1 Introduction

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1.1 A Century of Supported Liquids

Natural and synthesized solid materials are generally characterized by a nonuniform and undefined surface. The surface contains face atoms, corner atoms, edge atoms, ad-atoms, and defect sites, which together determine the surface properties of the material [1]. In many applications, these different sites display different properties, for example, with respect to their chemical activity. Often, only certain sites are advantageous with regard to the specific application of the material as in the case of, heterogeneous catalysts and adsorbents. Future development of more efficient catalysts and adsorbents in industrial processes will depend on the design of solid surfaces that allow all surface atoms to be most effective. At the same time, new technologies are required, which will lead to the design of completely new surface properties within solids [2].

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One possible way to achieve a uniform surface is by coating the solid support material with a thin liquid film, thereby defining the material properties by the liquid's properties. Such supported liquid phase (SLP) materials date back a 100 years ago till 1914, when BASF introduced a silica-supported V₂O₅-alkali/pyrosulfate SO₂ oxidation catalyst for sulfuric acid production (see Figure 1.1) [3]. This catalyst, which is still the standard system for sulfuric acid production today, can be described as a supported molten salt, as it consists of a mixture of vanadium alkali sulfate/hydrogensulfate/pyrosulfate complexes that are present under reaction conditions (400–600 °C) [4].

The concept of supported liquid catalysis is not restricted to liquid salts. In order to apply the concept of uniform surface properties and efficient catalyst immobilization, several authors investigated the SLP concept during the 1970s and 1980s [5–11]. However, later studies revealed that the evaporation of the loaded liquid cannot be avoided completely during operation. This is especially a problem when using water as the liquid phase [12–17]. In these supported aqueous phase (SAP) systems, the thin film of water evaporated quickly under reaction conditions, making the concept applicable only for slurry-phase reactions with hydrophobic reaction mixtures.

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Figure 1.1 Historical development of supported liquids in catalysis.

1.2 Supported Ionic Liquids

The supported ionic liquid phase (SILP) technology is a fundamental, new approach to obtain liquid containing solid materials that do not evaporate, made through surface modification of a porous solid by dispersing a thin film of ionic liquid (IL) onto it, as depicted in Figure 1.2 [18, 19]. ILs are salts consisting completely of organic cations and inorganic or organic anions (for further details see Chapter 2) [20]. Their better charge distribution and larger ion size compared to classical inorganic salts result in melting points below 100 °C. Owing to the extremely low vapor pressure of ILs, the surface of SILP materials is coated permanently, even



Figure 1.2 Schematic representation of an ionic liquid film supported on a porous material.



Figure 1.3 Categorization of materials based on supported ionic liquid films according to the phase behavior of the supported ionic liquid: (a) covalently attached monolayer and (b) multilayers of ionic liquid.

under elevated reaction conditions. By variation of anions and cations, solubility, reactivity, and coordination properties of the ILs can be changed according to the special requirements of the given application.

With respect to material and surface design, ILs are characterized by a highly pre-organized, homogeneous liquid structure with distinctive physicochemical characteristics and these – often unique – characteristics are exclusively governed by the combination of ions in the material [20]. Hence, by an appropriate choice of the ions (and eventually additives) contained in the IL material, it is possible to transfer specific properties of the fluid to the surface of a solid material by confining the fluid to the surface. Thus, the SILP concept allows custom-making of solid materials, resulting in uniform and well-defined surface topologies with definite properties and a controlled chemical reactivity. Importantly, the SILP concept thereby constitutes an attractive methodology to circumvent the lack of uniformity of solids in traditional material science. In addition, the approach provides a great potential to create materials with new surface properties, as the transfer of specific IL properties to solid surfaces may result in "designer surfaces" with properties that are impossible to realize with any present synthetic approach.

In principle, all ILs can be contacted with a solid surface and therefore, looking at the tremendous numbers of publications in the field of "ILs," exceeding 6700 in the year 2012, it is anticipated that the concept of "supported ILs" will benefit from this scientific input.¹⁾

A common method to immobilize ILs on surfaces is the covalent anchoring of a monolayer of IL onto a support – usually pretreated – as shown in Figure 1.3a. Here, the IL becomes part of the support material, thereby losing certain bulk phase properties such as solvation strength, conductivity, and viscosity. The IL can contain a certain functionality (e.g., acidity, hydrophobicity) that will render the support surface.

1) Literature search using SciFinder including the term "ionic liquid", March 2013.

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If multilayers of IL are immobilized onto a support, the bulk properties of the IL can be retained. In such SILP systems, depicted schematically in Figure 1.3b, functionalities can be incorporated by dissolving, for example, metal salts, acids, transition metal complexes, and nanoparticles.

Various efficient and recyclable systems based on the latter category have been developed, including supported ionic liquid catalysis (SILC), supported ionic liquid catalysts (SILCA), solid catalyst with ionic liquid (SCIL), solid catalysts with ionic liquid layer (SCILL), supported ionic liquid nanoparticles (SILPS), supported ionic liquid phase (SILP), supported ionic liquid phase catalyst (SILPC), ionic liquid crystalline-SILP (ILC-SILP), structured SILP (SSILP), supported ionic liquid like phase (SILLP), polymer-supported ionic liquid (PSIL), and supported ionic liquid membrane (SILM). All of these concepts try to use the intrinsic properties of IL bulk phases and can be regarded as derivatives of the general SILP concept, which itself is a branch of the "SLP-tree."

The synthesis of SILP materials is usually straightforward and the thin film of IL is fixed on the surface mainly by physisorption, and in a few cases by chemisorption [21]. The IL is mixed with the support and the catalyst complex (if applied) in a low-boiling solvent. The solvent is then removed by evaporation or freeze-drying, yielding a dry, free-flowing powder as the SILP catalyst. Depending on the amount of IL and the pore structure of the support material, film thicknesses between 3 and 30 nm can be accomplished. Detailed descriptions of support materials and synthetic methodologies are given in Chapters 3 and 4 while the structure and stability of these materials are discussed in Chapters 5 and 6. Solid-state NMR studies of different amounts of IL on silica support indicated that below a critical value of 10 vol% IL loading, small islands of ILs exist on the support [22]. At values higher than 10 vol%, complete surface coverage with IL was observed, which resembled the characteristics of the bulk IL. This is an important prerequisite for the efficient immobilization of homogeneous catalyst complexes that would lose activity and, more importantly, selectivity upon interaction with the support surface or in a constrained environment. Spectroscopic studies of SILP materials are summarized in Chapters 7 and 8 while Chapter 9 introduces tools for a-priori selection of suitable ionic liquids.

Form an engineering point of view these SILP materials offer some advantages compared to classical gas-liquid or liquid-liquid systems, especially

- a high surface area supplied by the support structure
- · a thin film of liquid that circumvents mass transport problems
- · adjustable solvent properties, for example, solubility
- thermal stability of most ILs up to 200 °C
- · application of fixed-bed or fluidized-bed reactor technology
- · efficient catalyst immobilization in defined environment.

1.3 Applications in Catalysis

In SILP catalysis, work is focused mainly on the immobilization of homogeneous transition metal complexes within the thin IL film. Homogeneous catalysts, in contrast to their heterogeneous counterparts, have a uniform molecular structure and can easily be modified by the use of dedicated ligands in terms of reactivity, selectivity, and stability [23]. The main drawback of homogeneous catalysis is the elaborate recycling of the dissolved catalyst from the reaction mixture, usually accomplished by distillation or extraction. This issue, which currently limits more applications of homogeneous catalysts in continuous processes, can be circumvented by the SILP technology.

The use of SILP systems in catalysis has been reviewed recently, including both liquid and gas-phase applications [21, 24]. With respect to the application of these solid materials in liquid phase slurry reactions, the leaching of IL from the support is the most crucial issue. The smallest cross-solubility of the IL in the liquid substrate or product phase will cause rapid removal of the thin film accompanied by leaching of the catalyst complex, resulting in lower catalyst activity.

This problem can be circumvented in a very elegant manner if the reaction is performed in SILP gas-phase contact. Since the IL does not have any technically relevant vapor pressure, it is not removed via gas-phase leaching, and catalyst stabilities have been found to be very high [25]. Moreover, the gas-phase has no solution power for the catalyst, which means that catalyst immobilization in SILP gas-phase systems does not require any dedicated ligand modification.

As this approach builds on the volatility of the reaction products it is clearly limited to feedstock and products with considerable vapor pressure. Note that every molecule that can be analyzed by gas chromatography is in principal accessible for SILP gas-phase reactions. The removal of high-boiling reactants from the SILP catalyst requires, however, a high amount of gas stripping, which is economically less attractive at least for the production of bulk chemicals. A suitable alternative for performing continuous reactions with high-boiling substrates is the combination of SILP catalysis with a supercritical fluid as the mobile extraction phase, in particular scCO₂ [26, 27]. A summary of catalytic gas and liquid phase applications is given in Chapters 10 to 18.

1.4 Applications in Separation

For gas purification, chloro-tin- and chloro-zinc-containing ILs have been immobilized on alumina supports to reversibly absorb sulfur compounds from gas streams [28]. These ILs have been tested initially for liquid–liquid biphasic extraction of sulfur from diesel or gasoline. Owing to the intrinsic high viscosity of all ILs, mass transport within these liquids is usually slow, making large-scale applications not feasible as large extractor and regenerator volumes would be required [29].

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By applying a thin film of the IL onto a silica or alumina support, mass transport could be enhanced by orders of magnitude because of the large interfacial exchange area on the one hand and the small diffusion time in the thin film of IL on the other. The sulfur content of the gas-condensate feed could be reduced below 10 ppm and the then-loaded SILP catalyst regenerated in vacuum. This loading–unloading procedure could be repeated several times without significant loss of performance, resulting in overall time-on-stream of 600 h [28]. Combinations of ILs can extend this flexibility spectrum even further, making SILP absorbers a promising alternative for gas-mask filters, off-gas purification (e.g. NO, SO₂), and CO₂ capture technology [30–33]. In refinery technology, the first commercial SILP process for mercury removal from hydrocarbon feed has been reported recently [34], while the important separation of ene/ane mixtures, for example, propene/propane, might be facilitated by the use of SILP materials or SILP-based membranes [35, 36]. Applications and future trends are highlighted in Chapter 22.

1.5 Coating of Heterogeneous Catalysts

In a strong analogy to the SILP technology, a concept called solid catalysts with ionic liquid layers has been discussed in the literature [37]. In this case, a solid heterogeneous catalyst is coated with a thin film of IL. In contrast to SILP catalysts, the support material itself is catalytically active and no homogeneous catalyst or dissolved nanoparticle is involved. It has been experimentally demonstrated that such systems may exhibit better selectivity and even higher activities than their uncoated analogs [38]. However, the origins of such selectivity and activity effects are yet unclear. The IL may influence the catalytic performance in a twofold manner. On the one hand, it can directly interact with the active centers comparable to the behavior of a ligand. These so-called cocatalytic effects have been extensively reported for catalytically active metal nanoparticles. Such interactions may even lead to decomposition of the IL under reaction conditions, with the co-adsorbed decomposition products further modifying the catalytic properties. On the other hand, the IL can modify the effective concentrations of the substrates and intermediates at the active sites, so that the solubility of liquids or gaseous reactants in the IL differs in an appropriate manner from that in the liquid organic phase, causing a "physical solvent effect." In addition, the IL can compete with the substrates for active sites on the catalyst surface, thereby blocking sites that lead to unwanted by-product formation [39]. The SCILL technology has been successfully applied in various hydrogenation reactions, resulting in better selectivity and enhanced activities. Examples of SCILL catalysis involving metal nanoparticles can be found in Chapter 14.

1.6 Monolayers of IL on Surfaces

The amount of IL can be reduced further compared to SILP and SCILL systems, in the extreme case, to only a monolayer or islands of IL coating the support [40]. The role of IL in these systems is to transfer a certain functionality of the IL to the support surface.

Such thin films of IL can obviously have no significant influence on substrate solubility. The IL is usually anchored onto the support via chemisorption, involving a surface reaction between the IL's cation and the surface. Other procedures have been reported in the literature and are highlighted in Chapter 4.

1.7 Conclusion

The field of ILs on surfaces is highly multidisciplinary, attracting experts from material sciences, synthetic chemistry, physical chemistry, chemical engineering as well as pharmaceutical sciences, electrochemistry, and bioengineering.

In summary, surface coating of solid materials with IL thin films constitutes a versatile and broadly applicable technology. However, the main markets for supported IL materials are expected in the fields of catalysis and separation as depicted in Figure 1.4.

Considering these benefits, it is estimated that SILP materials will contribute a substantial part of the catalyst and adsorbent markets within the next 10 years. A



Figure 1.4 Fields of application for ionic liquids on surfaces.

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market share of 5% for SILP catalysts, having significant advantages compared to classical heterogeneous or homogeneous systems, seems realistic. A similar share can be expected for adsorbents.

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