

Contents

Preface *xiii*

- 1 Introduction to Hydroxyapatite-based Materials in Heterogeneous Catalysis** *1*
Doan Pham Minh
- 1.1 Generality *1*
- 1.2 Hydroxyapatite: A New Family of Catalytic Materials in the Heterogeneous Catalysis *4*
- 1.2.1 Possible High Porous Volume and High Specific Surface Area *4*
- 1.2.2 High Thermal Stability *4*
- 1.2.3 Exceptional Ion Exchange Capacity *6*
- 1.2.4 Tunable Acid-base Properties *7*
- 1.2.5 High Affinity with Organic Compounds *8*
- 1.2.6 Formulation of HA-based Materials *8*
- 1.3 Opportunities and Challenges *11*
- References *14*
- 2 Synthesis and Characterization of Hydroxyapatite and Hydroxyapatite-Based Catalysts** *19*
Yousra EL Jemli, Karima Abdelouahdi, Doan Pham Minh, Abdellatif Barakat, and Abderrahim Solhy
- 2.1 Introduction *19*
- 2.2 HA Synthesis and Characterization *20*
- 2.2.1 HA Synthesis Routes *20*
- 2.2.1.1 Coprecipitation Method *20*
- 2.2.1.2 Sol–Gel Method *22*
- 2.2.1.3 Emulsion Methods *24*
- 2.2.1.4 Hydrolysis Methods *28*
- 2.2.1.5 Hydrothermal Methods *30*
- 2.2.1.6 Microwave (MW)-Assisted Methods *31*
- 2.2.1.7 Ball-Milling Method *32*
- 2.2.1.8 Sonochemical Method *34*
- 2.2.1.9 Dry Methods *35*

2.2.1.10	Other Methods	36
2.2.2	HA Structure	42
2.2.3	Physicochemical and Thermal Properties of HA	44
2.2.3.1	Thermal Stability	44
2.2.3.2	Solubility of HA	44
2.2.3.3	HA's Surface Functional Groups	45
2.2.3.4	Non-stoichiometric Calcium-Deficient or Calcium-Rich Hydroxyapatites	46
2.2.4	Substitutions in the Structure of HA	47
2.2.5	Modification and Functionalization of the HA's Surface	49
2.3	A Concise Overview on Synthesis and Characterization of HA-Based Catalysts	51
2.4	Summary and Conclusions	55
	References	55

3 Structure and Surface Study of Hydroxyapatite-Based Materials 73

Guyène Costentin, Christophe Drouet, Fabrice Salles, and Stéphanie Sarda

3.1	Introduction	73
3.2	Structure and Surface Properties of Hydroxyapatite: Overview	75
3.2.1	Apatite Structure and Model Studies	76
3.2.2	Specificities of Nonstoichiometric and/or Biomimetic Apatites	81
3.2.3	Relevance of Apatites in Catalysis	84
3.3	Advances in the Characterization of Structural and Surface Properties of Hydroxyapatite: Experimental and Computational Approaches	87
3.3.1	Structural and Compositional Characterization	87
3.3.2	Thermodynamic Properties and Thermal Stability	95
3.3.2.1	Overview of Apatites Thermodynamics	95
3.3.2.2	Thermal Behavior	98
3.3.3	Physicochemical and Interfacial Properties	100
3.3.3.1	Solubility and Evolution in Solution	100
3.3.3.2	Surface Charge	102
3.3.3.3	Interfacial Tension	103
3.3.4	Surface Reactivity	106
3.3.4.1	Nature of Acid and Base Sites	106
3.3.4.2	Influence of Substitution on Surface Reactivity	109
3.3.4.3	Low Temperature Ion Immobilization and Adsorption Properties in Aqueous Media or Wet Conditions	110
3.4	Conclusions	117
	References	117

4 Hydroxyapatite-Based Catalysts: Influence of the Molar Ratio of Ca to P 141

Zhen Ma

4.1	Introduction	141
4.2	Influence of Ca/P Ratio on the Performance of HA	143

- 4.2.1 Relatively Simple Reactions 143
- 4.2.2 More Complex Reactions 147
- 4.3 Influence of Ca/P Ratio on the Performance of HA-Supported Catalysts 152
 - 4.3.1 Relatively Simple Reactions 153
 - 4.3.2 More Complex Reactions 155
- 4.4 Concluding Remarks 156
- References 158

- 5 Kinetics and Mechanisms of Selected Reactions over Hydroxyapatite-Based Catalysts 163**
U.P.M. Ashik, Nurulhuda Halim, Shusaku Asano, Shinji Kudo, and Jun-ichiro Hayashi
 - 5.1 Introduction 163
 - 5.2 Oxidative Coupling of Methane 164
 - 5.3 Partial Oxidation of Methane 169
 - 5.4 Acetone to Methyl Isobutyl Ketone 173
 - 5.5 Ethanol Coupling Reaction 177
 - 5.6 Ethanol to Gasoline 180
 - 5.7 Glycerol to Lactic Acid 182
 - 5.8 Benzene to Phenol 183
 - 5.9 Transesterification 186
 - 5.10 Conclusion 188
 - References 189

- 6 Aerobic Selective Oxidation of Alcohols and Alkanes over Hydroxyapatite-Based Catalysts 201**
Guylène Costentin and Franck Launay
 - 6.1 Introduction 201
 - 6.2 Liquid Phase Reactions: Selective Aerobic Oxidation of Alcohols 202
 - 6.2.1 Apatite-Based Catalysts Efficient in the Aerobic Oxidation of Alcohols 203
 - 6.2.2 Apatite/Ru(III) Catalysts 204
 - 6.2.3 Apatite/Pd(0) Catalysts 211
 - 6.3 Gas Phase Reactions 214
 - 6.3.1 Partial Oxidation of Methane 214
 - 6.3.2 Alkane Oxidative Dehydrogenation Reactions 217
 - 6.3.2.1 Catalytic Performance of the Metal-Modified Hydroxyapatite in the ODH Reactions 218
 - 6.3.2.2 Metal Ion Modifications 219
 - 6.3.2.3 Activation Site and Mechanism 227
 - 6.4 Conclusions and Perspectives 229
 - References 232

7	Selective Hydrogenation and Dehydrogenation Using Hydroxyapatite-Based Catalysts 241
	<i>Vijay K. Velisoju, Hari Padmasri Aytam, and Venugopal Akula</i>
7.1	Introduction 241
7.2	HA as Catalyst Support in Hydrogenation Reactions 242
7.2.1	Hydrogenation of Biomass-Derived Compounds to Fuels and Fine Chemicals 242
7.2.2	Hydrogenation of Olefins and Nitro Compounds 245
7.2.3	Hydrogenation of Benzene, Phenol, and Diols 247
7.2.4	Selective Catalytic Reduction of Nitric Oxide 249
7.2.5	Higher Alcohol Synthesis by Simultaneous Dehydrogenation and Hydrogenation Reactions 249
7.2.6	Hydrogenation of Carbon Dioxide 252
7.2.6.1	CO ₂ Methanation 253
7.2.6.2	CO ₂ Fisher–Tropsch (FT) Synthesis 253
7.2.6.3	Alcohol Synthesis 255
7.2.6.4	Water–Gas Shift and Reverse Water–Gas Shift 255
7.2.7	Partial Conclusions 257
7.3	HA as Support in Dehydrogenation Reactions 257
7.4	Summary and Conclusions 262
	Acknowledgments 262
	References 263
8	Reforming Processes Using Hydroxyapatite-Based Catalysts 269
	<i>Zouhair Boukha, Rubén López-Fonseca, and Juan R. González-Velasco</i>
8.1	Introduction 269
8.2	Overview on the Nature of the Interactions of HA with Transition Metal Catalysts 271
8.3	HA-Supported Non-noble Metal Catalysts for Methane Reforming Reactions 274
8.3.1	Suitability of the HA-Based Catalysts 274
8.3.2	Effect of the Composition on the Performance of HA in the Reforming Reactions 281
8.3.3	Bimetallic Catalysts 284
8.4	Noble Metal Catalysts 286
8.5	Reforming of Other Hydrocarbons 287
8.6	Summary and Remarks 290
	Acknowledgments 291
	References 291

- 9 Hydroxyapatite-Based Catalysts for the Production of Energetic Carriers** 299
Othmane Amadine, Karim Dânoun, Younes Essamlali, Said Sair, and Mohamed Zahouily
- 9.1 Introduction 299
- 9.2 Biodiesel Production 300
- 9.2.1 Transesterification Reactions 301
- 9.2.2 Esterification Reaction for Biodiesel Production 307
- 9.2.3 Other Esterification Reactions 308
- 9.3 Hydrogen Production 312
- 9.3.1 Water–Gas Shift Reactions 312
- 9.3.2 Borohydride Hydrolysis Reaction 316
- 9.3.3 Ammonia Borane Hydrolysis Reaction 318
- 9.4 Catalytic Production of High Value-Added Energy Additives 319
- 9.4.1 *n*-Butanol and Its Derivative Chemicals 320
- 9.4.2 Fuel Additives from Furfural 324
- 9.4.3 Organic Carbonates Agents 326
- 9.4.4 Energy Additives from Alcohols via Guerbet Reaction 327
- 9.4.5 Other Value-Added Chemicals 329
- 9.5 Conclusion 329
- References 330
- 10 Hydroxyapatite-Based Catalysts in Organic Synthesis** 345
Michel Gruselle, Kaia Tônsuaadu, Patrick Gredin, and Christophe Len
- 10.1 Introduction 345
- 10.2 Synthesis and Characterization of HA and HA-Based Catalysts 346
- 10.2.1 Synthesis 346
- 10.2.1.1 Stoichiometric and Nonstoichiometric Apatites 346
- 10.2.1.2 Apatites as Catalyst Supports 346
- 10.2.1.3 HA as Macro-ligands for Catalytic Moieties 347
- 10.3 Apatites as Catalysts in C—C Bond Formation 347
- 10.3.1 Cross-coupling Reactions 347
- 10.3.2 Nucleophilic Carbon–Carbon Bond Forming Reactions 350
- 10.3.3 Multicomponent Reaction 352
- 10.4 Conclusions 361
- References 364
- 11 Electrocatalysis and Photocatalysis Using Hydroxyapatite-Based Materials** 373
Eric Puzenat and Mathieu Prévot
- 11.1 Photocatalysis with Hydroxyapatite-Based Materials 373
- 11.1.1 Basic Photocatalysis Principles 373

- 11.1.2 Hydroxyapatite Structure and Properties Implication in Photocatalysis 376
- 11.1.3 Single-Phase HA for Photocatalysis 377
- 11.1.4 Doped Photocatalytic HA 378
- 11.1.5 Multiphasic HA-Containing Photocatalyst 379
 - 11.1.5.1 HA—TiO₂ Biphasic Composites 380
 - 11.1.5.2 HA—TiO₂ Multiphasic Composites 381
 - 11.1.5.3 Other Photocatalytic HA-Containing Composites 381
- 11.1.6 Summary and Outlook 382
- 11.2 Electro catalysis with Hydroxyapatite-Based Materials 383
 - 11.2.1 Charge Transport Mechanism in Hydroxyapatites 384
 - 11.2.2 Electro catalytic Sensors 386
 - 11.2.3 Fuel Cell Application 396
 - 11.2.4 Electro catalytic Water Oxidation 401
 - 11.2.5 Summary and Outlook 403
- References 404

- 12 Magnetic Structured Hydroxyapatites and Their Catalytic Applications 413**
Tasnim Munshi, Smriti Rawat, Ian J. Scowen, and Sarwat Iqbal
 - 12.1 Introduction 413
 - 12.2 Magnetic HA 414
 - 12.2.1 Synthesis Route of Magnetic HA 415
 - 12.3 Catalysis 420
 - 12.3.1 Magnetic HA Nanoparticles as Active Catalysts for Organic Reactions 420
 - 12.3.2 HA Analogs and Their Catalytic Applications 425
 - 12.3.3 HA Catalysts and Green Chemistry 426
 - 12.4 Summary and Conclusions 430
 - References 431

- 13 Materials from Eggshells and Animal Bones and Their Catalytic Applications 437**
Abarasi Hart and Elias Aliu
 - 13.1 Introduction 437
 - 13.2 Chemical Composition and Properties of Eggshell and Animal Bones 441
 - 13.3 Eggshell and Animal Bones Materials 444
 - 13.3.1 Calcium Carbonate/Oxide/Phosphate 445
 - 13.3.2 Calcium Supplement 445
 - 13.3.3 Biofilter (Adsorbent) Biomaterial 446
 - 13.3.4 Hydroxyapatite Material 448
 - 13.4 Catalytic Applications of Eggshell and Animal Bones 451
 - 13.4.1 Catalytic Material Preparation from Eggshells and Animal Bones 451
 - 13.4.2 Catalytic Applications of Catalyst Derived from Eggshell and Animal Bones 454

- 13.4.2.1 Selective Catalytic Oxidation 455
- 13.4.2.2 Gasification of Biomass for Hydrogen Production 458
- 13.4.2.3 Reactive Carbon Dioxide Capture (Calcium Looping) 459
- 13.4.2.4 Water–Gas Shift (WGS) Reaction 460
- 13.4.2.5 Transesterification Reaction for Biodiesel Production 461
- 13.4.2.6 Eggshell Membranes (ESM) in Fuel Cell Applications 464
- 13.4.2.7 Catalytic Materials from Eggshells and Animal Bones in Organic Synthesis 465
- 13.4.2.8 Other Catalytic Applications 466
- 13.5 Conclusions 467
- References 468

14 Natural Phosphates and Their Catalytic Applications 481

Karima Abdelouahdi, Abderrahim Bouaid, Abdellatif Barakat, and Abderrahim Solhy

- 14.1 Introduction 481
- 14.2 Preparation and Characterization of Catalysts or Catalyst Supports from NP 482
- 14.3 Organic Synthesis Using NP and NP-Supported Catalysts 487
 - 14.3.1 Condensation Reactions 487
 - 14.3.1.1 Knoevenagel Reaction 487
 - 14.3.1.2 Claisen–Schmidt Condensation 491
 - 14.3.1.3 Michael Addition 494
 - 14.3.2 Transesterification Reaction 496
 - 14.3.3 Friedel–Crafts Alkylation 497
 - 14.3.4 Suzuki–Miyaura Coupling Reaction 499
 - 14.3.5 Hydration of Nitriles 501
 - 14.3.6 Synthesis of α -Hydroxyphosphonates 504
 - 14.3.7 Multicomponent Reactions (MCRs) 505
 - 14.3.7.1 Biginelli Reaction 505
 - 14.3.7.2 Synthesis of α -Aminophosphonates 506
 - 14.3.8 Oxidation Reactions 506
 - 14.3.8.1 Oxidative Cleavage of Cycloalkanones 506
 - 14.3.8.2 Oxidation of Benzyl Alcohol 509
 - 14.3.8.3 Epoxidation of Electron-Deficient Alkenes 510
 - 14.3.9 Hydrogenation Reactions 511
 - 14.3.9.1 Selective Hydrogenation of Crotonaldehyde 511
 - 14.3.9.2 Reduction of Aromatic Nitro Compounds 512
 - 14.3.10 Reforming of Methane 514
 - 14.3.11 Photooxidation of VOC Model Compounds 515
- 14.4 Conclusions 516
- References 516

Index 533

