

# Contents

<b>CHAPTER 1</b>	<b>Heterogeneous Catalysts .....</b>	<b>1</b>
1.1	Introduction .....	1
1.1.1	On the merits of industrial chemistry as a production activity .....	1
1.1.2	Catalysis and its role in industrial chemistry .....	2
1.1.3	Why solid catalysts? .....	3
1.1.4	Industrial catalytic materials.....	5
	References .....	7
<b>CHAPTER 2</b>	<b>Preparation of Solid Catalysts: A Short Summary .....</b>	<b>9</b>
2.1	Preparation of catalyst precursors .....	11
2.1.1	Choice of the starting compounds .....	11
2.1.2	Dry preparation procedures.....	11
2.1.3	Wet catalyst preparations and other slurry-phase preparation methods .....	13
2.1.4	Intermediate and final treatments in preparation chemistry .....	19
	References .....	20
<b>CHAPTER 3</b>	<b>Characterization of Real Catalytic Materials: An Overview .....</b>	<b>23</b>
3.1	Elemental composition of heterogeneous catalysts .....	24
3.1.1	Atomic absorption and emission spectroscopies.....	24
3.1.2	Inductively coupled plasma—mass spectrometry .....	24
3.1.3	X-ray fluorescence .....	25
3.1.4	Energy-dispersive X-ray analysis .....	25
3.2	Structural properties of inorganic materials and its characterization.....	25
3.2.1	XR diffraction .....	26
3.2.2	Electron diffraction .....	26
3.2.3	Neutron diffraction.....	27
3.2.4	Vibrational spectroscopies .....	27
3.2.5	X-ray absorption spectroscopy .....	28
3.2.6	UV—vis spectroscopic data.....	29
3.2.7	Magic angle spinning Nuclear Magnetic Resonance (NMR) techniques.....	29
3.3	Morphology characterization .....	30
3.3.1	Measurement of the surface area and analysis of porosity .....	30

3.3.2	Crystal size measurement .....	31
3.3.3	Electron microscopies .....	31
<b>3.4</b>	<b>Analysis of the surface structure and composition.....</b>	<b>32</b>
3.4.1	X-ray photoelectron spectroscopy .....	32
3.4.2	Direct surface analysis by conventional spectroscopies.....	33
3.4.3	Surface acidity and basicity characterization using probe molecules .....	33
3.4.4	Studies of the surface redox behavior .....	34
	References .....	34
<b>CHAPTER 4</b>	<b>Practical Application and Testing of Catalytic Materials: A Synthesis .....</b>	<b>37</b>
<b>4.1</b>	Shaping of catalysts for industrial catalytic reactions.....	38
<b>4.2</b>	Industrial heterogeneous catalytic reactors.....	41
4.2.1	Temperature control in catalytic reactors .....	41
4.2.2	Gas/solid and liquid/solid fixed-bed reactors .....	41
4.2.3	Monolithic reactors .....	45
4.2.4	Catalytic membrane reactors .....	46
4.2.5	Gas/solid fluidized and transported bed reactors.....	46
4.2.6	Raiser reactors and circulating fluidized bed reactors .....	46
4.2.7	Slurry liquid/solid and gas/liquid/solid reactors.....	48
<b>4.3</b>	Deactivation of solid catalysts .....	48
4.3.1	Poisoning .....	50
4.3.2	Coking .....	50
4.3.3	Sintering .....	50
4.3.4	Phase transitions and solid-state reactions .....	51
4.3.5	Breaking of extrudates .....	51
4.3.6	Erosion or breaking of monoliths .....	51
<b>4.4</b>	Regeneration of reversibly deactivated catalysts.....	51
4.4.1	Techniques for regeneration.....	51
4.4.2	Regeneration of catalysts and the reactors .....	52
<b>4.5</b>	Laboratory evaluation of the catalytic activity .....	53
<b>4.6</b>	Operando methodologies.....	53
	References .....	55
<b>CHAPTER 5</b>	<b>Acid and Basic Catalysts: Fundamentals .....</b>	<b>57</b>
<b>5.1</b>	Acido-basicity in liquid phases. Fundamentals and hystorical perspective .....	58
5.1.1	Acido-basicity in diluted water solutions.....	58
5.1.2	Protonic acidity in highly concentrated water solutions and in dry conditions.....	62

5.1.3 Brønsted basicity in nonprotic solvents.....	66
5.1.4 Lewis acidity and basicity .....	69
5.1.5 Hard and soft acidity and basicity (HSAB) and nucleophilicity .....	71
5.1.6 Gas phase acidity and basicity.....	72
<b>5.2</b> Reactant activation and acid–base catalysis in liquid phases....	73
5.2.1 Reactant activation and acid–base catalysis in diluted water solutions .....	73
5.2.2 Activation of weak basic molecules by acids .....	74
5.2.3 Catalysis in liquid superbasic conditions .....	78
<b>5.3</b> The surface acidity and basicity of solids .....	79
5.3.1 Structural chemistry versus surface chemistry of solids: a fundamental approach.....	79
5.3.2 Characterization techniques of surface acidity and basicity of solids .....	80
5.3.3 Methods measuring adsorption/desorption energies .....	88
5.3.4 IR spectroscopic methods .....	91
5.3.5 NMR spectroscopic methods .....	92
5.3.6 Catalytic probe reactions .....	93
5.3.7 Strength, amount, and distribution of surface acid and basic sites on the ideal surface of a solid.....	95
<b>5.4</b> Heterogeneous versus homogeneous acid–base catalysis .....	96
References .....	96

## **CHAPTER 6 Metal Oxides as Acid-Base Catalytic Materials .... 103**

<b>6.1</b> Chemistry of metal oxides .....	104
6.1.1 “Bulk” acidity and basicity.....	104
6.1.2 Structural chemistry of metal oxides.....	109
6.1.3 Covalent versus ionic oxides .....	121
6.1.4 Amorphous versus crystalline metal oxides.....	122
6.1.5 Redox behavior, thermal stability, magnetism and electronic conduction .....	122
6.1.6 Effect of particle size in the solid-state chemistry of oxides .....	124
<b>6.2</b> Composition effect on the surface acido-basicity of metal oxides: an overview .....	125
<b>6.3</b> Acido-basicity of supports for catalysts.....	128
<b>6.4</b> Metal oxides as acid and basic catalytic materials.....	129
6.4.1 Supported alkali oxides.....	129
6.4.2 Magnesia and other alkali-earth oxides.....	131

6.4.3	Aluminas .....	136
6.4.4	Lanthana and rare-earth oxides .....	150
6.4.5	Silicas .....	151
6.4.6	Titanias .....	161
6.4.7	Zirconias .....	166
6.4.8	Ceria .....	171
6.4.9	Niobia .....	172
6.4.10	Tungsten trioxide (tungsta) .....	173
<b>6.5</b>	<b>Mixed metal oxides and their acido-basicity .....</b>	<b>174</b>
6.5.1	Silica–aluminas .....	174
6.5.2	Alumina-rich silica–aluminas and silicated aluminas ....	178
6.5.3	Aluminated silicas .....	179
6.5.4	Combinations of silica, titania, alumina, ceria and zirconia .....	179
6.5.5	Calcined hydrothalcites and spinels .....	180
	References .....	182
<b>CHAPTER 7</b>	<b>Zeolites and Other Structurally Microporous Solids as Acid–Base Materials .....</b>	<b>197</b>
7.1	Zeolites .....	198
7.1.1	Structural chemistry of zeolites .....	198
7.1.2	Preparation chemistry of synthetic zeolites .....	201
7.1.3	Natural zeolites and their surface-related applications ...	201
7.1.4	Alkali and alkali earth cationic zeolites and their industrial applications .....	204
7.1.5	Protonic zeolites: acidity and shape selectivity .....	212
7.1.6	Some particular protonic zeolites applied in the industry .....	216
7.2	Aluminophosphates (AlPOs) .....	234
7.3	Silicoaluminophosphates (SAPOs) .....	234
7.4	Metal heteroatom containing aluminophosphates (MAPOs) ...	237
7.5	Very large-pore zeolitic inorganic materials .....	237
7.6	Zeolite-like titanosilicates .....	237
7.7	Metal Organic Frameworks (MOFs) and similar materials .....	239
	References .....	241
<b>CHAPTER 8</b>	<b>Other Solid Acid and Basic Catalytic Materials .....</b>	<b>251</b>
8.1	Acid–base catalytic materials from minerals .....	252
8.1.1	Clays as catalytic materials .....	252
8.1.2	Chemically modified clays .....	255

8.1.3 Pillared clays (PILC) and acidic porous clay heterostructures .....	256
8.1.4 Chalcareous minerals .....	258
8.1.5 Basic silicate clays .....	258
<b>8.2 Halide salts and halided oxides .....</b>	<b>259</b>
8.2.1 Solid chlorided catalytic materials .....	259
8.2.2 Fluorided inorganic solids.....	262
<b>8.3 Sulfides, (oxy)nitrides, carbides, phosphides as acid–base materials .....</b>	<b>265</b>
<b>8.4 Heteropolyacids and polyoxometallates .....</b>	<b>267</b>
<b>8.5 Solid carbonates, phosphates, sulfates and other salts .....</b>	<b>270</b>
<b>8.6 Supported inorganic acids.....</b>	<b>272</b>
8.6.1 Solid phosphoric acid.....	272
8.6.2 Silica sulfuric acid .....	273
8.6.3 Supported triflic acid.....	274
8.6.4 Supported ionic liquids .....	274
<b>8.7 Supported alkali and earth metals or organometallics as “basic catalysts” .....</b>	<b>275</b>
<b>8.8 Organo-inorganic hybrid materials .....</b>	<b>275</b>
<b>8.9 Carbon-based materials .....</b>	<b>276</b>
8.9.1 Carbon materials .....	277
8.9.2 Carbon materials as catalysts supports.....	282
8.9.3 Modified carbons as catalysts .....	283
<b>8.10 Polymeric solid acids and bases (ion exchange resins) .....</b>	<b>284</b>
References .....	287

## **CHAPTER 9 Metal Catalysts for Hydrogenations and Dehydrogenations..... 297**

<b>9.1 Bulk metal catalysts .....</b>	<b>302</b>
9.1.1 Surface science studies on metal monocrystal faces and model surfaces .....	302
9.1.2 Unsupported metal nanoparticles.....	304
<b>9.2 Supported metal catalysts.....</b>	<b>304</b>
9.2.1 Supports for metal catalysts.....	304
9.2.2 Supported metal nanoparticles.....	306
9.2.3 Isolated and very highly dispersed metal centers.....	308
<b>9.3 Fundamentals of hydrogenation/dehydrogenation.....</b>	<b>309</b>
9.3.1 Adsorption of hydrogen on metals .....	309
9.3.2 Adsorption of organic substrates on metals .....	310
9.3.3 Hydrogenation of hydrocarbons .....	311

9.3.4	Fundamentals of dehydrogenation.....	312
9.3.5	Steam-reforming and related processes.....	312
<b>9.4</b>	<b>Metal catalysts for hydrogenation and dehydrogenation</b>	
	reactions.....	313
9.4.1	Iron-based metal catalysts .....	313
9.4.2	Cobalt-based metal catalysts .....	314
9.4.3	Nickel-based metal catalysts .....	316
9.4.4	Copper-based catalysts.....	321
9.4.5	Ruthenium-based catalysts .....	326
9.4.6	Rhodium-based catalysts .....	327
9.4.7	Palladium-based catalysts .....	327
9.4.8	Rhenium metal in catalysis.....	331
9.4.9	Iridium-based catalysts .....	331
9.4.10	Platinum-based catalysts.....	331
9.4.11	Gold-based catalysts for water–gas shift.....	335
	References .....	335

## **CHAPTER 10 Catalysts for Hydrogenations, Dehydrogenations and Metathesis: Sulfides and Oxides ..... 345**

<b>10.1</b>	<b>Metal oxides in hydrogenation and dehydrogenation</b>	
	reactions.....	346
10.1.1	Iron oxide-based catalysts for hydrocarbon dehydrogenation and water gas-shift.....	348
10.1.2	Chromia–alumina for alkane dehydrogenation and hydrodealkylation.....	351
10.1.3	Gallium oxide-based catalysts for dehydrogenations .....	352
10.1.4	Zinc oxide for dehydrogenation reactions.....	353
10.1.5	Oxide-based catalysts for carboxylic acid hydrodeoxygenation .....	353
10.1.6	Oxide catalysts for catalytic transfer hydrogenation ..	354
<b>10.2</b>	<b>Sulfide catalysts.....</b>	<b>354</b>
10.2.1	Adsorption of hydrogen on metal sulfides .....	355
10.2.2	Layered bulk sulfides and their applications.....	356
10.2.3	Supported bimetallic sulfides.....	360
10.2.4	Other sulfide catalysts.....	362
10.2.5	Hydrocracking catalysts.....	364
10.2.6	Other catalytic materials for hydrotreatings.....	365
<b>10.3</b>	<b>Olefin metathesis catalysts.....</b>	<b>366</b>
10.3.1	Heterogeneous tungsten-based metathesis catalysts ...	366

10.3.2 Heterogeneous rhenium-oxide metathesis catalysts....	367
10.3.3 Molybdenum-based metathesis catalysts.....	368
References .....	368
<b>CHAPTER 11 Oxidation Catalysts.....</b>	<b>375</b>
<b>11.1 Fundamentals of oxidation catalysis.....</b>	<b>376</b>
11.1.1 Oxidation reactions .....	376
11.1.2 The oxidant and the configurations of heterogeneously catalyzed oxidations .....	377
11.1.3 Mechanisms of the heterogeneously catalyzed oxidations .....	377
11.1.4 Adsorption/reaction/activation of oxygen on bulk metals .....	379
11.1.5 Supported metal catalysts .....	382
11.1.6 Adsorption/reaction/activation of oxygen on metal oxides .....	383
11.1.7 The activation of the substrate.....	384
<b>11.2 Transition-metal mixed oxides for selective and total     oxidation reactions .....</b>	<b>385</b>
11.2.1 Metal molybdates for selective oxidations.....	385
11.2.2 Antimony oxide-based catalysts.....	390
11.2.3 Vanadium oxide-based catalysts.....	391
11.2.4 Oxide catalysts for oxidative dehydrogenations .....	395
11.2.5 Heteropolyacids for selective oxidations.....	396
11.2.6 Zeolite catalysts for the abatement of NO <sub>x</sub> and N <sub>2</sub> O.....	397
11.2.7 Oxide catalysts for total oxidations.....	398
<b>11.3 Metal catalysts for oxidation reactions.....</b>	<b>400</b>
11.3.1 Metal gauzes for selective oxidation catalysis.....	400
11.3.2 Silver catalysts for selective oxidations .....	401
11.3.3 Other noble metal-based catalysts for gas-phase selective oxidations of organics .....	402
11.3.4 Noble metal catalysts for selective oxidations in the liquid phase .....	402
11.3.5 Metal catalysts for ammonia selective catalytic oxidation to nitrogen.....	403
11.3.6 Metal catalysts for methane partial oxidation to syngas .....	403
11.3.7 Metal catalysts for CO oxidation .....	404

11.3.8	Combustion catalysts for energy generation .....	405
11.3.9	Noble metal catalysts for total oxidation for VOC abatement .....	406
11.3.10	Noble metals for catalytic wet oxidation .....	407
11.3.11	Catalysts for the aftertreatment of engines' waste gases .....	407
<b>11.4</b>	<b>Catalysts for oxidation reactions in the presence of chlorine .....</b>	<b>409</b>
11.4.1	Catalysts for the oxidation of HCl to Cl <sub>2</sub> .....	409
11.4.2	Catalysts for the oxychlorination of ethylene .....	409
11.4.3	Catalytic combustion of dioxins and other chlorinated organics .....	410
<b>11.5</b>	<b>Catalysts for the production and use of hydrogen peroxide .....</b>	<b>410</b>
11.5.1	The direct synthesis of hydrogen peroxide .....	410
11.5.2	Catalytic oxidations with H <sub>2</sub> O <sub>2</sub> .....	411
	References .....	412
<b>CHAPTER 12</b>	<b>Polymerization Catalysts and Heterogenized Homogeneous Catalysts .....</b>	<b>421</b>
<b>12.1</b>	<b>Solid polymerization catalysts .....</b>	<b>421</b>
12.1.1	Ziegler–Natta-type catalysts .....	421
12.1.2	Phillips-type catalysts .....	423
12.1.3	Heterogenized “single-site” polymerization catalysts .....	423
<b>12.2</b>	<b>Supported or heterogenized homogeneous catalysts .....</b>	<b>426</b>
	References .....	426
<b>CHAPTER 13</b>	<b>Heterogeneous Catalysts and Biomass Conversion .....</b>	<b>429</b>
<b>13.1</b>	<b>Heterogeneous catalysts and the future of industrial chemistry .....</b>	<b>429</b>
<b>13.2</b>	<b>Biomasses as raw materials for industrial chemistry .....</b>	<b>430</b>
<b>13.3</b>	<b>Heterogeneous catalysts and conversion of vegetable oils and animal fats .....</b>	<b>430</b>
13.3.1	Heterogeneous catalysts and biodiesel production .....	430
13.3.2	Heterogeneous catalysts and glycerol conversion to useful products .....	431
13.3.3	Hydrogenations of vegetable oils .....	432
13.3.4	Heterogeneous catalysts and pyrolysis of vegetable oils .....	433

13.3.5 Chemicals from triglycerides .....	433
13.3.6 Conversion of fatty acids and their salts .....	433
<b>13.4 Heterogeneous catalysts and the conversion</b>	
of lignocellulosics .....	434
13.4.1 Heterogeneous catalysts and the pyrolysis	
of lignocellulosic matter .....	434
13.4.2 Heterogeneous catalysts and upgrading of biooils.....	436
13.4.3 Heterogeneous catalysis and the gasification	
of lignocellulosic matter .....	437
13.4.4 Heterogeneous catalysis and the conversion	
of cellulose and hemicellulose .....	437
13.4.5 Heterogeneous catalysis and the conversion	
of lignin to chemicals .....	440
<b>13.5 Heterogeneous catalysts and industrial chemistry</b>	
from renewables .....	441
References .....	443
Index .....	447