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Editorial

Ionic Liquids in Catalysis

Hieronim Maciejewski [1,2]

[1] Faculty of Chemistry, Adam Mickiewicz University, Uniwersytetu Poznańskiego 8, 61-614 Poznań, Poland; maciejm@amu.edu.pl
[2] Adam Mickiewicz University Foundation, Poznań Science and Technology Park, Rubież 46, 61-612 Poznań, Poland

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Ionic liquids play a larger and larger as well as more and more diversified role in catalysis [1–4], which is reflected by the fact that the number of literature reports on this subject increases annually by over 400 items. In the case of catalytic reactions, the ionic liquids enable us to obtain higher selectivities and yields and, first and foremost, they allow easy isolation of catalysts from the post-reaction mixture. Until now, the most popular application of ionic liquids is their use as a solvent and immobilizing agent. Their low vapor pressure and high thermal stability make them an alternative to classic organic solvents (the so-called green alternative). Nevertheless, at the beginning of this century, some critical voices were raised that pointed to the often complicated synthesis of the ionic liquids, which was also waste-generating and expensive. The shortcomings of ionic liquids also included their low biodegradability (or its absence) and sometimes their toxicity [5–7]. This is why a search has been made for the development of synthesis methods with a limited amount of waste (or waste-free ones), based first of all on the use of biodegradable and non-toxic starting materials, often of natural origin [8–11]. Due to the selection of new methods of synthesis, as well as the application of renewable and biodegradable raw materials, a larger and larger group of derivatives is considered safe and environmentally friendly, and the application trends include more and more areas. At present, one can notice a keen interest in two areas of the applications of ionic liquids. One of them is biotransformation (in a broad sense) that is used in the processing of biomass and lignocellulosic waste to obtain valuable chemical products [12–14]. The other widely developing trend is obtaining heterogeneous catalytic systems with the participation of ionic liquids, i.e., SILPC or SILCA (Supported Ionic Liquids Phase Catalysts or Supported Ionic Liquids Catalysts) [15–17] and SCILL (Supported Catalysts with Ionic Liquid Layer) [15,18–20] as well as catalysts in which ionic liquid makes a structural element [21–24]. In systems of this type, all problems observed in the case of catalysis in homogeneous systems are eliminated. First of all, there is no problem with the isolation of catalyst which is heterogeneous. Since in the case of SILPC and SCILL, the ionic liquid covers the supports with a thin layer, a small amount of the ionic liquid is needed which results in a considerable cost reduction (despite the high price of ionic liquids). Moreover, due to the thinness of the layer, the liquid viscosity does not influence the process course and mass transfer is not a problem. Such a form of catalyst can be applied in the continuous flow reactors what also influences the process economics.

The subject of papers published in this Special Issue reflects the two dominating trends of interest. The first one concerns biomass processing and the synthesis and application of ionic liquids from biorenewable resources. Parajo et al. presented an effective (one or two-step) method for the processing of eucalyptus wood towards producing furfural and levulinic acid with the use of acidic ionic liquid (C_3SO_3Hmim)HSO_3 as a catalyst [25]. Bengoa et al. described the processing of cellulose (obtained from municipal and industrial sewage) into valuable levulinic acid, while also using a Brønsted acidic ionic liquid as a catalyst [26]. During the conversion of cellulose to levulinic acid, 5-hydroxymethylfurfural (5-HMF) is formed as a by-product. By rehydration reaction of the latter, it can be converted into levulinic acid. The process of cellulose degradation towards 5-HMF and glucose in the presence of DES (deep eutectic solvents based on oxalic acid/choline chloride) and metal chlorides ($CrCl_3$ or $SnCl_4$) has been presented by Zhang's research group [27]. Brønsted acidic ionic liquids based on trimethylamine and sulfuric acid were employed as a solvent and catalyst in the synthesis of bis(2-ethylhexyl) terephthalate which is used as a plasticizer in the manufacture of plastics coming into contact with food. This new approach, which is characterized by the replacement of conventional acids and organometallic compounds with ionic liquids, was described by Chrobok's research group [28]. Bouquillon et al. presented the synthesis of a series of biobased ionic liquids with natural carboxylates (proline-based ionic liquids) [29]. These compounds were employed as a solvent and basic catalyst in Michael reactions.

The second group of papers concerns the synthesis and activity of heterogeneous catalytic systems. In the review article [30], the most important issues of heterogeneous catalysis with the participation of ionic liquids were presented. The methods of synthesis and exemplary trends in the application of SILP (SILCA), SCILL, and porous ionic liquids were described in the review. Subsequent papers concern the application of heterogeneous systems in particular types of reactions. Vucetic et al. described the use of PdCl2-containing SILCA as a catalyst for a Heck reaction [31]. The catalyst showed high stability and activity in the reaction between butylacrylate and iodobenzene and enabled its multiple use. A highly active SILP material that contained a rhodium complex was applied in the synthesis of monofunctional derivatives of disiloxanes. The above catalyst, described in the paper by Kukawka et al. [32], was characterized by high stability that enabled at least 50 catalytic runs without loss of activity. Orlińska et al. presented a new SCILL catalytic system with N-hydroxyphthalimide as an active component and applied it in the oxidation of ethylbenzene [33]. In the next two papers, heterogeneous catalysts containing ionic liquids as structural elements were described. Bartlewicz et al. [34] presented a rhodium complex ligated by imidazolium-substituted phosphine that showed high activity for hydrosilylation of alkynes. A series of anionic platinum complexes obtained by a simple reaction of piperidinium or pyrrolidinium ionic liquids with platinum compounds were presented by Jankowska-Wajda et al. [35]. The complexes prepared in such a way appeared to be very active catalysts for hydrosilylation of different olefins. It is worth mentioning that their high activity was maintained even after multiple use. Szyling et al. [36] described an effective immobilization of a ruthenium complex in ionic liquids and applied the obtained complex as a catalyst for the selective synthesis of (E)-alkenyl boronates via borylative coupling of olefins with vinyl boronic acid pinacol ester. Additional application of $scCO_2$ to the extraction of the product significantly reduced catalyst leaching, due to which it could be used many times.

All the above papers showed the great importance of ionic liquids in practice and that their catalytic application is growing wider and wider; particularly, they can play various functions in catalysis. In addition to the known advantages of the application of ionic liquids, the development of advanced methods of their synthesis from biorenewable natural resources results in their biodegradable and environmentally friendly character. For this reason, one can expect further development of their application, including in different catalytic processes.

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