Contents

Preface *xiii*

1 Introduction to Solid Base Catalyst *1*
Indu Sindhu, Ravi Tomar, and Anshul Singh
1.1 Introduction *1*
1.2 History and Main Facts on Solid Base Catalysts *2*
1.3 Literary Perspective of Solid Base Catalyst *3*
1.4 Solid Basic Sites *4*
1.5 Types of Solid Base Catalysts *5*
1.5.1 Metal Oxides *5*
1.5.1.1 Alkaline Earth Oxides *5*
1.5.1.2 Zirconium Oxides *6*
1.5.1.3 Rare Earth Oxides *7*
1.5.1.4 Titanium Oxides *9*
1.5.1.5 Zinc Oxide *9*
1.5.1.6 Alumina *10*
1.5.1.7 Mixed Oxides *10*
1.5.1.8 Alkali Metal-Loaded Metal Oxides *10*
1.5.2 Zeolites *11*
1.5.3 Mesoporous Materials *13*
1.5.4 Clay Minerals (Hydrotalcite) *13*
1.5.5 Oxynitride *14*
1.5.6 Calcined Metal Phosphates *14*
1.6 Why Solid Base Catalysts Have Fascinated the Scientific Community? *16*
1.7 Advantages and Disadvantages of Solid Base Catalysts Over Inorganic/Organic Bases *17*
1.8 Role of Solid Base Catalysts in Green Chemistry *18*
1.9 Future Prospects for Solid Base Catalysts *20*
1.10 Conclusion *20*
References *21*

2 Synthesis of Solid Base Catalysts *27*
Chetna Kumari, Nishu Dhanda, Nirmala Kumari Jangid, and Sudesh Kumar
2.1 Introduction *27*
2.2 K_2O/Al_2O_3–CaO *27*
2.2.1 Preparation of K_2O/Al_2O_3–CaO *28*
2.2.1.1 Preparation of Al_2O_3–CaO Mixed Oxides Basic Support *28*
2.2.1.2 Potassium Nitrate Loading with Calcined Mixed Oxides Basic Support *28*
2.2.2 Catalytic Activity of K_2O/Al_2O_3–CaO in the Knoevenagel Condensation Process for the Preparation of Benzylidene Barbituric and Benzylidenemalononitrile Derivatives *28*
2.2.3 Catalytic Activity of K_2O/Al_2O_3–CaO for the Preparation of Pyrano[2,3-*d*]pyrimidinone Derivatives *29*
2.3 Solid Base Fly Ash *30*
2.3.1 Synthesis *30*
2.3.2 Catalytic Activity of SBFA *30*
2.3.3 Condensation Between Benzaldehyde and Cyclohexanone *31*
2.3.4 Catalyst Regeneration *31*
2.4 Calcined Water Sludge *31*
2.4.1 Catalyst Preparation *32*
2.5 Oxides of Rare Earth *32*
2.5.1 Preparation *32*
2.6 Titanium Dioxide *33*
2.6.1 Preparation *33*
2.7 Zinc Oxide *34*
2.7.1 Preparation *34*
2.8 Alkaline Earth Oxides *34*
2.8.1 Preparation *35*
2.8.1.1 Conventional Method for MgO Catalyst *35*
2.8.1.2 Effects of Starting Magnesium Salt *35*
2.8.1.3 Preparation of MgO by Sol–Gel Method *36*
2.8.1.4 Preparation of Mesoporous MgO *36*
2.8.1.5 Catalytic Activity for Claisen–Schmidt Reaction *37*
2.9 Hydrotalcite *38*
2.9.1 Synthesis of Hydrotalcite *38*
2.9.1.1 Coprecipitation Method *38*
2.9.1.2 Sol–Gel Method *39*
2.9.1.3 Michael Addition *39*
2.10 Comparison of Different Solid Base Catalysts *39*
2.11 Conclusion *42*
Conflicts of Interest *42*
Acknowledgment *42*
References *42*

3 Advanced Characterization Techniques for Solid Base Catalysts: An Overview *51*
Neelam Sharma, Suman Swami, Sakshi Pathak, Aruna, and Rahul Shrivastava
3.1 Introduction *51*
3.2 Traditional Characterization Techniques for Solid Base Catalyst *55*
3.2.1 Titration Method *55*
3.2.2 IR Analysis *56*
3.2.3 Scanning Electron Microscopes *58*
3.3 Advanced Characterization Techniques for Solid Base Catalyst *59*
3.3.1 Fourier Transform Infrared Spectroscopy (FT-IR) *59*
3.3.2 Field Emission Scanning Electron Microscopes (FE-SEM) *62*
3.3.3 Transmission Electron Microscope (TEM) *66*
3.3.4 X-ray Diffraction (XRD) Analysis *68*
3.3.5 Thermogravimetric Analysis (TGA) *73*
3.3.6 Brunauer–Emmett–Teller BET Surface Area Pore Diameter Analysis [Gas Interaction and Surface Area Measurement: (Brunauer–Emmett–Teller (BET), Barrett–Joyner–Halenda (BJH) N_2 Adsorption–Desorption Isotherms)] *78*
3.3.7 X-Ray Photoelectron Spectroscopy (XPS) *83*
3.3.8 X-Ray Fluorescence (XRF) *85*
3.4 Protocol for Characterization of Catalyst *87*
3.4.1 Sample Preparation *87*
3.4.1.1 XRD *87*
3.4.1.2 FT-IR *88*
3.4.1.3 FE-SEM *88*
3.4.1.4 TEM *88*
3.4.1.5 BET *89*
3.4.1.6 TGA *89*
3.5 Characterization of Some Basic Sites of Solid Base Catalyst with Suitable Example *89*
3.6 Conclusion *91*
Acknowledgment *92*
References *92*

4 Advanced Solid Catalysis for Biomass Conversion into High Value-Added Chemicals *97*
Urja, Amanpreet Kaur Jassal
4.1 Introduction *97*
4.2 Advanced Solid Catalysis *99*
4.2.1 Types of Solid Catalysts *100*
4.2.2 Methods for the Synthesis of Solid Catalysts *103*
4.3 Biomass, Its Composition, and Properties *105*

4.4 Biomass Conversion into High Value-Added Chemicals *107*
4.5 Utilization of Solid Catalysts for Biomass Conversion into High Value-Added Chemicals *111*
4.6 Electrocatalytic Conversion of Biomass into High Value-Added Chemicals *113*
4.7 Challenges in Design of Solid Catalysts for Biomass Conversion into High Value-Added Chemicals *116*
4.8 Advantages of High Value-Added Chemicals *118*
4.9 Summary and Future Prospectus *119*
Acknowledgments *119*
References *119*

5 Applications of Solid Basic Catalysts for Organic Synthesis *129*
Aditi Tiwari, Anirudh Singh Bhathiwal, and Anjaneyulu Bendi
5.1 Introduction *129*
5.2 Solid-Based Catalyst for Organic Synthesis *131*
5.2.1 Metal Oxides *131*
5.2.2 Zeolites *134*
5.2.3 Clays *136*
5.2.4 Solid-Supported Basic Catalysts *137*
5.3 Conclusion *144*
List of Abbreviations *144*
Consent for Publication *144*
Conflict of Interest *145*
Acknowledgment *145*
References *145*

6 Multicomponent Reactions for Eco-compatible Heterocyclic Synthesis Over Solid Base Catalysts *153*
Amanpreet Singh and Jasdeep Kaur
6.1 Introduction *153*
6.2 Multicomponent Reactions (MCRs) *154*
6.2.1 The Biginelli Multicomponent Reaction *155*
6.2.2 The Hantzsch Multicomponent Reaction *156*
6.2.3 The Mannich Multicomponent Reaction *156*
6.2.4 The Passerini Multicomponent Reaction *156*
6.2.5 The Ugi Multicomponent Reaction *156*
6.2.6 The Gewald Multicomponent Reaction *156*
6.3 Solid Base Catalysts for Organic Reactions *156*
6.4 Characterization Techniques for Solid Base Catalysts *158*
6.5 Heterocycle Synthesis Using Solid Base-Catalyzed MCRs *159*
6.6 Conclusion and Future Trends *165*
Acknowledgment *165*
References *165*

7 Industrial Applications of Solid Base Catalysis *169*
Navdeep Kaur and Nibedita Banik
7.1 Introduction to Solid Base Catalysis *169*
7.1.1 Definition and Characteristics of Solid Base Catalysts *169*
7.1.2 Importance in Industrial Catalysis *171*
7.1.3 Comparison with Solid Acid Catalysts *171*
7.2 Biodiesel Production *171*
7.2.1 Transesterification Reactions *174*
7.2.2 Catalysts and Mechanisms *175*
7.2.3 Industrial-scale Biodiesel Production *176*
7.3 Hydrogenation and Dehydrogenation Reactions *178*
7.3.1 Role of Solid Base Catalysts *178*
7.3.2 Case Studies: Hydrogenation of Oils and Dehydrogenation of Hydrocarbons *179*
7.3.3 Catalytic Mechanisms *181*
7.4 Bimolecular Reactions *182*
7.4.1 Dialkyl Carbonate Synthesis *183*
7.4.2 Catalyst Selection and Reaction Pathways *183*
7.4.3 Applications and Industrial Scale-Up *184*
7.5 Methanol and DME Synthesis *185*
7.5.1 Importance of Methanol and DME *185*
7.5.2 Catalysts and Reaction Conditions *187*
7.5.3 Technological Advancements *187*
7.6 Transesterification of Esters *188*
7.6.1 Role in Chemical and Petrochemical Industries *188*
7.6.1.1 Producing Biodiesel *189*
7.6.1.2 Specialized Chemical Production *189*
7.6.1.3 Procedures for Polymerization *189*
7.6.1.4 Engineering Reactions and Catalysis *189*
7.6.1.5 Resource Efficiency and Waste Reduction *190*
7.6.2 Catalysts for Transesterification *190*
7.7 Alkylation and Isomerization Reactions *190*
7.7.1 Solid Base Catalysis in Petrochemical Processes *190*
7.7.2 Environmental and Economic Implications *193*
7.7.2.1 Economic Implications *194*
7.8 Environmental Applications *195*
7.8.1 Sulfur Removal from Flue Gas *195*
7.8.2 NO_x Reduction in Catalytic Converters *196*
7.8.3 Waste Remediation and Pollution Control *196*
7.9 Dehydration Reactions *197*
7.9.1 Dehydration of Alcohols to Olefins *197*
7.9.2 Dehydration of Alkanes *199*
7.9.3 Industrial Significance and Process Optimization *200*
7.10 Sulfur Removal in Fuel Refining *200*

7.10.1 Hydrodesulfurization (HDS) Catalysts *201*
7.10.2 Sulfur Removal Mechanisms *202*
7.10.3 Impact on Clean Fuel Production *202*
7.11 Processing Methods *202*
7.11.1 Impregnation Method *203*
7.11.2 Precipitation and Coprecipitation Method *203*
7.11.3 Sol–Gel Method *204*
7.11.4 Hydrothermal Process *206*
7.11.5 Vapor Phase Deposition Method *207*
7.12 Use of Solid Base Catalyst in Various Industries *208*
7.12.1 Biodiesel Production (Refer to Section 2) *209*
7.12.2 Petrochemical Industries (Refer to Section 6.1) *209*
7.12.3 Environmental Applications (Refer to Section 8) *210*
7.12.4 Catalytic Cracking in Refining *210*
7.12.5 Biomass Conversion *210*
7.12.6 Water Treatment *210*
7.12.7 Catalytic Decomposition of Ammonia *212*
7.12.8 Aldol Condensation and Knoevenagel Reactions *212*
7.12.9 Hydrogenation Reactions (Refer to Section 3) *212*
7.13 Socioeconomic Impact of Using Solid Base Catalyst *213*
7.14 Challenges and Future Prospects *214*
7.14.1 Current Challenges in Solid Base Catalysis *214*
7.14.2 Emerging Technologies and Materials *215*
7.14.3 Prospects for Sustainable Industrial Catalysis *216*
7.15 Conclusion *216*
7.15.1 Summary of Key Points *216*
7.15.2 Outlook for Continued Research and Development *217*
References *218*

8 Silica-Supported Heterogenous Catalysts: Application in the Synthesis of Tetrazoles *233*
Suman Swami, Neelam Sharma, and Rahul Shrivastava
8.1 Introduction *233*
8.1.1 General Synthetic Protocol for Tetrazoles *234*
8.2 Silica-Supported Heterogenous Catalysts for Tetrazole Synthesis *236*
8.2.1 Generalized Reaction Mechanism of Silica-Supported Heterogenous-Catalyzed Tetrazole Synthesis *252*
8.2.1.1 Via [3 + 2] Cycloaddition *253*
8.2.1.2 Via One-Pot Multicomponent Reaction of Amine, Triethyl Orthoformate, and Azide *254*
8.3 Future Perspective of Silica-Supported Catalysts in Tetrazole Synthesis *255*
8.4 Conclusion *256*
Acknowledgment *256*
References *257*

9 Theoretical Insights on Reduction of CO_2 Using Functionalized Ionic Liquid at Gold Surface *259*
Shanmugasundaram Kamalakannan, Muthuramalingam Prakash, and Majdi Hochlaf
9.1 Introduction to Heterogeneous Catalysts for CO_2RR Applications *259*
9.2 Computational Methodology *261*
9.3 Characterization of Functionalized Ionic Liquids Interacting with CO_2 *262*
9.3.1 Studies of CO_2 Interacting with ILs in Gas Phase *262*
9.3.2 Geometries and Energetics of CO_2 Interacting with Solid–Liquid Interface *264*
9.4 CO_2 Catalytic Activation at IL@Au(111) Liquid–Solid Interface Model *265*
9.4.1 CO_2 interacting with $[EMIm\text{-}Z]^+[DCA]^-$@Au(111) Interface *265*
9.4.2 CO_2 Interacting with $[EMIm\text{-}Z]^+[SCN]^-$@Au(111) Interface *267*
9.5 Charge Transfer and Charge Density Analyses at the Interface *268*
9.5.1 Charge Redistribution Between CO_2 and Interfacial Medium *268*
9.5.2 Interfacial Charge Transfer Analysis of CO_2@Interface *268*
9.5.3 Electronic Structure Analysis of CO_2 at the IL@Au(111) Interface *270*
9.6 Application: Conversion of CO_2 into HCOOH *272*
9.7 Conclusion *272*
References *274*

10 Mixed Metal Oxides as Solid Base Catalysts: Fundamentals and Their Catalytic Performance *279*
Naveen Kumar, Sauraj, and Naveen Chandra Joshi
10.1 Introduction *279*
10.2 Why Mixed Metal Oxides (MMOs)? *280*
10.3 Mixed Metal Oxides (MMOs) *281*
10.4 Synthesis Aspect of MMO Catalysts *282*
10.5 Characterization Techniques for MMO Catalysts *285*
10.6 Catalytic Applications of MMO Catalysts *289*
10.6.1 Applications in Industrially Important Reactions *290*
10.6.2 Applications in Organic Synthesis *297*
10.6.3 Applications in Green Chemistry *299*
10.6.4 Applications in Environmental Catalysis *303*
10.7 Challenges and Future Scope of Mixed Metal Oxides *304*
10.8 Conclusion *305*
References *306*

11 Recent Advances in Conversion of Carbon Dioxide into Value-Added Product over the Solid Base Catalyst *317*
Rajan Singh and Kamal K. Pant
11.1 Introduction *317*
11.2 CO_2 Hydrogenation to Methane *319*

11.2.1 Thermodynamics of CO_2 Hydrogenation to Methane *319*
11.2.2 Catalyst for Methane Synthesis *320*
11.2.3 Proposed Reaction Pathways for CO_2 Hydrogenation to Methane *321*
11.3 CO_2 Hydrogenation to Methanol *323*
11.3.1 Thermodynamics of CO_2 Hydrogenation to Methanol *323*
11.3.2 Catalytic System for CO_2 Hydrogenation to Methanol *324*
11.3.3 Reaction Pathways for Methanol Synthesis *328*
11.3.3.1 HCOO Pathway *329*
11.3.3.2 COOH Pathways *331*
11.3.3.3 RWGS+ CO Hydrogenation Pathways *331*
11.4 CO_2 Hydrogenation to Dimethyl Ether *332*
11.4.1 Thermodynamics of Single-Step DME Synthesis *332*
11.4.2 Catalysts for Single-Step DME Synthesis by CO_2 Hydrogenation *333*
11.4.3 Mechanism of CO_2 Hydrogenation to DME *337*
11.5 CO_2 Hydrogenation to Light Olefins *337*
11.5.1 Catalysts for Light Olefin Synthesis by CO_2 Hydrogenation *338*
11.5.1.1 Reverse Water–Gas Shift (RWGS)-Mediated Pathway *338*
11.5.1.2 Methanol-Mediated Pathways *340*
11.5.2 Mechanism of CO_2 Hydrogenation to Olefins *341*
11.6 Conclusions and Future Prospects *343*
References *344*

Index *351*