	
6.1	Introduction	141
6.1.1	Biological Motors	142
6.1.2	Artificial Catalytic Nanomotors	142
6.2	The Propulsion Mechanism of Catalytic Nanomotors	144
6.2.1	Diffusiophoresis	144
6.2.2	Self-Electrophoresis	145
6.2.3	Bubble Propulsion	148
6.2.4	Interfacial Tension Gradients	149
6.2.5	Bioelectrochemical Propulsion	150
6.3	Advanced Design of Catalytic Nanomotors	151
6.3.1	Dynamic Shadowing Growth	151
6.3.2	Rotary Si–Pt Nanorod Nanomotors	151
6.3.3	L-Shaped Nanorod Nanomotors	152
6.3.4	Rolling Nanospring	153
6.3.5	Hinged Nanorods	154
6.4	Applications, Challenges, and Perspectives	157
	References	158
<b>7</b>	<b>Rational Design and High-Throughput Screening of Metal Open Frameworks for Gas Separation and Catalysis</b>	<b>161</b>
	<i>David Farrusseng and Claude Mirodatos</i>	
7.1	Introduction	161
7.2	MOF General Features and Brief State of the Art	162
7.2.1	A Building Block Construction	162
7.2.2	Robust Open, Functionalized, and Sizeable Frameworks	162
7.2.3	MOFs Synthesis	164
7.2.4	Adsorption Properties of MOF	166
7.2.5	Rational Strategies to Design MOFs for Targeted Applications	167
7.3	Combinatorial Design of MOF for CO <sub>2</sub> Capture in a PSA Process	167
7.3.1	Process Specifications	167
7.3.2	General Properties of MOFs for CO <sub>2</sub> Adsorption	168
7.3.3	MOF Design for CO <sub>2</sub> Capture	171
7.3.3.1	“Structural” Route for Design Strategy	171
7.3.3.2	“Functionalization” Route for Design Strategy	172
7.3.4	Combinatorial Screening Methodology at IRCELYON	173
7.3.5	Combinatorial Synthesis	174
7.3.5.1	Protocol	174
7.3.5.2	Method Validation	174
7.3.5.3	Screening of Metal-BTC System	175
7.3.6	Characterization of Representative Samples	177
7.3.7	HT Testing and CO <sub>2</sub> –CH <sub>4</sub> Isotherms of Selected Samples	178
7.4	MOF Design for Catalytic Application	179

7.4.1	Properties of MOF in Catalysis	179
7.4.1.1	Lewis Acid Catalysis	180
7.4.1.2	Brönsted Acid Catalysis	181
7.4.1.3	Basic and Enantioselective Catalysis	182
7.4.1.4	C–C Coupling	183
7.4.1.5	Metal Catalysis	183
7.4.1.6	Wall Functionalization	183
7.4.1.7	Postfunctionalization	184
7.4.2	MOFs – Are They “Heterogenized” Catalysts or Solid Catalysts?	185
7.4.2.1	Engineering of Structural Defects in MOF	185
7.4.2.2	Probing Acid Centers by Alkylation Reactions	185
7.4.2.3	Catalyst Characterization	187
7.4.2.4	General Statements on MOF Application for Catalysis	188
7.5	Conclusion	188
	References	189
<b>8</b>	<b>Design of Bimetallic Catalysts: From Model Surfaces to Supported Catalysts</b>	<b>195</b>
	<i>Jeffrey P. Bosco, Michael P. Humbert, and Jingguang G. Chen</i>	
8.1	Introduction	195
8.2	Experimental and Theoretical Methods	196
8.2.1	Experimental Techniques	196
8.2.2	DFT Modeling	199
8.3	Results and Discussion	199
8.3.1	UHV and DFT Studies on Pt-Ni Model Surfaces	199
8.3.1.1	Adsorption and Desorption of Hydrogen	200
8.3.1.2	Disproportionation and Hydrogenation of Cyclohexene	202
8.3.2	Characterization and Reactor Studies of Supported Pt-Ni Catalysts	205
8.3.2.1	TEM and EXAFS Characterization of Ni/Pt/Al <sub>2</sub> O <sub>3</sub> Catalysts	205
8.4	Conclusions	211
	References	211
<b>9</b>	<b>Self-Assembled Materials for Catalysis</b>	<b>213</b>
	<i>Kake Zhu, Donghai Wang, and Jun Liu</i>	
9.1	Introduction	213
9.2	Mesocale Design	214
9.2.1	Inclusion of Heteroatoms	216
9.2.1.1	Acid Sites	216
9.2.1.2	Dispersed Metal Oxides	219
9.2.2	Embedded Nanoparticles	220
9.2.3	Nonsiliceous Mesoporous Materials	221
9.2.3.1	Molecule Self-Assembly to Mesoporous Catalysts	222
9.2.3.2	Nanoparticles Self-Assembly to Mesoporous Catalysts	222

9.2.4	Self-Assembly of Zeolite Seeds into Mesophase	223
9.2.5	Organic Functional Groups as Catalysts	224
9.3	Designing Catalysts at the Nanoparticle Surfaces	225
9.3.1	Polyoxometalates: Nanoparticles with Cations	225
9.3.2	Dendrimer-Stabilized Metal Nanoparticles	226
9.4	Perspectives	226
	References	227
<b>10</b>	<b>Theory-Aided Catalyst Design</b>	<b>231</b>
	<i>Matthew Neurock</i>	
10.1	Introduction	231
10.2	Catalytic Descriptors	234
10.2.1	Electronic Descriptors	234
10.2.2	Energetic Descriptors	235
10.2.3	Adsorption Energies or Binding Energies	236
10.2.4	High-Throughput Screening	238
10.3	High-Throughput Simulation and Design	242
10.3.1	NO Decomposition	244
10.3.2	Vinyl Acetate (VAM) Synthesis	249
10.4	Controlled Patterning	252
10.5	Catalyst Synthesis and Stability	252
10.6	Conclusions	253
	References	254
<b>11</b>	<b>Use of <i>In Situ</i> XAS Techniques for Catalysts' Characterization and Design</b>	<b>259</b>
	<i>Christophe Geantet and Jean-Marc M. Millet</i>	
11.1	Introduction	259
11.2	The X-Ray Absorption Techniques	260
11.2.1	Principles and Feasibility	260
11.2.2	Data Acquisition	262
11.2.3	Spectral Analysis and Interpretations	263
11.3	Recent Applications of X-Ray Absorption Techniques to the Design of Heterogeneous Catalysts	265
11.3.1	Time Resolution	265
11.3.2	High-Resolution XANES	271
11.3.3	High Detection Sensitivity	277
11.3.4	Spatial Resolution	278
11.3.5	Coupling of Techniques	280
11.4	Perspective	285
11.4.1	Time-Resolved Ultrafast X-Ray Absorption Spectroscopy	286
11.4.2	X-Ray Emission Spectroscopy (XES) and Resonant Inelastic X-Ray Scattering Spectroscopy (RIXS)	287
11.5	Conclusions	290
	References	291

<b>12</b>	<b>Catalyst Design Through Dual Templating</b>	<b>295</b>
	<i>Moises A. Carreon and Vadim V. Guliants</i>	
12.1	Introduction	295
12.2	Surfactant-Assisted Self-Assembly of Mesoporous Metal Oxides	297
12.2.1	Fundamentals	297
12.2.2	Thermal Stability Considerations	297
12.2.3	Mesostructuring via Evaporation-Induced Self-Assembly	299
12.3	Colloidal Sphere Templating of Macroporous Metal Oxides	301
12.4	Dual Templating of Metal Oxides	303
12.5	Catalytic Applications	305
12.5.1	Mesoporous Metal Oxides	305
12.5.2	Macroporous Metal Oxides	310
12.5.3	Metal Oxides Obtained via Dual Templating	311
12.6	Concluding Remarks	312
	References	313
	<b>Index</b>	<b>315</b>