Contents

Preface *XV*
List of Contributors *XVII*

1 Introduction *1*
Rasmus Fehrmann, Marco Haumann, and Anders Riisager
1.1 A Century of Supported Liquids *1*
1.2 Supported Ionic Liquids *2*
1.3 Applications in Catalysis *5*
1.4 Applications in Separation *5*
1.5 Coating of Heterogeneous Catalysts *6*
1.6 Monolayers of IL on Surfaces *7*
1.7 Conclusion *7*
References *8*

Part I Concept and Building Blocks *11*

2 Introducing Ionic Liquids *13*
Tom Welton
2.1 Introduction *13*
2.2 Preparation *13*
2.3 Liquid Range *14*
2.4 Structures *16*
2.4.1 The Liquid/Solid Interface *17*
2.4.2 The Liquid/Gas Interface *19*
2.5 Physical Properties *20*
2.5.1 The Liquid/Solid Interface *21*
2.5.2 The Liquid/Gas Interface *21*
2.5.3 Polarity *22*
2.5.4 Chromatographic Measurements and the Abraham Model of Polarity *24*
2.5.5 Infinite Dilution Activity Coefficients *24*
2.6 Effects of Ionic Liquids on Chemical Reactions *26*
2.7 Ionic Liquids as Process Solvents in Industry *29*
2.8 Summary *30*
References *31*

3 Porous Inorganic Materials as Potential Supports for Ionic Liquids *37*
Wilhelm Schwieger, Thangaraj Selvam, Michael Klumpp, and Martin Hartmann
3.1 Introduction *37*
3.2 Porous Materials – an Overview *39*
3.2.1 History *39*
3.2.2 Pore Size *40*
3.2.3 Structural Aspects *41*
3.2.4 Chemistry *43*
3.2.5 Synthesis *43*
3.3 Silica-Based Materials – Amorphous *48*
3.3.1 Silica Gels *48*
3.3.2 Precipitated Silicas *49*
3.3.3 Porous Glass *49*
3.4 Layered Materials *51*
3.5 Microporous Materials *52*
3.5.1 Zeolites *52*
3.5.2 AlPOs/SAPOs *54*
3.5.3 Hierarchical Porosity in Zeolite Crystals *55*
3.6 Ordered Mesoporous Materials *56*
3.6.1 Silica-Based Classical Compounds *58*
3.6.2 PMOs *60*
3.6.3 Mesoporous Carbons *61*
3.6.4 Other Mesoporous Oxides *61*
3.6.5 Anodic Oxidized Materials *62*
3.7 Structured Supports and Monolithic Materials *63*
3.7.1 Monoliths with Hierarchical Porosity *64*
3.7.2 Hierarchically Structured Reactors *65*
3.8 Conclusions *66*
References *66*

4 Synthetic Methodologies for Supported Ionic Liquid Materials *75*
Reinout Meijboom, Marco Haumann, Thomas E. Müller, and Normen Szesni
4.1 Introduction *75*
4.2 Support Materials *76*
4.3 Preparation Methods for Supported Ionic Liquids *77*
4.3.1 Incipient Wetness Impregnation *77*
4.3.2 Freeze-Drying *79*
4.3.3 Spray Coating *80*
4.3.4 Chemically Bound Ionic Liquids *82*
4.3.5 IL–Silica Hybrid Materials *89*
4.4 Summary *91*
References *91*

Part II Synthesis and Properties *95*

5 Pore Volume and Surface Area of Supported Ionic Liquids Systems *97*
Florian Heym, Christoph Kern, Johannes Thiessen, and Andreas Jess
5.1 Example I: [EMIM][NTf_2] on Porous Silica *98*
5.2 Example II: SCILL Catalyst (Commercial Ni catalyst) Coated with [BMIM][$OcSO_4$] *99*
Acknowledgments *103*
Symbols *104*
Abbreviations *104*
References *104*

6 Transport Phenomena, Evaporation, and Thermal Stability of Supported Ionic Liquids *105*
Florian Heym, Christoph Kern, Johannes Thiessen, and Andreas Jess
6.1 Introduction *105*
6.2 Diffusion of Gases and Liquids in ILs and Diffusivity of ILs in Gases *106*
6.2.1 Diffusivity of Gases and Liquids in ILs *106*
6.2.2 Diffusion Coefficient of Evaporated ILs in Gases *108*
6.3 Thermal Stability and Vapor Pressure of Pure ILs *109*
6.3.1 Drawbacks and Opportunities Regarding Stability and Vapor Pressure Measurements of ILs *109*
6.3.2 Experimental Methods to Determine the Stability and Vapor Pressure of ILs *110*
6.3.3 Data Evaluation and Modeling Methodology *110*
6.3.3.1 Evaluation of Vapor Pressure and Decomposition of ILs by Ambient Pressure TG at Constant Heating Rate *110*
6.3.3.2 Evaluation of Vapor Pressure of ILs by High Vacuum TG *114*
6.3.4 Vapor Pressure Data and Kinetic Parameters of Decomposition of Pure ILs *116*
6.3.4.1 Kinetic Data of Thermal Decomposition of Pure ILs *116*
6.3.4.2 Vapor Pressure of Pure ILs *116*
6.3.5 Guidelines to Determine the Volatility and Stability of ILs *118*
6.3.6 Criteria for the Maximum Operation Temperature of ILs *118*
6.3.6.1 Maximum Operation Temperature of ILs with Regard to Thermal Decomposition *118*
6.3.6.2 Maximum Operation Temperature of ILs with Regard to Evaporation *120*
6.4 Vapor Pressure and Thermal Decomposition of Supported ILs *120*
6.4.1 Thermal Decomposition of Supported ILs *121*
6.4.2 Mass Loss of Supported ILs by Evaporation *123*
6.4.2.1 Evaporation of ILs Coated on Silica (SILP-System) *123*
6.4.2.2 Evaporation of ILs Coated on a Ni-Catalyst (SCILL-System) *132*
6.4.2.3 Evaluation of Internal Surface Area by the Evaporation Rate of Supported ILs *132*

6.4.3 Criteria for the Maximum Operation Temperature of Supported ILs *134*
6.4.3.1 Maximum Operation Temperature of Supported ILs with Regard to Thermal Stability *134*
6.4.3.2 Maximum Operation Temperature of Supported ILs with Regard to Evaporation *135*
6.5 Outlook *137*
Acknowledgments *138*
Symbols *138*
Abbreviations *140*
References *140*

7 Ionic Liquids at the Gas–Liquid and Solid–Liquid Interface – Characterization and Properties *145*
Zlata Grenoble and Steven Baldelli
7.1 Introduction *145*
7.2 Characterization of Ionic Liquid Surfaces by Spectroscopic Techniques *146*
7.2.1 Types of Interfacial Systems Involving Ionic Liquids *146*
7.2.2 Overview of Surface Analytical Techniques for Characterization of Ionic Liquids *146*
7.2.3 Structural and Orientational Analysis of Ionic Liquids at the Gas–Liquid Interface *147*
7.2.3.1 Principles of Sum-Frequency Vibrational Spectroscopy *147*
7.2.4 Cation-Specific Ionic Liquid Orientational Analysis *148*
7.2.5 Anion-Specific Ionic Liquid Orientational Analysis *154*
7.2.6 Ionic Liquid Interfacial Analysis by Other Surface-Specific Techniques *157*
7.2.7 Ionic Liquid Effects on Surface Tension *162*
7.2.8 Ionic Liquid Effects on Surface Charge Density *163*
7.3 Orientation and Properties of Ionic Liquids at the Solid–Liquid Interface *165*
7.3.1 Surface Orientational Analysis of Ionic Liquids on Dry Silica *165*
7.3.2 Cation Orientational Analysis *166*
7.3.3 Alkyl Chain Length Effects on Orientation *167*
7.3.4 Competing Anions and Co-adsorption *168*
7.3.5 Computational Simulations of Ionic Liquid on Silica *168*
7.3.6 Ionic Liquids on Titania (TiO_2) *170*
7.4 Comments *172*
References *173*

8 Spectroscopy on Supported Ionic Liquids *177*
Peter S. Schulz
8.1 NMR-Spectroscopy *178*
8.1.1 Spectroscopy of Support and IL *178*

8.1.2 Spectroscopy of the Catalyst *183*
8.2 IR Spectroscopy *186*
References *189*

9 A Priori Selection of the Type of Ionic Liquid *191*
Wolfgang Arlt and Alexander Buchele
9.1 Introduction and Objective *191*
9.2 Methods *191*
9.2.1 Experimental Determination of Gas Solubilities *192*
9.2.1.1 Magnetic Suspension Balance *192*
9.2.1.2 Isochoric Solubility Cell *194*
9.2.1.3 Inverse Gas Chromatography *195*
9.2.2 Prediction of Gas Solubilities with COSMO-RS *196*
9.2.3 Reaction Equilibrium and Reaction Kinetics *197*
9.3 Usage of COSMO-RS to Predict Solubilities in IL *198*
9.4 Results of Reaction Modeling *201*
9.5 Perspectives of the A Priori Selection of ILs *202*
References *205*

Part III Catalytic Applications *209*

10 Supported Ionic Liquids as Part of a Building-Block System for Tailored Catalysts *211*
Thomas E. Müller
10.1 Introduction *211*
10.2 Immobilized Catalysts *212*
10.3 Supported Ionic Liquids *214*
10.4 The Building Blocks *215*
10.4.1 Ionic Liquid *215*
10.4.2 Support *216*
10.4.3 Catalytic Function *218*
10.4.3.1 Type A1 – Task Specific IL *219*
10.4.3.2 Type A2 – Immobilized Homogeneous Catalysts and Metal Nanoparticles *219*
10.4.3.3 Type B – Heterogeneous Catalysts Coated with IL *221*
10.4.3.4 Type C – Chemically Bound Monolayers of IL *221*
10.4.4 Additives and Promoters *222*
10.4.5 Preparation and Characterization of Catalysts Involving Supported ILs *222*
10.5 Catalysis in Supported Thin Films of IL *222*
10.6 Supported Films of IL in Catalysis *223*
10.6.1 Hydrogenation Reactions *224*
10.6.2 Hydroamination *225*
10.7 Advantages and Drawbacks of the Concept *228*
10.8 Conclusions *229*

Acknowledgments *229*
References *229*

11 Coupling Reactions with Supported Ionic Liquid Catalysts *233*
Zhenshan Hou and Buxing Han
11.1 Introduction *233*
11.2 A Short History of Supported Ionic Liquids *234*
11.3 Properties of SIL *234*
11.4 Application of SIL in Coupling Reactions *235*
11.4.1 C–C Coupling Reactions *235*
11.4.1.1 Stille Cross Coupling Reactions *235*
11.4.1.2 Friedel–Crafts Alkylation *235*
11.4.1.3 Olefin Hydroformylation Reaction *236*
11.4.1.4 Methanol Carbonylation *237*
11.4.1.5 Suzuki Coupling Reactions *237*
11.4.1.6 Heck Coupling Reactions *239*
11.4.1.7 Diels–Alder Cycloaddition *241*
11.4.1.8 Mukaiyama reaction *242*
11.4.1.9 Biglinelli Reaction *242*
11.4.1.10 Olefin Metathesis Reaction *243*
11.4.2 C–N Coupling Reaction *243*
11.4.2.1 Hydroamination *243*
11.4.2.2 N-Arylation of N-Containing Heterocycles *244*
11.4.2.3 Huisgen [3+2] Cycloaddition *244*
11.4.3 Miscellaneous Coupling Reaction *244*
11.5 Conclusion *246*
References *246*

12 Selective Hydrogenation for Fine Chemical Synthesis *251*
Pasi Virtanen, Eero Salminen, Päivi Mäki-Arvela, and Jyri-Pekka Mikkola
12.1 Introduction *251*
12.2 Selective Hydrogenation of α,β-Unsaturated Aldehydes *251*
12.3 Asymmetric Hydrogenations over Chiral Metal Complexes Immobilized in SILCAs *257*
12.4 Conclusions *261*
References *261*

13 Hydrogenation with Nanoparticles Using Supported Ionic Liquids *263*
Jackson D. Scholten and Jairton Dupont
13.1 Introduction *263*
13.2 MNPs Dispersed in ILs: Green Catalysts for Multiphase Reactions *264*
13.3 MNPs Immobilized on Supported Ionic Liquids: Alternative Materials for Catalytic Reactions *267*
13.4 Conclusions *275*
References *275*

14 Solid Catalysts with Ionic Liquid Layer (SCILL) *279*
Wolfgang Korth and Andreas Jess
14.1 Introduction *279*
14.2 Classification of Applications of Ionic Liquids in Heterogeneous Catalysis *280*
14.3 Preparation and Characterization of the Physical Properties of the SCILL Systems *283*
14.3.1 Preparation of SCILL Catalysts *283*
14.3.2 Nernst Partition Coefficients *284*
14.3.3 Pore Volume and Surface Area of the SCILL Catalyst with [BMIM][$OcSO_4$] as IL *287*
14.4 Kinetic Studies with SCILL Catalysts *287*
14.4.1 Experimental *287*
14.4.2 Hydrogenation of 1,5-Cyclooctadiene (COD) *288*
14.4.2.1 Reaction Steps of 1,5-COD Hydrogenation on the Investigated Ni Catalyst *288*
14.4.2.2 Influence of ILCoating of the Ni Catalyst on the Selectivity of COD Hydrogenation *288*
14.4.2.3 Influence of IL Coating of the Catalyst on the Rate of COD Hydrogenation *291*
14.4.2.4 Influence of Pore Diffusion on the Effective Rate of COD Hydrogenation *293*
14.4.2.5 Influence of Pore Diffusion on the Selectivity of COD Hydrogenation *295*
14.4.2.6 Stability of the IL Layer and Deactivation of IL-Coated Catalyst *297*
14.4.3 Hydrogenation of Octine, Cinnamaldehyde, and Naphthalene with SCILL Catalysts *297*
14.4.4 Hydrogenation of Citral with SCILL Catalysts *298*
14.5 Conclusions and Outlook *300*
Acknowledgments *300*
Symbols Used *300*
Greek Symbols *301*
Abbreviations and Subscripts *301*
References *302*

15 Supported Ionic Liquid Phase (SILP) Materials in Hydroformylation Catalysis *307*
Andreas Schönweiz and Robert Franke
15.1 SILP Materials in Liquid-Phase Hydroformylation Reactions *307*
15.2 Gas-Phase SILP Hydroformylation Catalysis *311*
15.3 SILP Combined with $scCO_2$ – Extending the Substrate Range *319*
15.4 Continuous SILP Gas-Phase Methanol Carbonylation *322*

15.5 Conclusion and Future Potential *323*
References *324*

16 Ultralow Temperature Water–Gas Shift Reaction Enabled by Supported Ionic Liquid Phase Catalysts *327*
Sebastian Werner and Marco Haumann
16.1 Introduction to Water–Gas Shift Reaction *327*
16.1.1 Heterogeneous WGS Catalysts *327*
16.1.2 Homogeneous WGS Catalysts *329*
16.2 Challenges *332*
16.3 SILP Catalyst Development *332*
16.4 Building-Block Optimization *333*
16.4.1 Catalyst Precursor *334*
16.4.2 Support Material *335*
16.4.3 IL Variation *337*
16.4.4 Catalyst Loading *338*
16.4.5 IL Loading *339*
16.4.6 Combination of Optimized Parameters *340*
16.5 Application-Specific Testing *341*
16.5.1 Restart Behavior *341*
16.5.2 Industrial Support Materials *343*
16.5.3 Elevated Pressure *345*
16.5.4 Reformate Synthesis Gas Tests *346*
16.6 Conclusion *348*
References *348*

17 Biocatalytic Processes Based on Supported Ionic Liquids *351*
Eduardo García-Verdugo, Pedro Lozano, and Santiago V. Luis
17.1 Introduction and General Concepts *351*
17.1.1 Enzymes and Ionic Liquids *351*
17.1.2 Supported ILs for Biocatalytic Processes *353*
17.1.3 Reactor Configurations with Supported ILs for Biocatalytic Processes *355*
17.2 Biocatalysts Based on Supported Ionic Liquid Phases (SILPs) *356*
17.3 Biocatalysts Based on Covalently Supported Ionic Liquid-Like Phases (SILLPs) *360*
17.4 Conclusions/Future Trends and Perspectives *365*
Acknowledgments *365*
References *365*

18 Supported Ionic Liquid Phase Catalysts with Supercritical Fluid Flow *369*
Rubén Duque and David J. Cole-Hamilton
18.1 Introduction *369*
18.2 SILP Catalysis *369*

18.2.1 Liquid-Phase Reactions *369*
18.2.2 Gas-Phase Reactions *370*
18.2.3 Supercritical Fluids *371*
18.2.4 SCF IL Biphasic Systems *372*
18.2.5 SILP Catalysis with Supercritical Flow *375*
References *381*

Part IV Special Applications *385*

19 Pharmaceutically Active Supported Ionic Liquids *387*
O. Andreea Cojocaru, Amal Siriwardana, Gabriela Gurau, and Robin D. Rogers
19.1 Active Pharmaceutical Ingredients in Ionic Liquid Form *387*
19.2 Solid-Supported Pharmaceuticals *389*
19.3 Silica Materials for Drug Delivery *389*
19.4 Factors That Influence the Loading and Release Rate of Drugs *391*
19.4.1 Adsorptive Properties (Pore Size, Surface Area, Pore Volume) of Mesoporous Materials *391*
19.4.1.1 Pore Size *391*
19.4.1.2 Surface Area *392*
19.4.1.3 Pore Volume *392*
19.4.2 Surface Functionalization of Mesoporous materials *392*
19.4.3 Drug Loading Procedures *394*
19.4.3.1 Covalent Attachment *394*
19.4.3.2 Physical Trapping *394*
19.4.3.3 Adsorption *395*
19.5 SILPs Approach for Drug Delivery *395*
19.5.1 ILs Confined on Silica *395*
19.5.2 API-ILs Confined on Silica *396*
19.5.2.1 Synthesis and Characterization of SILP Materials *396*
19.5.2.2 Release Studies of the API-ILs from the SILP Materials *399*
19.6 Conclusions *402*
References *402*

20 Supported Protic Ionic Liquids in Polymer Membranes for Electrolytes of Nonhumidified Fuel Cells *407*
Tomohiro Yasuda and Masayoshi Watanabe
20.1 Introduction *407*
20.2 Protic ILs as Electrolytes for Fuel Cells *409*
20.2.1 Protic ILs *409*
20.2.2 Thermal Stability of Protic IL *410*
20.2.3 PILs Preferable for Fuel Cell Applications *411*
20.3 Membrane Fabrication Including PIL and Fuel Cell Operation *411*
20.3.1 Membrane Preparation *411*
20.3.2 Fuel Cell Operation Using Supported PILs in Membranes *414*

20.4 Proton Conducting Mechanism during Fuel Cell Operation *415*
20.5 Conclusion *417*
Acknowledgments *418*
References *418*

21 Gas Separation Using Supported Ionic Liquids *419*
Marco Haumann
21.1 SILP Materials *419*
21.1.1 SILP-Facilitated GC *423*
21.2 Supported Ionic Liquid Membranes (SILMs) *428*
21.2.1 Gas Separation *429*
21.2.2 Gas Separation and Reaction *437*
21.3 Conclusion *440*
References *441*

22 Ionic Liquids on Surfaces – a Plethora of Applications *445*
Thomas J. S. Schubert
22.1 Introduction *445*
22.2 The Influence of ILs on Solid-State Surfaces *445*
22.3 Layers of ILs on Solid-State Surfaces *446*
22.4 Selected Applications *446*
22.5 Sensors *447*
22.6 Electrochemical Double Layer Capacitors (Supercapacitors) *449*
22.7 Dye Sensitized Solar Cells *451*
22.8 Lubricants *452*
22.9 Synthesis and Dispersions of Nanoparticles *453*
References *454*

Part V Outlook *457*

23 Outlook – the Technical Prospect of Supported Ionic Liquid Materials *459*
Peter Wasserscheid
23.1 Competitive Advantage *460*
23.2 Observability *462*
23.3 Trialability *462*
23.4 Compatibility *463*
23.5 Complexity *463*
23.6 Perceived Risk *464*
References *465*

Index *467*