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Supported ionic liquids in catalysis

Boris V. Romanovsky, Irina G. Tarkhanova

Department of Chemistry, Lomonosov Moscow State University
Leninskie Gory 1, 119991 Moscow, Russian Federation

Catalysis using supported ionic liquids is nowadays a rapidly developing field of research. This review considers published data devoted to the methods of synthesis of supported ionic liquid-based catalytic materials. The results of investigations of the physicochemical properties of these materials and their catalytic activities and selectivities in liquid- and gas-phase reactions are discussed. The review covers publications of the last five years and also includes earlier works that have not been reflected, for some reason, in numerous reviews and monographs dealing with this subject.
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I. Introduction

Over the last decade, academic and industrial interest in using ionic liquids (ILs) in catalysis has clearly and consistently shifted to their application as not only alternatives to traditional solvents, but also essential components of catalytic materials.[1,2] Ultrathin layers of ILs supported on porous supports through covalent bonding or adsorption either exhibit high intrinsic catalytic activity [Supported Ionic Liquid Catalyst (SILC) systems] or serve as peculiar 2D solvents and stabilizers for an introduced active compound [Supported Ionic Liquid Phase (SILP) systems]. Whereas in the early 2000s, there were approximately ten references to SILC and SILP systems in the scientific and patent literature, since 2010 several analytical reviews and tens of original research articles on these promising materials have been published annually.[2–10]

The reasons for the rapidly growing research interest in supported ILs are quite obvious. First, the consumption of ILs, which are still rather costly, is sharply reduced when they are used as nanofilms deposited on large surface area supports. Second, since high viscosity of ILs and the resulting low diffusion coefficients of solubilized molecules can induce kinetic limitations on their interaction, switching to nanofilms minimizes the undesirable retardation of fast reactions due to diffusion. Third, from a practical point of view, the possibility to conduct a catalytic proccess in a continuous mode, rather than a batch one, thus multiplying the output of the reaction system, is a substantial factor.

For some reason, recent monographs and reviews do not cover studies on the use of supported ILs in catalysis of such processes as synthesis of haloalkanes and haloarenes, oxidation of heteroorganic compounds, isomerization of hydrocarbons and other. In this regard, the aim of the present review was to give an analytical consideration of investigations in these areas as well as to assess the recently published works on synthetic routes to supported IL-based catalytic materials, investigation of their physicochemical properties as well as catalytic activities and selectivities in liquid- and gas-phase reactions.

II. Synthesis of supported ionic liquid-based catalysts: general principles

There are two severely different synthetic approaches to immobilization of ILs on porous supports and fabrication of heterogenous catalysts based on such systems. The first one comprises the formation of an ultrathin film of a physically adsorbed IL on a highly developed surface of a porous support. The adsorbed IL plays the role of a highly polar reaction medium and contains a catalytically active component, transition metal complex

B.V.Romanovsky. Doctor of Chemical Sciences, Professor at the Division of Physical Chemistry of the Department of Chemistry, MSU.
Telephone: +7(495)939–2054, e-mail: bvromanovsky@mail.ru
I.G.Tarkhanova. Doctor of Chemical Sciences, Leading Researcher, Head of the Laboratory of Molecular-organized Catalytic Systems at the Division of Chemical Kinetics of the same Department.
Telephone: +7(495)939–3498, e-mail: itar_msu@mail.ru
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or metal nanoparticles, which are introduced either into the IL prior to film formation or into the already formed adsorption layer (SILP technology).[11–15]

According to the second, also widely used approach, an IL layer with a catalytically active metal complex such as $[Al_2Cl_7]^-$, $[RuO_4]^-$, $[SnCl_5]^-$ *etc.* as the anion is created on the surface of the support (SILC technology).[16–18] The first example of using the latter technology was described by Wu *et al.*[19] as early as in 1996. The hydrodechlorination catalyst was obtained as follows. A layer of IL, tetra-n-butylammonium chloride, was deposited onto a silica surface and, after that, palladium, cobalt or copper chlorides were introduced into the layer. Indeed, upon dissolution, these chlorides react with two chloride anions of the adsorbed IL to give tetrachloride complex anions $[MCl_4]^{2-}$. In the early 2000s, catalytic materials based on ILs with chloroaluminate anions supported on various porous substrates were successfully used as catalysts for the reactions of many organic compounds.[20, 21]

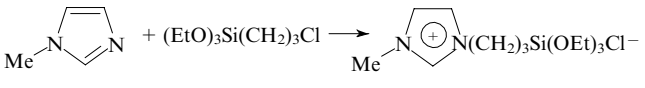
As a matter of fact, the results of those particular works inspired a rapid development of a new trend in catalysis: preparation, investigation and application of supported ionic liquid-based catalytic materials.

A doubtless advantage of SILP and SILC materials as catalysts, apart from the relatively inexpensive preparation route, is primarily the minimization of mass transfer effects in such high-viscosity media as ILs owing to the nanolayer nature of their coating of a porous support surface. When ILs are used as reaction media, diffusion limitations could substantially inhibit fast reactions. Moreover, an almost perfect uniformity of the catalytic sites is achieved in the ILs deposited in nanofilms, but this is never observed in traditional catalytic materials; meanwhile, it is a key factor of high selectivity of molecular catalysts.

From the practical standpoint, the possibility of well-directed tuning the solubility of ILs in common polar and non-polar solvents by selecting the appropriate ion pair is also of great importance. Such matching makes it possible to prevent leaching of the IL active layer from the catalyst in liquid-phase processes. Finally, from the engineering standpoint, catalysts based on supported layers of ILs are most efficient for conducting vapour- and gas-phase processes in continuous reaction units, which have larger productivity than batch units.

Another strategy of supported IL synthesis is based on the formation of organized monomolecular layers such as Langmuir–Blodgett films on supports by forming a covalent or ionic bond between the ionic liquid and the surface. In the former case, the IL in which the cation bears a functional 'anchor' trimethoxy or triethoxy group is first obtained by quaternization of a corresponding organic base such as *N*-methylimidazole (MIM) with 3-choloropropyltriethoxysilane (CPTES) (Scheme 1).

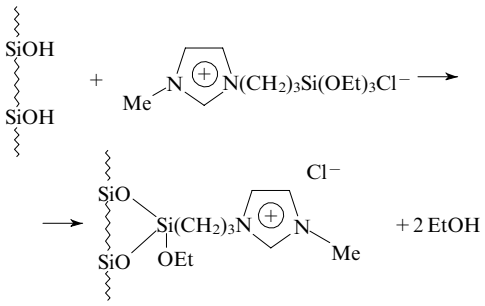
Scheme 1



MIM CPTES

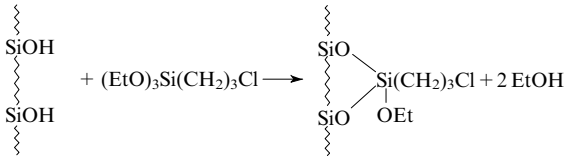
Modification of the silica support having reactive OH groups at a surface with a functionalized IL results in the formation of stable Si–O–Si chemical bonds between the IL cation and the surface (Scheme 2).

Scheme 2



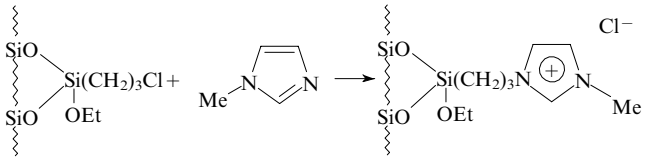
In the covalent grafting of IL to the surface, instead of functionalization of the ionic liquid cation, functionalization of the surface bearing OH groups to which the would-be linker is grafted may first take place (Scheme 3).

Scheme 3



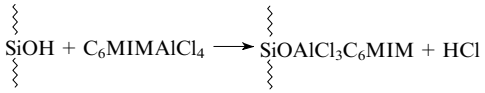
In this case, covalent immobilization of the IL occurs *via* quaternization of methylimidazole base by the linker grafted to the support surface (Scheme 4).

Scheme 4



Ionic liquid immobilization *via* ionic bond formation between the surface-grafted ionic liquid anion and its cation can be illustrated by the results reported by DeCastro *et al.*[20] The ionic bond of the cation of the imidazolium ionic liquid $[C_6MIM]^+[AlCl_4]^-$ (C_6 is hexyl) was formed upon the reaction of its anion with the support OH groups (Scheme 5).

Scheme 5



It is clear that from the preparative standpoint, covalent or ionic immobilization of an IL on a support is a lot more complicated than deposition by adsorption. However, an evident advantage of chemical bonding of IL is minimization (or even elimination) of the highly undesirable leaching of the catalyst into the reaction medium during the catalytic process. In the case of physical adsorption of an IL on a support, this effect usually complicates the repeated use of the catalytic material.[22]

Noteworthy is one more factor that largely affects the performance of the catalytic materials based on both adsorbed and covalently attached ILs. This is the coverage of the porous support surface by the modifying ionic liquid. If the IL is deposited by adsorption, the layer thickness can vary between a few and tens of nanometres, depending on the total pore volume occupied by the IL. If the IL amount is <5 vol.%, it can aggregate as nanodroplets rather than form a solid film, *i.e.* a fraction of the support surface remains unoccupied. If the IL content is >10 vol.%, a solid nanofilm is usually formed.[23] Unlike the adsorption method, no segregation effect is observed using covalent immobilization of ILs on the support in Langmiur–Blodgett monolayers (Fig. 1).

Samples of palladium-containing catalysts were obtained through either covalent bonding or adsorption of an IL on the mesoporous molecular sieve SBA-15, before divalent palladium salts were introduced into the modified support and Pd^{2+} ions were reduced to the metallic state. In the former case, the reduced palladium metal nanoparticles were uniformly distributed in mesopores of the support (Fig. 1 *a*), while in the latter case, they were mainly hosted in IL droplets located near to mesopore openings (Fig. 1 *b*). It should be pointed out that the reduction with hydrogen was conducted at an elevated temperature, when surface tension of the IL was insufficient for IL to form nanodroplets instead of a solid layer on the support surface. After palladium reduction and cooling to room temperature, at which the resulting catalytic material was investigated by TEM, the IL always segregated into nanodroplets, together with metal Pd^0 nanoparticles.

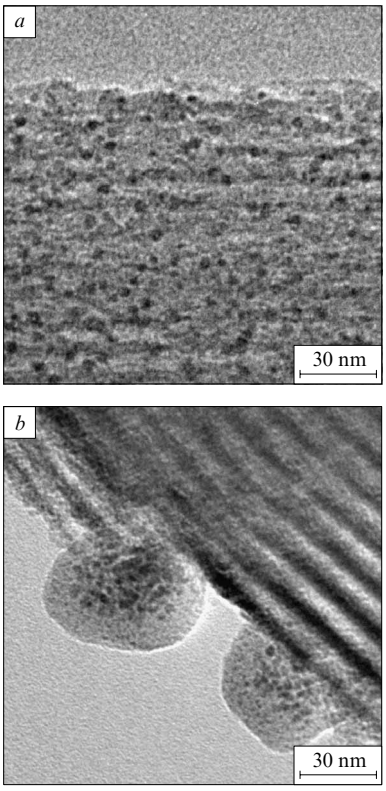


Figure 1. TEM images of palladium-containing imidazolium IL-based catalysts supported on silica by covalent grafting (*a*) and physical adsorption (*b*).[24]

Finally, essentially different preparative methods of catalytic materials with supported ionic liquids (through physical adsorption or covalent bonding) may have different impacts not only on the state of the IL modifier, but also on the particle morphology of porous supports. Impregnation of IL from a non-corrosive solvent can hardly cause any significant morphological changes of such materials. Quite a different situation takes place with covalent bonding of IL to the support, which implies participation of the functional OH groups located not only in the pores of the support, but also on its surface. The issue of how sensitive the morphology of a porous support is to the reaction medium during chemical immobilization of IL was studied[24] using scanning electron microscopy (SEM) in relation to a silica support, mesoporous molecular sieve SBA-15.

Comparison of the SEM images of initial and modified support samples revealed no changes in original silica particles after physisorption of an imidazolium ionic liquid. On the contrary, as follows from the micrographs shown in Fig. 2, chemical modification of the support with the ionic liquid induces dramatic changes of the support particles. The chemical grafting of IL to the silicate surface through the reaction between functional ethoxy groups of the imidazolium cation and silanol groups of the outer surface of the particles results not only in fragmentation of the extended fibrous particles of the support, but also in significant change in the particle shape to cylindrical or irregular. The greater the IL concentration in the silicate, the more pronounced the size and shape alterations.

It has been shown[25,26] that in the formation of covalently attached monolayers of palladium-containing IL on silica surfaces, the conditions of support preparation, particularly the temperature of SBA-15 hydrothermal treatment, play a significant role. Mild heat treatment conditions (120 °C instead of 150 °C) lead to increase in the surface area, pore volume and pore diameter, resulting in increased amounts of grafted IL.

In contrast to above-mentioned methods of covalent bonding and physisorption, there exists a third route to immobilize ILs on silica supports, namely, the sol–gel synthesis, which makes it possible to encapsulate the ILs within the support framework.[10,25–31] In this case, it is possible to impregnate up to 40% of the total modifier amount into the pores; therefore, the material becomes more resistant to IL leaching-out by various solvents.

For hybrid silica materials containing $C_{8-16}MIM-SiO_2$ fragments (C_{8-16} are hydrocarbon substituents having from 8 to 16 carbon atoms), it was shown that the formation kinetics and texture features of the material are greatly influenced by the length of hydrocarbon substituent.[26] In particular, among the modified SBA-15, the largest surface area is inherent in methylimidazolium substituted with $C_{12}H_{25}$, while the substituent with eight carbon atoms results in this value being twice smaller. However, this particular material has the largest pore size (D), which exceeds this parameter for $C_{10}MIM-SiO_2$ and $C_{12}MIM-SiO_2$ by a factor of 1.5–2. $C_{16}MIM-SiO_2$ has the largest pore volume.

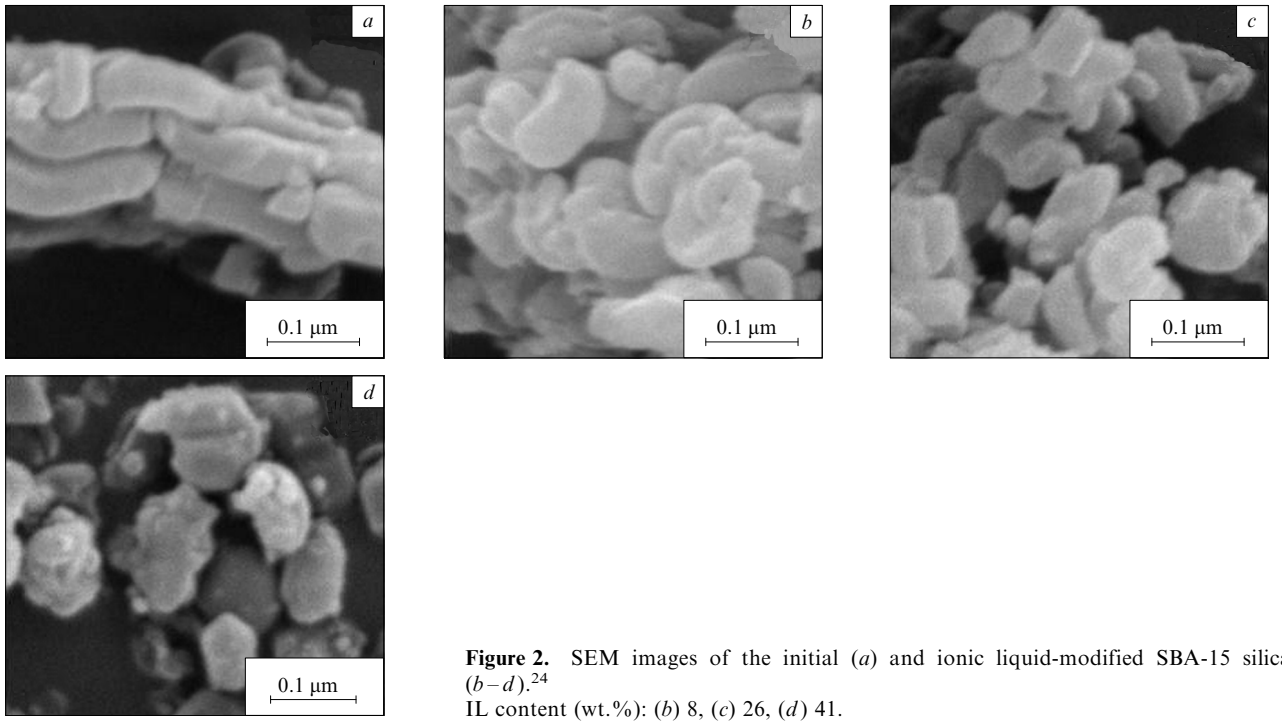


Figure 2. SEM images of the initial (*a*) and ionic liquid-modified SBA-15 silica (*b* – *d*).[24]
IL content (wt.%): (*b*) 8, (*c*) 26, (*d*) 41.

Obviously, this variability of texture features has a considerable impact on the catalytic properties of the modified silica.[26]

Of much importance for practical applications is heterogenization of palladium comlexes on the surfaces of dilelectric supports such as glass fibres, perlite or glass fibre fabrics. This treatment can serve to activate the surface for the subsequent preparation of partially or fully metal-coated materials, which have unique properties and are widely utilized in many fields.[32, 33]

In addition to mineral supports, polymer-based materials such as polyelectrolytes can also be used as substrates. In this case, the interaction between the supported IL and the surface is of solely ionic nature, which opens up prospects for application of the resulting composites as heterogenous catalysts for processes in non-polar organic media. Binding of ILs to molecules with chiral moieties (amino acids, first of all, proline, alkaloid derivatives, carbohydrates, *etc.*) makes it possible to obtain organocatalysts for highly selective asymmetric catalysis.[34] Ionic environment facilitates the separation of the catalyst from the products, and also often promotes higher reaction rates, owing to stabilization of ionic intermediates of many organocatalytic reactions.[35]

III. Liquid-phase reactions over catalysts with supported ionic liquids

III.1. Redox reactions

III.1.a. Oxidation of sulfur-containing compounds

One of the promising trends is to apply the supported ILs for oxidative desulfurization of petroleum feedstock.[36 – 44] Efficient removal of toxic sulfur compounds is due to the ability of heterogenous systems to adsorb both the reactants (sulfides) and reaction products (sulfoxides and sulfones). Such materials, acting as catalysts and adsorbents simultaneously, can remove up to 99% of sulfur-containing compounds from fuels in one step under mild reaction conditions. Various efficient catalysts, generally imidazolium ILs bearing anionic complexes of transition metal, have been proposed for peroxidation of model sulfur compounds.[40 – 49]

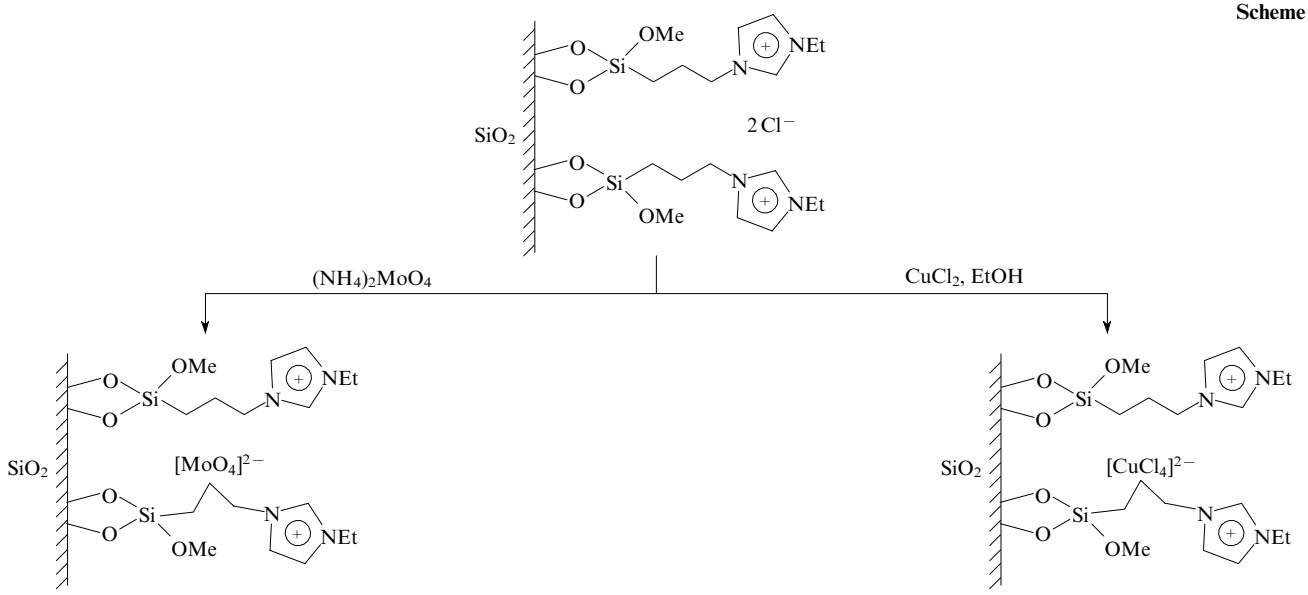
Catalytic compositions incorporating ILs and molybdenum or tungsten heteropolyacid anions deposited on mineral supports have gained widespread use. The active catalytic sites of these systems are molybdenum or tungsten peroxo complexes, which are formed from oxides or metallates, as well as phospho(silico)molybdates and tungstates upon the reaction with hydrogen peroxide.[36, 37, 40, 44]

A series of works addressed the synthesis and comparative analysis of catalytic properties of copper-, molybdenum- and tungsten-containing 3-ethyl-1-propyl imidazolium derivatives supported on mineral (silica-based) materials; the catalysts were tested in the oxidation of sulfides with hydrogen peroxide.[50, 51] The methods for preparation of catalysts based on 3-ethyl-1-propylimidazolium molybdates and tungstates were developed and samples containing ethylpropylimidazolium chlorocuprate complexes with various oxidation states of Cu were obtained on supports with different textural characteristics (Scheme 6).[51]

When a wide-pore support (Silochrome, $D = 40 – 45$ nm) is used, the Cl^- ion in the grafted 3-ethyl-1-propylimidazolium chloride can be replaced in one step by a molybdenum-containing anion. In the case of a Perlkat mesoporous silica gel ($D = 5 – 10$ nm), the degree of chloride replacement was less than 50% under similar conditions.

The efficacy of the proposed methods for covalent attachment of the catalyst complex to the support surface was confirmed by chromatography – surface-assisted laser desorption/ionization (SALDI) mass spec-

Scheme 6



trometry.[52] As follows from analysis of mass spectra, positive ions correspond to the ethylpropylimidazole (EtPrIM) fragment. Apart from the mentioned major ion and lighter products of imidazolium decomposition, SALDI mass spectrum exhibited peaks that corresponded to EtPrIMSi and EtPrIMSiOMe species. The formation of these species indicates a strong binding of imidazolium to the surface, mainly, *via* two linker groups, as shown in Scheme 6.

The methods mentioned above can serve for the preparation of meta- and polytungstates and molybdates as well as heteropolyacid derivatives.[51] The formation of various species is suggested by chromatography–mass spectrometry data. The SALDI mass spectra of the samples containing 3-ethyl-1-propyl imidazolium phosphomolybdate and metamolybdate are shown in Fig. 3. The ion peaks present in the mass spectrum obtained by the authors (Fig. 3 *a*) correspond to the fragments of phosphomolybdic heteropolyacid. The major signal in Fig. 3 *b* corresponds to the $[MoO_4]^-$ ion, the contents of $[Mo_2O_6]^-$ and $[Mo_3O_9]^-$ cluster ions are markedly lower.[51]

Methyl phenyl sulfide and thiophene, typical sulfur compounds occuring in petroleum fractions, were used as model substrates. The most active and stable catalysts for methyl phenyl sulfide oxidation are those based on 3-ethyl-1-propylimidazolium polymolybdates. In the case of 100 : 1 substrate to molybdenum molar ratio, full conversion of the sulfide can be achieved after 3 h, the catalytic activity being retained for at least three successive cycles. Compositions containing alkylammonium and imidazolium phosphomolybdic acid derivatives, as well as tungstates and chlorocuprates were tested as catalysts for thiophene oxidation. Comparison of the results with published data demonstrated that the catalytic activity of the samples containing both phosphomolybdic acid and IL is many times higher than that for heterogenized heteropolyacids without IL.[53] Copper-

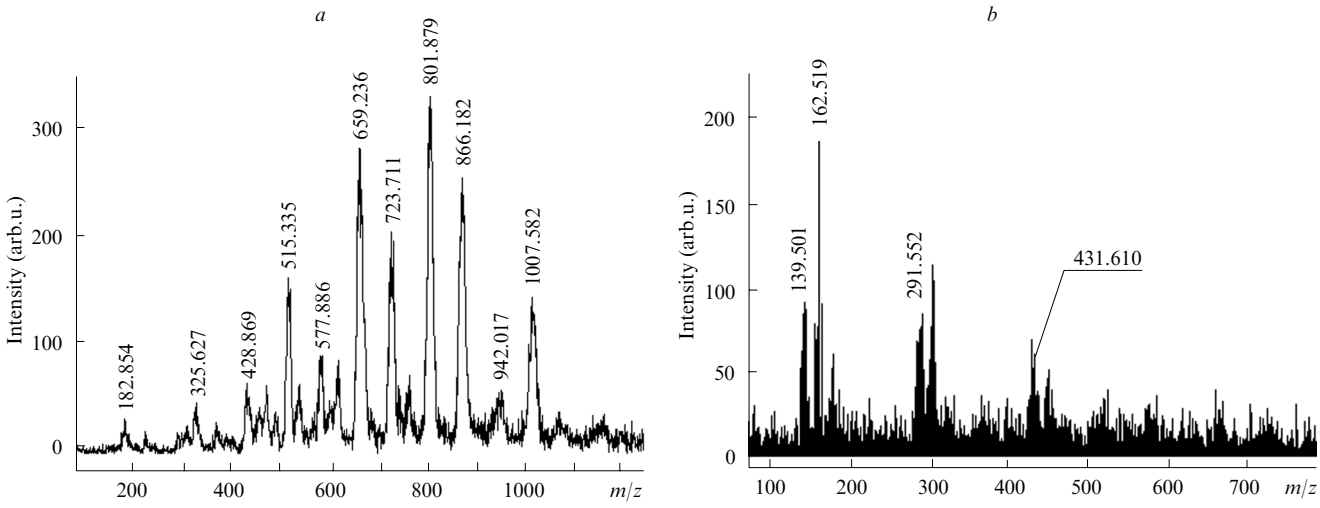


Figure 3. SALDI mass spectra (negative ion detection mode) of samples containing imidazolium phosphomolybdate (*a*) and molybdate (*b*).[51]

Table 1. Activities and stabilities of the catalysts based on anionic chlorocuprate complexes in the oxidation of n-dodecylthiol by atmospheric oxygen in isooctane, 20 °C, [Cu] = 2 mol.%.[56]

Organic IL cation	KSK		Silochrome		Perlkat	
	TOF /h^{-1}	TON	TOF /h^{-1}	TON	TOF /h^{-1}	TON
3-Ethyl-1-propylimidazolium	26	130	36	200	41	220
N-Propylpyridinium	12	76	39	80	54	330
Propyltriethylammonium	0.3	0.5	12	15	6	12

and tungsten-containing catalysts proved even more active towards thiophene oxidation.

The activity of copper compounds is determined by the valence state of the metal and the nature of the support. Catalysts prepared from CuCl and imidazolium on Silochrome (the degree of thiophene oxidation reached 70% within 3 h) are most active, while the activity of catalysts on a Perlkat mesoporous silica gel turned out to be three times lower. The reason for so different catalyst performances as prepared using two different supports is attributable to different oxidation states of copper on Silochrome: according to X-ray photoelectron spectroscopy, the percentages of Cu^+ ions were 90% and 15% of the total copper content in the case of Silochrome and Perlkat, respectively. This means that ILs on the wide-pore Silochrome stabilize Cu^+ ions more efficiently; therefore, the resulting compositions are efficient in sulfur removal. High efficacy of monovalent copper compounds is attributed to adsorption of thiophene on Cu^+ ions prior to oxidation. Such interaction with π-complex formation is used in the extraction of thiophene derivatives into ionic liquids.[39, 54]

The stabilization effect of different valence states of copper in anionic halide complexes on the surfaces of IL-modified mineral supports has been reported previously.[55 – 58] In particular, this was employed[56 – 58] for preparation of catalysts for thiol oxidation in hydrocarbons. These catalysts contained grafted *N*-propylpyridinium, 3-ethyl-1-propylimidazolium and propyltriethylammonium cations and chloride anions of copper(II) salt. Silica gels with various specific surface areas (s) and pore sizes were utilized as supports: Perlkat (s = 450 m^2 g^{-1}, D = 5 – 10 nm), KSK (s = 300 m^2 g^{-1}, D = 12 – 15 nm) and Silochrome (s = 120 m^2 g^{-1}, D = 40 – 45 nm). Catalysts based on pyridinium and imidazolium on the support having the largest surface area and smallest pore size (Perlkat) proved to be most efficient. The catalytic activity and stability data such as turnover frequencies (TOF) and turnover numbers (TON) of the catalytic reactions are summarized in Table 1.

The experimental results could be explained considering both the structural pecularities of copper complexes on the surface and the mechanism of thiol oxidation over Cu catalysts. This is a multielectron process involving the formation of bi- and polynuclear copper thiolate complexes.[59, 60] The first step is the reaction between the Cu^{2+} complex and thiol, resulting in the formation of Cu^+ complex and RS$^\bullet$ free radicals, which recombine to produce the corresponding disulfide. Next, the Cu^+ complex reacts with oxygen yielding H_2O_2, then the latter decomposes with regeneration of the initial Cu^{2+} complex; this is the rate-limiting step. The Cu^+ oxidation proceeds faster on the Perlkat support, since the formation of polynuclear complexes is favoured in this case, owing to reduced pore diameter of the support (Fig. 4). This conclusion is in good agreement with spectral data. The copper chloride complex with propyltriethylammonium on KSK or Silochrome, exhibiting low activity, has an absorption maximum at 430 nm, the spectral region corresponding to isolated complexes.[57, 61, 62] The samples containing *N*-propylpyridinium and 3-ethyl-1-propylimidazolium on Perlkat have absorption maxima in the longer wavelength region (λ = 460 – 470 nm), corresponding to absorption of aggregated species; according to chromatography – mass spectrometry data (Fig. 4), these species are represented by bi- and trinuclear ionic clusters, $[Cu_2Cl_3]^{2-}$ and $[Cu_3Cl_4]^-$.

The negative ions manifested in the SALDI mass spectrum of 3-ethyl-1-propylimidazolium cholorocuprates on the Perlkat silica gel correspond to $[CuCl_2]^-$, $[CuCl_3]^-$, $[Cu_2Cl_3]^-$, $[Cu_3Cl_4]^-$ and $[Cu_3Cl_5]^-$ species, polynuclear ionic clusters obviously predominating.

In summary, using thiols as an example, it was demonstrated that the natures of a support and organic IL cation have a significant impact on the catalytic performance of the resulting compositions. Targeted design of such systems makes it possible to obtain active catalysts for alkali-free oxidation of thiols by atmospheric oxygen. It is worth mentioning that only few examples of using ILs for this type of reactions can be encountered in the literature (mostly in Merox type processes).[63] At the same time, the papers concerning

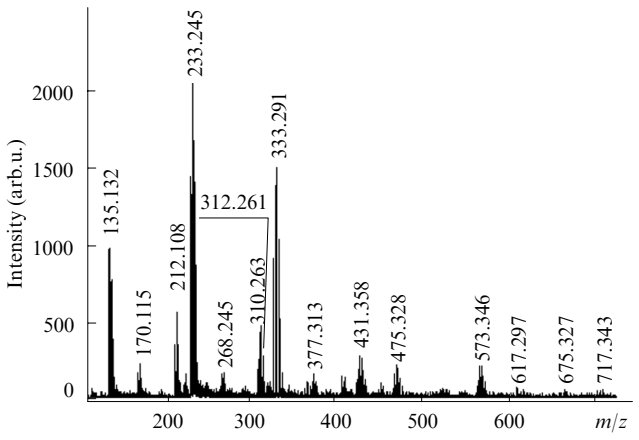


Figure 4. SALDI mass-spectrum (negative ion detection mode) of 3-ethyl-1-propylimidazolium chlorocuprates on Perlkat silica gel.

the development of heterogenous catalysts for alkali-free oxidation published over the last few years indicate a growing interest in such processes due to increasing environmental standards in the petrochemical industry.[64–67] In this connection, IL-based catalysts immobilized on solid supports seen to be promising for application in desulfurization of hydrocarbon feedstocks by oxidation of sulfides and thiophene, as well as thiols and hydrogen sulfide.

III.1.b. Phenol oxidation

Phenol and its derivatives are among the most hazardous chemical toxicants occuring in industrial effluents. Their neutralization (primarily, of phenol itself) is one of the most acute problems. It is being solved by environment-friendly catalysis using atmospheric oxygen or comparatively cheap water-soluble peroxides such as hydrogen peroxide.[68] In terms of oxidative efficacy, transition metals, primarily iron, can compete with noble metals (main components of oxidative catalytic systems); however, the former failed to find widespread application due to irreversible loss during homogeneous catalysis in aqueous media.[69,70]

Targeted design of IL-based supported catalytic materials, accomplished by matching the pairs of ions, enables one to obtain a highly hydrophobic IL with catalytically active transition metal ions in its anion component. This opens up real prospects for utilization of the considered compositions in aqueous solutions without irreversible leaching of active metal ions. This type of comparative investigations of the catalytic activity and stability of various Fe^{3+}-containing materials as catalysts of phenol oxidation in aqueous solutions with hydrogen peroxide have been reported.[71–74] Iron(III) chloride was deposited onto a non-modified surface of MCM-41 molecular sieve ($FeCl_3$/MCM sample), the same support chemically modified with grafted NH_2-containing molecules ($FeCl_3$/NH_2/MCM sample) and also the support modified with supported imidazolium IL ($FeCl_3$/IL/MCM sample).

In the first case, ferric chloride was physically adsorbed on the surface of the support; in the second sample, $FeCl_3$ molecules were held by the coordination bond between Fe^{3+} ion and NH_2 group of the modifier. In the third sample, $FeCl_3$ introduced into the grafted IL layer formed the tetrachloride complex, $[FeCl_4]^-$, with its Cl^- anion, which was electrostatically bound to the cation of the ionic liquid. The formation of this anionic complex upon ferric chloride introduction into the supported IL layer was confirmed by XANES (X-Ray Absorption Near Edge Structure) method for the discussed sample and for $FeCl_3 \cdot 6H_2O$. Indeed, the -3 eV shift of the absorption edge of the former relative to that of the latter is determined by the appearance of an additional electron-withdrawing Cl^- ligand in the Fe^{3+} coordination sphere.[72]

The different nature of the forces that retain Fe-containing particles on the porous support surface can give a good explanation to the substantial difference in phenol oxidation kinetics in the presence of these samples and their stability as the catalysts of the process. For the $FeCl_3$/MCM and $FeCl_3$/NH_2/MCM samples, a significant induction period is observed, associated with iron transition from the porous support into the aqueous solution where Fe^{3+} cations exhibit high catalytic activity in homogeneuos phenol oxidation with hydrogen peroxide. As a result, the $FeCl_3$/MCM and $FeCl_3$/NH_2/MCM samples recovered from the reaction mixture and extracted with acetone lose up to 80%–90% of the initial catalytic activity in the second cycle, and have no oxidative activity in the third cycle because of complete leaching of the active component. On the contrary, in the case of $FeCl_3$/IL/MCM sample, no induction period was observed, and in the second and third cycles after the extractive recovery, the catalytic activity decreased by 5% and 12% only. The maintenance of the total iron content in the catalytic material was confirmed by X-ray fluorescence analysis of the recovered $FeCl_3$/IL/MCM catalyst.[73]

In summary, heterogenization of iron(III) chloride in the ionic form through physical adsorption, as well as coordination bonding to NH_2 groups cannot produce a stable heterogeneous catalyst, because iron is extensively leached from the support, thus exhibiting catalytic activity only in the homogeneous phase. In contrast, iron(III) chloride embedded into the grafted layer of imidazolium IL does perform heterogeneous catalysis in aqueous medium, owing to tetrachloride $[FeCl_4]^-$ complex formed, which plays a role of anion of the grafted IL bound to the support surface *via* ionic bonds, so that this efficiently prevents iron ions from transfer to the solution.[74]

III.1.c. Synthesis of metal nanoparticles on the surface

Materials featuring thin-film metal coatings with high adhesion to the insulator are widely used in microelectronics, optics and magnetic technology.[75–78] To prepare these materials, it is necessary to initiate the metallization process: deposition of metal nanoparticles (*e.g.*, palladium nanoparticles) on the insulator surface. Palladium activation affords metallic particles of 3–20 nm size, which are evenly distributed over the surface in a single layer at a concentration of 400 μm^{-2}; this corresponds to the optimal conditions for subsequent treatment stages.[77,78] A method for direct activation of metallization of insulating materials using ILs with $PdCl_4^{2-}$ counter-ion has been developed.[32,33] Heterogenization of ammonium and pyridinium tetrachloropalladates on the glass fibre surface was

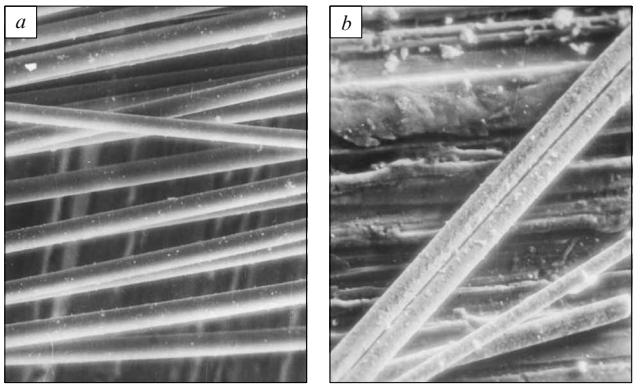


Figure 5. Micrographs of nickelated glass fibres (500-fold magnified).[32]
Activation by $[n\text{-}C_{10}H_{21}NC_5H_5]_2PdCl_4$ (*a*) and $PdCl_2$ in concentrated hydrochloric acid (*b*).

carried out by chemical grafting *via* organic cation. The resulting complex provided sufficiently strong binding of $PdCl_4^{2-}$ ions to the sample surface, so that up to 95% of palladium was retained on the surface after 2-h extraction with water. When direct surface activation was performed only by a Na_2PdCl_4 solution or by an acidified $PdCl_2$ solution, no strong binding of the catalyst was observed, almost 50% of the adsorbed $PdCl_4^{2-}$ ions being leached into water upon extractive treatment.

The results of chemical nickel-plating of glass fibres 7 – 10 μm in diameter demonstrated that the samples obtained by direct preliminary activation with $PdCl_4^{2-}$-containing ionic liquids had a smooth fine-grained defectless coating, unlike the fibres obtained by direct activation with an acidified $PdCl_2$ solution (Fig. 5).

III.2. Reactions of haloalkanes

The pioneering study dealing with the catalytic application of supported metal-containing ILs [19] was devoted to the reactions of choloroalkanes. The authors produced catalyst for CCl_4 hydrodechlorination using silica-supported tetra(n-butyl)ammoium chloride in combination with palladium, cobalt and copper chlorides. Later, polymers such as polystyrene were proposed as supports.[79, 80] Polystyrene-supported imidazolium ILs were studied in detail as catalysts for nucleophilic substitution of a halogen atom in haloalkanes yielding various products, including fluorinated ones.[79 – 82] Apart from high catalytic activity of such systems, their promising application particularly in fluorination reactions was highlighted, owing to the resistance of polystyrene to fluoride ions and acids, in contrast to inorganic supports.

Another attractive field of application of supported ILs is associated with the synthesis of halogen derivatives using polyhalomethanes as the halogen source. The early works on the Kharasch halogenation of alkanes over supported ILs were reported by Sasaki *et al.*[83, 84] The addition of CCl_4 to the double bond was illustrated by the reaction with styrene; anionic chloride complexes of copper, nickel, iron and platinum attached to Aerosil-supported alkyl imidazolium cations were used as catalysts (Scheme 7).

Scheme 7

$$CCl_4 + PhCH{=}CH_2 \longrightarrow PhCHClCH_2CCl_3$$

Another trend in utilization of polyhaloalkanes as halogen source is aliphatic halogenation, a reaction with a similar mechanism (Scheme 8).[22, 55, 57, 85, 86]

Scheme 8

$$CHal_4 + RH \longrightarrow CHHal_3 + RHal$$

R = Alk; Hal = Cl, Br

A distinctive feature of the considered process compared with the Kharasch reaction is higher temperature (170 – 200 °C instead of 100 °C for CCl_4), which poses certain limitations to the composition of the IL used. Namely, when alkyl ammonium chlorocuprates having long carbon chains (C_{5+}) are used without a support, resinification of the IL, due to chlorination of alkyl substituents, and catalyst deactivation are observed.[87] The use of imidazolium and 3-ethyl-1-propylammonium derivatives on supports with different porosity has been

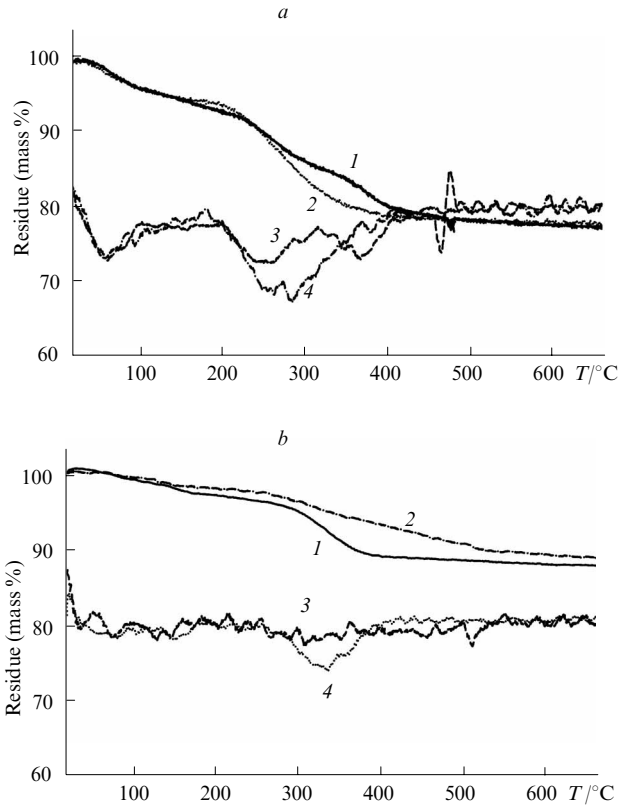


Figure 6. Integral (*1*, *2*) and differential (*3*, *4*) TGA curves of tetraalkylammonium clorocuprate-based samples on silica gel prepared by adsorption (*a*) and covalent linkage (*b*).[22]
(*1*, *3*) in air; (*2*, *4*) under argon.

reported.[22, 57] With ILs on mineral suports, the stability of catalytic compositions was considerably enhanced. A covalent attachment proved to be more efficient than simple adsorption. The results of thermogravimetric analysis (TGA) of ILs containing chlorocuprate anions and alkyl cations with similar compositions — $Et_3(ClCH_2CH_2)N^+$ and $Et_3Pr^nN^+$— are shown in Fig. 6. In the former case, the sample was obtained by adsorption on the KSK silica gel, while in the latter case, covalent bonding of the cation to the surface was employed.

A comparison showed that for the sample prepared by adsorption, the mass loss in air starts below 200 °C, while for the covalently linked IL, it starts in the 250 – 350 °C range. The catalytic activity and stability of the samples in the reaction also depend on the method of metal comlex embedding. The largest yield was achieved using the supported IL based on tetraalkylammonium (Table 2). Under the investigated conditions, the main products of reaction bewtween decane and CCl_4 were isomeric monocholorodecanes.

An analogous reaction of decane bromination with CBr_4 has been studied.[85] Tetraalkyl ammonium and 3-ethyl-1-propylimidazolium bromocuprates supported on KSK silica gel were used as catalysts. It was found that many process features observed for chlorination are also true for bromination. This conclusion is supported by the close contents of reaction products in both cases and high activity of the catalysts as proposed for chlorina-

Table 2. Yields of chlorodecanes over chlorocuprate IL-based catalysts prepared by different methods after successive cycles (175 °C, 5 h, [Cu] = 1.5 mol.%).[22]

Organic cation of IL	Sample preparation on KSK silica gel	Yield of chlorodecanes (%) in successive cycles				
		1	2	3	4	5
(2-Chloroethyl)triethylammonium	Physisorption	52	38	34	31	23
Propyltriethylammonium	Covalent linkage	59	55	58	57	–
3-Ethyl-1-propylimidazolium	The same	52	51	53	52	–

tion in the bromination reaction. The similarity extended also to the fact that the highest activity was demonstrated by propyltriethylammonium-based catalyst, which, however, showed poor stability, associated with partial bromination of the organic cation during the catalytic reaction. An improved stability was observed for 3-ethyl-1-propylimidazolium-based catalyst. At a relatively low temperature (130 °C), it demonstrated a catalytic activity comparable with the previously reported value for chlorine-containing catalysts of radical chain reaction of alkanes with CCl_4 at 180–190 °C. For three hours at decane : CBr_4 molar ratio of 10 : 1, the reaction proceeded selectively, yielding monosubstituted bromoalkanes as the main products. Introduction of donor additives (EtOH or Pr^nOH) substantially improved the product yield (from 35% to 60%). The yields of bromination products depended on the reaction temperature in a complex way featuring an extremum: the onset of the reaction could already be detected at 130–140 °C, the maximum yield of products was produced at 150–155 °C, and further increase in temperature to 180 °C led to decreased yields of monobromodecanes. According to the authors, lowering of the product yield is attributable to the catalyst degradation (in particular, due to bromination of ligands in the catalytic complex), as well as dehydrobromination of bromodecanes promoted by catalyst components. This was confirmed by formation of hydrogen bromide along with catalyst resinification following the high-temperature reaction. In order to understand the differences in the catalytic activity of alkylammoium- and imidazolium-based ILs, the compositions of the catalysts were studied by chromatograhy–SALDI mass spectrometry.

As follows from the qualitative comparison of the spectra, in the propyltriethylammonium bromocuprate-based sample, mainly mononuclear $CuBr^+$ ions and NR_4Br^+ ions are detected, the rest of the signals originating from amine fragmentation. In the spectrum of 3-ethyl-1-propylimidazolium-based sample, polynuclear $[Cu_2Br]^+$, $[Cu_2Br_2]^+$ and $[Cu_3Br_2]^+$ ions predominate. Organic component is responsible for a peak at 137 in the spectrum, which corresponds to 3-ethyl-1-propylimidazolium ion. In summary, as in the case of chlorine-containing ILs, the nature of the organic cation determines the nuclearity of halocuprates formed, which, in its turn, influences the catalytic activity of supported IL samples.

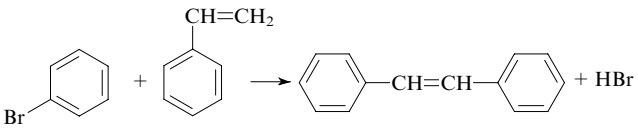
III.3. Reactions of fine organic synthesis

III.3.a. Heck reaction

The Heck cross-coupling reaction is one of the most efficient synthetic approaches to the formation of C–C bonds between organic molecules, generally catalyzed by palladium-containing compounds or materials.[88,89] Utilization of ILs immobilized on porous supports as the medium for this reaction makes it possible not only to substantially lower the consumption of the expensive palladium complex that is used in the homogenuous version, but also to remarkably increase the environmental performance of the process.[89] Temirbulatova *et al.*[90] prepared the Heck reaction catalyst by chemical grafting of 1-methyl-3-(3-trimethoxypropyl)imidazolium chloride to the surface of MCM-41 mesoporous molecular sieve, followed by introduction of $PdCl_2$ into the grafted IL layer and reduction of Pd^{2+} to the metallic state. Here, the TGA results in the temperature range of 200–1000 °C for the molecular sieve support (1.8 mmol of hydroxyl groups per g of the support) and elemental N,C-analysis of ionic liquid-modified sample (1.94 mmol of IL per g of the support) were used to determine the degree of involvement of the hydroxyl coating of the MCM-41 sieve to be ~ 50%. This estimate is based on analysis of ^{29}Si NMR spectrum recorded for the grafted IL sample. Three partially overlaping signals within the −70 to −50 ppm range indicate that IL binding to the surface is not a single-point one: the reaction of alkoxyl groups of the grafted IL with the OH groups of MCM-41 yields one to three Si–O–Si bonds between the cation and the support. By deconvolution of the experimental spectrum and determination of integral intensities of signals, the average number of chemical bonds between the IL and surface was estimated to be about two.

The palladium content in the resulting catalyst was found to be 8.5 wt.%, which corresponds to stoichiometric formation of $PdCl_4^-$ anions, which neutralize the charge of every pair of grafted IL cations. Catalytic cross-coupling of phenyl bromide with styrene to afford stilbene (Scheme 9) was carried out in dimethylformamide at 140 °C under argon flow for 24 h; tri-n-butylamine was used to bind HBr.

Scheme 9



Under these conditions, the yield of stilbene was 81 mol.%, which corresponds to TOF = 110 h^{-1}. It is of interest to compare this value with the respective parameter of homogeneously catalyzed Heck reaction. In the medium of imidazolium IL at the same temperature in the presence of palladium acetate and triethylamine as a proton-binding base, the reactant conversion reached 94%, but the TOF value was only 2.6 h^{-1}, *i.e.*,

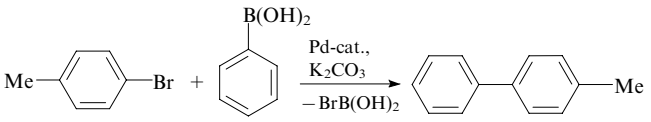
it was 40 times lower.[91] Such a large difference in the catalytic activity for heterogeneous and homogeneous catalysis is most likely due to mass transfer conditions in the ultrathin layer on the support surface, as compared with the bulk IL.

III.3.b. Suzuki reaction

Numerous heterogeneous IL-based catalytic compositions have been proposed for the preparatively important Suzuki reaction, which is the reaction between an aryl halide and an arylboronic acid to give biaryls.[92 – 96] These catalysts generally contain Ni^{2+} or Pd^{2+} imidazolium derivatives as precursors; carbene species generated under the action of promoters serve as active sites.[92]

A comparative analysis of palladium-containing compositions prepared by two methods as catalysts for the Suzuki – Miyaura reaction (Scheme 10) has been reported.[25, 26]

Scheme 10



The first method was based on ion exchange of IL anion for tetrachloropalladate by adsorption from aqueous solutions of K_2PdCl_4 on $C_3MIM-SBA\text{-}15$ and $C_{8-16}MIM-SiO_2$. The second method included adsorption of palladium acetate on $C_3MIM-SBA\text{-}15$ and $C_{8-16}MIM-SiO_2$ from dimethyl sulfoxide. The natures of the support and the metal salt were found to considerably affect the catalytic properties of the samples. The use of supports with covalently attached ionic liquids produced highly active catalysts by ion exchange. Active catalytic systems were also produced by complexation of palladium acetate with a supported IL (Table 3).

As can be seen, utilization of the material based on SBA-15 modified with $[C_3MIM-Si(OEt)_3]Cl$ provides higher activity for $K_2PdCl_4/C_3MIM-SBA\text{-}15$ samples, compared with $Pd(OAc)_2/C_3MIM-SBA\text{-}15$. At the same time, the conversion of 4-bromotoluene is higher for the $Pd(OAc)_2/C_{12}MIM-SiO_2$ samples obtained by the sol – gel technique than for $K_2PdCl_4/C_{12}MIM-SiO_2$. This difference was explained by different accessiblity of IL molecules for palladium carbene complex formation. In general, the proposed synthesis of the modified silicate containing IL in its pores proved efficient for the preparation of Pd-containing catalyst for Suzuki reaction.

III.3.c. Hydroamination of unsaturated compounds

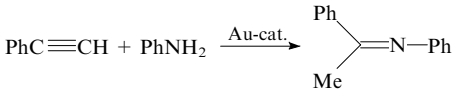
The hydroamination of organic compounds is one of useful techniques of fine organic synthesis to obtain nitrogen-containing compounds that have gained widespread use in industry. In the heterogeneous catalytic approach, nanosized particles of noble metals generally serve as the active component.[97, 98] Here, the key problem is to stabilize the thermodynamically unstable ultradispersed metal phase in the reaction system. Meanwhile, ILs are almost perfect media for hydroamination, since a highly polar IL inhibits the aggregation of metal nanoparticles, which has an undesirable impact on the catalyst activity and selectivity and, consequently, prevents its repeated use.

Table 3. Characteristics of the Suzuki – Miyaura reaction (see Scheme 10) (1% Pd, 1.5 h).[26]

Pd precursor	IL support	T/°C	Conversion of 4-MeC_6H_4Br (%)
$Pd(OAc)_2$	$C_3MIM-SBA\text{-}15$	120	18
		150	20
K_2PdCl_4	$C_3MIM-SBA\text{-}15$	150	36
$Pd(OAc)_2$	$C_{12}MIM-SiO_2$	80	37
K_2PdCl_4	$C_{12}MIM-SiO_2$	80	19

These problems have been covered in detail by Isaeva *et al.*,[99] who prepared gold-containing catalysts by IL immobilization on the mesoporous molecular sieve MCM-41 ($s = 1030\ m^2\ g^{-1}$) or chitosan-modified KSK silica gel ($s = 240\ m^2\ g^{-1}$) followed by $HAuCl_4$ introduction into the adsorbed ionic liquid layer and reduction of gold to the metallic state and used them for phenylacetylene hydroamination. Common ILs, such as butylmethylimidazolium hexafluorophosphate ($[BMIM]PF_6$) or tetrafluoroborate ($[BMIM]BF_4$), and a novel IL, 1-[(2*R*, 3*S*, 4*R*, 5*R*)-2,3,4,4,6-pentahydroxyhexyl]-1-ethylpyrrolidonium bromide ([Q]Br), synthesized by the authors from glucose, were adsorbed on the mentioned supports. Liquid-phase hydroamination of phenylacetylene with aniline affording *N*-(1-methylbenzylidene)aniline (imine) was chosen as a model reaction (Scheme 11).

Scheme 11



Trace amounts of water in the reaction mixture drastically decreased the process selectivity to the desired product because of imine hydrolysis to acetophenone.

As can be seen from the data presented in Table 4, for gold contents of 1wt.% (or higher), the TOF values, which characterize the productivity of a single gold atom on a metal nanoparticle surface, are of the same order of magnitude and depend neither on the support type, nor on the nature of the modifying IL. When the content of active metal is lowered by an order of magnitude, the TOF value decreases by the same factor, indicating a sensitivity of hydroamination reaction to the particle size of the catalytic system, *i.e.* the size effect is observed. Interestingly, when silica gel with grafted chitosan layer coated with glucosamine IL was used as the support, the catalytic material featuring 5 wt.% Au provided both high reactant conversion in hydroamination and superior selectivity (see Table 4). This result is apparently related to a specific type of bonding between the structurally similar elements of the chitosan layer on the support surface Ch/SiO_2 and the adsorbed [Q]Br ionic liquid, as has been noted by Isaeva *et al.*[99]

In addition, a comparison of data on the active metal dispersity, obtained from scanning electron microscopy, and selectivities of the studied catalysts containing variable amounts of the metal suggests that the key

Table 4. Characteristics of phenylacetylene hydroamination with aniline in the presence of gold-containing catalysts (T = 110 °C, toluene).[99]

Support	IL	[Au] (wt.%)	TOF /h^{-1}	Time /h	Conversion (%)	Yield (%)	
						imine	acetophenone
MCM-41	[BMIM]PF_6	0.1	5.8×10^2	24	6.0	5.6	0.4
MCM-41	[Q]Br	1	6.1×10^3	30	88.2	44.8	43.4
MCM-41	[BMIM]BF_4	1	8.5×10^3	20	97.0	65.9	31.1
Ch/SiO_2	[Q]Br	5	7.6×10^3	19	96.0	89.5	6.5

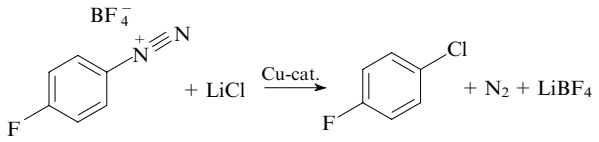
Note. The following abbreviations are used: Ch/SiO_2 is chitosan-modified KSK silica gel.

factor behind the efficiency of catalytic hydroamination is the optimized size of gold nanoparticles, being 12–15 nm.

III.3.d. Sandmeyer reaction

The Sandmeyer reaction is one of the few examples of radical processes widely applied in preparative chemistry.[100–104] The classic case of this reaction is the interaction of a halide ion with aryl diazonium salts promoted by copper compounds. Utilization of this version for synthetic purposes has a number of limitations associated with the necessity to use equimolar amounts of copper, elevated temperatures and, in some cases, concentrated acids. Recently, a novel catalytic composition has been proposed that includes CuCl and $CuCl_2$ mixture with nitrogen-containing organic compounds (*N*,*N*,*N*′,*N*′-tetramethylethylenediamine, phenanthroline or bipyridine).[105] These systems proved fairly efficient in bromination and catalyzed the introduction of the so-called pseudohalides, cyano- and thiocyano-groups,[106] into the aromatic ring affording compounds that are of interest as intermediates for pharmacology. Later, highly active and stable catalytic systems were proposed for selective Sandmeyer halogenation proceeding under mild conditions in the presence of small catalytic quantities of copper (Scheme 12).[107]

Scheme 12



These catalysts are silica-supported ILs composed of copper(I) and copper(II) chloride complex anions and tetraalkylammonium and imidazolium cations. It was determined by X-ray photoelectron spectroscopy that the majority of catalysts synthesized using CuCl actually contained mixtures of mono- and divalent copper derivatives, the ratio of two copper forms depending on the nature of both the support and the organic cation. For the most active catalyst, the ratio of di- to monovalent copper was 2:1. Further studies revealed that this ratio is most favourable for catalysis. The catalyst demonstrated not only remarkable activity, but also good stability: in the reaction with LiCl, the product yield remained almost constant (at least after three successive cycles).

III.4. Isomerization of hydrocarbons

Isomerizartion of C_5–C_6 hydrocarbons over the ionic liquid catalyst $[Et_3NH]^+[AlCl_4]^-$ supported on a zeolite-containing wide-pore silica gel or γ-alumina has been reported.[108] It was demonstrated that for the isomerization of cyclohexane, pentane or pentane–n-hexane mixture, the most efficient catalytic system is that based on the aluminosilicate support, while for the isomerization of n-hexane, the highest catalytic activity is observed for the γ-Al_2O_3-based catalyst. At temperatures of 60–100 °C and a pressure of 0.101 MPa, the conversion of alkanes over such catalysts is <65%, and for the transformation of n-hexane, the selectivity to isohexanes reaches 70%. It was pointed out[108] that for cyclohexane isomerization, unlike that of n-alkanes and their mixtures, no noticeable formation of by-products is observed, the selectivity to methylcyclopentane being at least 95% for all investigated catalytic systems.

It was also found that when IL bearing $[AlCl_4]^-$ anions is used as both the catalyst and the solvent, the equilibrium product composition is achieved within several hours,[109] whereas in the case of supported IL, this does not take place. This result was attributed to possible diffusion retardation of the chemical process in the pores of the heterogeneous catalyst.

On the grounds of analysis of transformation products of the studied hydrocarbons over supported $[Et_3NH]^+[AlCl_4]^-$ ionic liquid as the catalyst, three possible mechanisms of hydrocarbon molecule isomerization are considered.[109] First, in view of high isomerizing activity of aliminium chloride, which is present in the IL anion, one cannot rule out the possibility of the catalytic reaction proceeding *via* the classic carbenium ion mechanism that involves hydrogen transfer from the substrate to the aprotic site on the aluminium atom. Nonetheless, since the IL cation contains the H^+ ion, a carbonium ion mechanism can be realized by the attack of a superacidic hydrogen ion on the C–H bond of the hydrocarbon molecule to give non-classical five-coordinate carbocation intermediate and subsequent elimination of molecular hydrogen to produce a carbenium ion. Finally, a longer chain of elementary reaction steps is also possible, involving intermediate products such as haloalkanes, which can efficiently initiate the proper isomerization step.[110]

IV. Gas-phase alkene hydrogenation reactions over catalysts with supported ionic liquids

Like hydroformylation,[111–113] hydrogenation of unsaturated compounds[114] on heterogeneous catalysts based

on supported ILs is one of the first gas-phase processes carried out in a continuous mode using a flow-type reactor.[115] A doubtless advantage of this type of process over a batch process (apart from the quite obvious enhancement of productivity and elimination of the stage of catalyst separation from the reaction mixture), particularly for the supported IL systems, is the possibility to completely prevent IL loss, due to a negligible partial vapour pressure of ionic liquids even at elevated temperatures.[116]

Meanwhile, the use of various synthetic routes to prepare supported IL-based catalytic materials, namely, adsorption and covalent immobilization, can have specific influence on their key parameters — catalytic activity and selectivity. The catalytic properties of two series of palladium-containing catalysts prepared by both covalent bonding of IL to the surface of the SBA-15 molecular-sieve silicate support and physisorption were compared in the gas-phase hex-1-ene hydrogenation. First of all, it was found that apart from the main hydrogenation product, hexane, certain amounts of isomerization products, isohexenes, are formed over such catalysts. Besides, while selectivity to hexane for the more active samples of the first series was 92% – 95%, for the catalysts of the second series with an equal content of metallic palladium, it did not exceed 30% – 50%. The considered result is, most likely, associated with the 'island' structure of the adsopbed IL, as mentioned previously.

Indeed, the small portions of molecular sieve surface free from the adsorbed IL, which contain some OH groups, can well be responsible for occurrence of the competing isomerization of the initial alkene. At the same time, due to the chemical reaction of alkoxy groups with OH groups of the surface, the number of acid sites remaining on the surface is insufficient for isomerization products to be formed in significant quantities.

Rather unexpected results have been obtained [117] in a study of the catalytic hydrogenation in a broad temperature range with catalysts of both series with different metallic palladium and imidazolium IL contents. Experimental results are shown in Fig. 7. The temperature was raised stepwise for two samples with masses selected in such a way that they contained equal amounts of palladium. The two series of samples (covalently bound or adsorbed IL) differed not only in their catalytic activities, but first of all in the pattern of temperature dependence of the activity. In particular, in the former case, the temperature dependences of hex-1-ene conversion were common saturation curves, in the latter case, the dependences featured a well-defined inflection point, the position of which shifted to higher temperatures with increasing mass fraction of the metal. Here, it is important to note that in both curves, no temperature hysteresis was observed, *i.e.* the conversions for the forward and reverse direction of temperature variation coincided within the accuracy of measurements. Taking this into consideration, it can be speculated that such an unusual shape of conversion temperature curves in the vicinity of inflection points is rather associated with macroscopic factors and not with specific changes in the intrinsic activity of catalytic sites of metallic palladium. Indeed, the TEM micrographs shown in Fig. 1 demonstrate a considerably different distributions of metal nanoparticles for the samples prepared by covalent immobilization and adsorption of IL layers on the support.

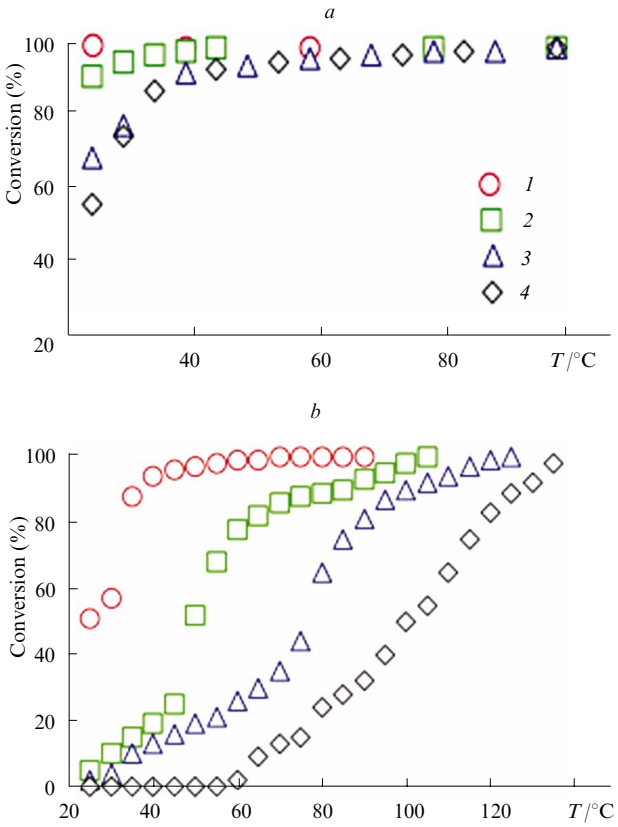


Figure 7. Temperature dependences of hex-1-ene conversion over samples with covalently grafted (*a*) or physically adsorbed (*b*) imidazolium IL.[24]
(*a*) Pd content (wt.%): (*1*) 0.5, (*2*) 1.1, (*3*) 2.2, (*4*) 5.5;
IL content (wt.%): (*1*) 11, (*2*) 11, (*3*) 26, (*4*) 41.
(*b*) Pd content (wt.%): (*1*) 2.2, (*2*) 0.5, (*3*) 5.0, (*4*) 6.5;
IL content, (wt.%): (*1*) 17, (*2*) 11, (*3*) 33, (*4*) 50.

Most likely, at temperatures close to room temperature, wetting of a silica surface by a polar ionic liquid is insufficient for an IL solid film to form. However, at elevated temperature, the surface tension of the IL decreasse noticeably and, as a result, its spreading over the inner surface of the support occurs, producing a continuous ultrathin layer within the pores. It can be assumed that the spreading effect of the IL dramatically changes the conditions of mass transfer to the catalyst nanoparticles, which is hindered within the IL droplets, and is in contrast greatly favoured in reaction medium nanofilms. It is the effect of spontaneous spreading of the IL at a certain critical temperature that promotes the activation of the process after the inflection point in the conversion temperature curves (Fig. 7).

V. Conclusion

Analysis of the information concerning the use of supported ionic liquids in heterogeneous catalysis demonstrates the great theoretical and applied potential offered by this field of catalytic chemistry. Undoubtedly,

among the most important and promising trends of theoretical and experimental research should be gaining more in-depth and extensive knowledge of the physicochemical aspects of IL interaction with surfaces of both inert and catalytically active supports. This would enable targeted and scientifically substantiated fabrication of essentially new catalytic materials based on supported ILs for relevant chemical processes. Additionally, of special interest is the possiblity to use these materials in highly selective asymmetric catalysis of pharmacochemical processes. For this purpose, it is crucial to determine the toxicity of supported IL-based catalytic materials. It should be noted that numerous publications have covered the toxicity of individual ILs as solvents,[118 – 122] paying particular attention to imidazolium and pyridinium derivatives. It is assumed that hydrophobic ILs can be accumulated in soils and hydrophilic ILs can enter water bodies. Meanwhile, it is obvious that strong covalent bonding of IL cations or anions to the surface of mineral supports almost completely eliminates its leaching and getting into the ecosystem. There is no doubt that a more hazardous situation arises for adsorbed ILs; however, by appropriate selection of solvents, leaching can be easily minimized. In any case, for the development of pharmacochemical processes, this issue requires a thorough investigation.

It is important to note that utilization of supported ILs as components of catalytic materials makes it possible to substantially improve their key parameters (in particular, the efficiency of noble metal use) by forming a uniform set of active sites on the surface and thereby lowering the impact of mass transfer effects. The enhancement of another parameter, *e.g.*, catalytic site stability, can be achieved by lowering the surface mobility of metal sites within the IL layer and their agglomeration. Equally important results should be expected from utilization of the concept of supported ILs in such a rapidly developing field of catalytic chemistry as nanocatalysis, where the morphological uniformity of the particles rather than the nano-size of the active phase is the key factor for a chemical process on the surface. Finally, a relatively poorly studied synergistic effect, arising from cooperative interaction of the immobilied IL, the support and catalytically active sites, opens up new opportunities for the targeted design of reaction systems having enhanced catalytic activity and selectivity.

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