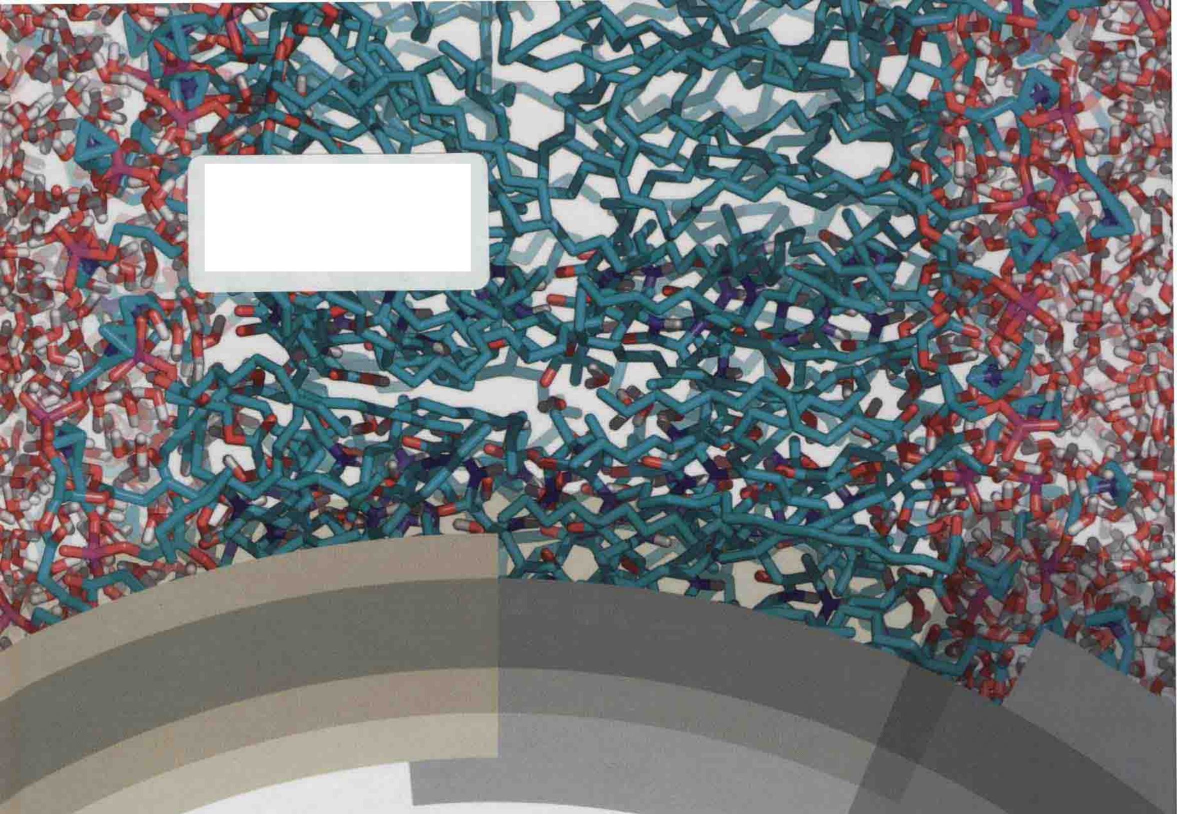

RSC Catalysis Series

Catalysis in Ionic Liquids

From Catalyst Synthesis to Application

Edited by Chris Hardacre and Vasile Parvulescu

ROYAL SOCIETY
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Preface

This book provides an up to date review of the state of the art of catalytic reactions in ionic liquids as well as the formation of catalytic materials using ionic liquid methods. Catalytic reactions were amongst the first to be undertaken in these neoteric solvents with electrocatalytic studies being reported in the 1960s. Thereafter, there has been an explosion in the interest in this area starting with carbon–carbon bond forming reactions utilizing ionic liquids as the catalyst as well as the solvent in Friedel–Crafts, Heck and Diels–Alder reactions. From there the field moved onto study gas–liquid reactions, asymmetric processes and the conversion of biomass. A wide range of catalysts have been utilized and modified to be compatible with ionic liquid processes including homogeneous complexes, nanoparticles, supported metal heterogeneous catalysts, supported ionic liquid based catalysts, zeolites, enzymes, electrocatalysts and photocatalysts. In the vast majority of cases, the ionic liquid based processes have been compared with analogous molecular derived systems with significant advantages being demonstrated, for example, in rate, selectivity, recycle of the catalyst or work up procedures. In a number of cases, the ionic liquid based systems have enabled new reactions to be undertaken. Due to the wide range of ionic liquids available and the ability to functionalise the cation and the anion to tailor their physical and chemical properties, the field of catalysis in ionic liquids has been transformed over the last 20 years from both the perspective of novel materials synthesis as well as reactivity-selectivity profiles. The chapters provide a perspective on how ionic liquid properties can be modified by structural changes to enable the catalytic materials and processes to be controlled. In addition, the reviews provide a summary of where our understanding lies in these systems. The complex nature of the interactions involved and the potential these systems have to change many industrial processes provide significant opportunities for future study.

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This is particularly true in the translation of the technologies under study from the bench scale to pilot and full scale industrial utilization where the recovery of the ionic liquids, their toxicity and their added value to a process, for example, are critical. We would like to thank all the authors for their hard work in reviewing the subject matter for this book and for providing their insight into the future.

Christopher Hardacre and Vasile I. Parvulescu

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Simon Doherty

CHAPTER 1

Catalytic Conversion of Biomass in Ionic Liquids

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1.1 Introduction

The fossil fuel-based economy is facing several problems and challenges, which involve the increasing emissions of CO_2, decreasing reserves, and increasing energy prices.[1] These challenges have driven the search for new transportation fuels and bioproducts to substitute the fossil carbon-based materials. Biomass is defined as organic matter available on a renewable basis, and it includes forest and mill residues, agricultural crops and wastes, wood and wood wastes, animal wastes, livestock operation residues, aquatic plants, and municipal and industrial wastes.[2] Biomass is deemed a sustainable and green feedstock for the production of fuels and fine chemicals, although perhaps not always in the way they are proposed to be used.

A major source of biomass is lignocellulosic biomass, which is particularly well suited for energy applications because of its large-scale availability, low cost, and environmentally benign production. Lignocelluloses are composed of cellulose, hemicellulose, lignin, extractives, and several inorganic materials, of which the first three biopolymers are the main components. The cellulose microfibrils that are present in the hemicellulose–lignin matrix are often associated in the form of bundles or macrofibrils.[3] The structure of these naturally occurring cellulose fibrils is mostly crystalline in nature and

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highly resistant to attack by enzymes. In addition, the presence of lignin also impedes enzymatic hydrolysis, as enzymes bind onto the surface of lignin and hence do not act on the cellulose chains.[4]

Usually, conversion of lignocellulosic biomass is carried out in the presence of catalysts, such as strong liquid and solid acids. Various types of lignocellulosic biomass, such as wood chips, sawdust, corncobs, and walnut shells, have been tentatively processed by liquid acid-catalyzed hydrolysis[5–8] with H_2SO_4, HCl, H_3PO_4, *etc.* Despite the relatively high catalytic activity of these liquid acids in the hydrolysis of cellulosic materials, by and large their uses are still uneconomical because the process suffers from severe corrosion, a requirement for special reactors, and costly separation and neutralization of waste acids.[9]

Recently, attention has been paid to the use of solid catalysts in the depolymerization of lignocellulosic biomass. Several types of solid acids, such as Nafion, Amberlyst, $-SO_3H$ functionalized amorphous carbon or mesoporous silica, H-form zeolites like HZSM-5, heteropolyacids, and even metal oxides (*e.g.*, γ-Al_2O_3) have been explored for their catalytic performance in the hydrolysis of lignocellulosic biomass.[10–13] It has been shown that solid Brønsted acids are efficient catalysts for the hydrolysis of lignocellulosic biomass.[14,15]

The ability of ionic liquids (ILs, now defined as salts with melting points below 100 °C[16]) to dissolve biomass provides new opportunities for the pretreatment and conversion of lignocellulosic biomass. In 2002, we reported that certain ILs, such as 1-butyl-3-methylimidazolium chloride ($[C_4mim]Cl$) can dissolve cellulose by as much as 25 wt% without any pretreatment.[17] Since then, increasing numbers of scientific papers, patents, and conference abstracts in this area have been published, and ILs have become one of the "hot-topics" in polysaccharide research. Up to now, ILs have been shown to be able to dissolve a number of pure biopolymers, including cellulose,[17–22] hemicellulose,[23] lignin,[24,25] chitin,[26] starch,[27] silk,[28] wool,[29] as well as a variety of raw biomass, such as wood,[30,31] bagasse,[32,33] corn stover,[34] wheat straw[35] and shrimp shell.[26] Not only is the dissolution of biomass in ILs widely studied, but also its conversion into value-enhanced products has drawn the attention of scientists.

In this chapter, the catalytic dissolution and degradation of pure cellulose, lignin (including lignin model compounds), hemicellulose, and raw lignocellulosic biomass materials in the presence of ILs will be reviewed. Several challenges in this area will also be addressed.

1.2 Catalytic Dissolution of Lignocellulosic Biomass

Lignocellulosic biomass presents a greater challenge for dissolution because of the tight, covalent, hydrogen bonded matrix of carbohydrate polymers (cellulose and hemicellulose) and phenolic polymers (lignin),[36] resulting in insolubility in common solvents. Various pretreatment methods for lignocelluloses have been developed to open the compact structure and make