Chapter 11
Catalysis with Room Temperature Ionic Liquids Mediated Metal Nanoparticles

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ABSTRACT

There has been still a growing interest in ionic liquids (ILs) for catalysis, in particular considering their tremendous success made over the past decades. Indeed, ILs for catalysis has been a main subject in chemistry and technology, and a rough estimate is that more than 6000 publications involving IL catalysis have been reported in the past fifteen years. Since there have been a large number of excellent reviews and books concerning the catalysis in ILs, in this chapter the authors mainly focus on the IL immobilized nano- or super-fine metal particles for catalysis, which could bridge or fill the gap between homogeneous and heterogeneous catalysis. Detailed IL-immobilized catalyst preparation, characterization and their application in hydrogenation, C-C coupling, oxidation, etc. will be discussed.

INTRODUCTION

Over the past 30 years, perhaps the most exciting scientific and technological progress in chemical science and chemical engineering is the discovery and recognition of ionic liquids (ILs). As a matter of fact, ILs are not new and the first room temperature IL $[EtNH_3][NO_3]$ that has a melting point of 12 °C was described as early as 1914, and was primarily prepared for electric conductivity measurements (Sugden & Wilkins, 1929). Generally, RTILs are defined as those molten salts composing of bulky organic cations (such as imidazolium, pyridinium, quaternary ammonium, phosphonium, *etc.*,) and inorganic or organic anions, which melt around 100°C or below as an arbitrary temperature limit. A series of typical ILs are shown in Figure 1.

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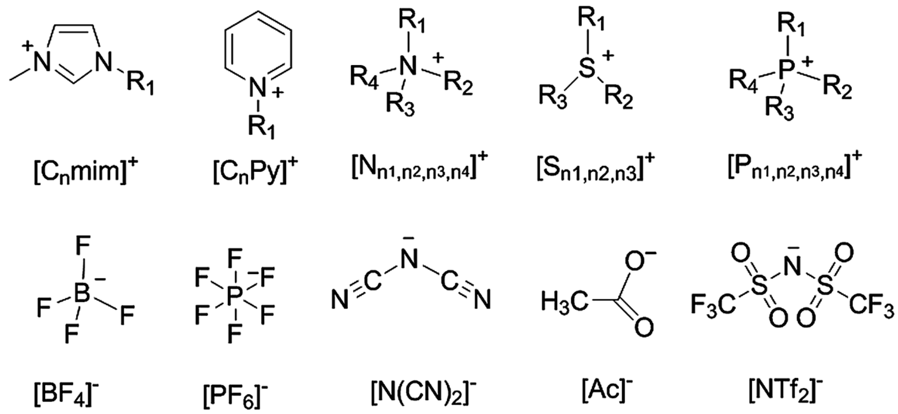
Figure 1. Typical structure of commercially available ILs



Catalytic reactions in ILs have been examined for about 30 years, and the first example of RTILs for catalysis is using dialkylimidazolium chloroaluminate ILs as catalysts for Friedel-Crafts reactions in 1986 (Boon, Levisky, Pflug, & Wilkes, 1986). Although the chloroaluminate ILs are relatively cheaper and exhibit good catalytic performance, they are air and water sensitive, which limited their further application in catalysis as well as in many other fields. In the 1990s, a significant milestone was passed as the imidazolium salts incorporated the tetrafluoroborate or hexafluorophosphate anions to form air- and water-stable ILs (Wilkes & Zaworotko, 1992). Since then, ILs began to bring a green revolution in the fields of catalytic science and all kinds of 'green' catalytic reactions or processes in or by ILs were gradually established.

No doubt that ILs have achieved great success in catalysis by acting as reaction media, catalysts, or both. Most often the reasons for this achievement include: 1) ILs could control both the direction and selectivity of chemical reactions due to their special "ionic environment", including stronger electrostatic field, peculiar micro-environment, existence of multidimensional weak interactions; 2) ILs could provide a two-phase systems for reaction, or the catalyst could be entrapped or ''immobilized" with ILs allowing catalytic system recycle; 3) ILs could be designed by varying the structures of both the anion and cation to modulate the physical and chemical properties, which made them apply to various catalytic systems; 4) ILs could endow a catalytic reaction with green character compared with organic solvents because of their lower vapor pressure and less combustibility (Hallett & Welton, 2011; Parvulescu & Hardacre, 2007; Welton, 1999; Q. Zhang, Zhang, & Deng, 2011). In a word, using ILs as catalysts or reaction media or both, unexpected catalytic performance, new reactions and new catalyst materials could be achieved, and even the current situation of catalytic science and technology may be changed greatly.

Up to now, ILs have pervaded in nearly every branch of catalytic science and technology, and in the past ten years the numbers of IL publications for catalysis have been significantly increasing. It is to say that ILs have been successfully involved in conventional homogeneous and heterogeneous catalysis. Furthermore, the incorporation of ILs into nano- or super-fine particle catalysis could also provide a possibility or platform to explore those fascinating catalysis, which could bridge or fill the gap between homogeneous and heterogeneous catalysis.

In this chapter, we will focus on IL immobilized nano- or super-fine particles, and the IL-immobilized nanocatalyst preparation, characterization and their application in various reactions will be discussed in