Posters
New water soluble Pd-Imidate complexes: Catalysts for efficient modification of nucleosides in neat water.

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Abstract: The direct reactions between the precursors trans-[Pd(Imidate)2(SMe2)2] and 1,3,5-triaza-7-phosphaadamantane (PTA) yield new water-soluble palladium(II) complexes trans-[Pd(Imidate)2(PTA)2]. These new complexes have revealed as excellent catalysts for environmentally friendly, efficient cross-coupling of synthetically challenging substrates like the antiviral nucleosides in neat water as solvent. Besides this our research group has also been interested in the development of industrially feasible (column-free) scale-up processes for the synthesis of modified nucleosides having commercial relevance.

\[ \text{Precatalyst (1.0 mol\%) } \xrightarrow{\text{H}_2\text{O, Base}} \text{N-imidate} = \text{succinimidate (suc), maleimidate (mal), phthalimidate (phthal), or saccharinate (sacc)} \]

References:
Biological drain cleaning agent based on hair-degrading microbial products (proteases, reducing agents, detergents)

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Commercially available drain cleaning agents are mainly based on chemicals like sodium hydroxide, aluminum, potassium nitrate and detergents. This alkaline and caustic composition is necessary to cleave protein molecules (e.g. in hair), fat and oils but has several sanitary disadvantages for the consumer and can chemically damage drain materials. Biological drain cleaning agents have already been developed but mainly fall through the degradation of substances like hair which are highly resistant to chemical and enzymatic damage because of their high content of disulfide bridges. The first approach of this project was to find disulfide-reductases or hair-degrading proteases, respectively. Microorganisms which are able to produce hair-degrading proteases were collected in the environment and selected according to scientific literature. The proteases or protease-combinations with detergents, reducing agents and other substances, respectively, were tested for activity against keratinous substrates using scanning electron microscopy and amino acid analysis by high-performance thin-layer chromatography with prechromatographic dansylation. In the following, standardized equipment and defined obstructions were invented for testing composed cleansers based on the previously tested proteases in combination with detergents, reducing agents, lipases and further substances. The activities of the diverse proteases and cleansers differed in their effect on hair and on the standardized obstructions. It was demonstrated that some proteases are able to efficiently damage hair either in combination with other cleanser substances or without them. The addition of reducing agents had a remarkable influence on the degradation of hair. The addition of effective detergents to the cleanser enabled the hydrophobic components in the standardized obstructions to resolve in the aqueous environment and expose the contained hair to the proteases. The resolution potential was measured by determining the chemical oxygen demand (COD) in the aqueous solution where the standardized obstructions were incubated.
Chiral α-hydroxyketones are important building blocks for the synthesis of several biologically active compounds such as pharmaceuticals, agrochemicals, and pheromones. Various chemical and biocatalytical approaches for their synthesis are described in literature. Enzymatic routes show great potential with lower amounts of waste, higher stereoselectivities and overall yields compared to the chemical methods.\[1\] Among the enzymatic strategies kinetic resolution of racemic α-hydroxyketones catalyzed by lipases is advantageous as (i) there is no need for a coenzyme or a cofactor and (ii) high substrate loadings are possible thanks to comparably high stability of lipases in organic solvents. Typical disadvantages of kinetic resolutions are a maximum conversion of 50% and difficult product purification. However, both can be eliminated by establishing a dynamic kinetic resolution (DKR).\[2\] Herein, we report DKR of racemic benzoin and derivatives thereof by coupling a lipase from \textit{Pseudomonas stutzeri} (commercial Lipase TL) with the chemo-catalyst TUD-1\[3\]. The combination of both catalysts in a heterogeneous formulation leads to a yield and enantioselectivity of >99% and high recyclability.\[4\]

As reaction solvent 2-MeTHF\[5\] and deep eutectic solvents (DESs)\[6\] were chosen since they have been described as environmentally friendly and cost-effective alternatives to conventional solvents. For achieving high productivities the parameters e.g. (i) temperature, (ii) solvent and (iii) water activity\[7\] are crucial. Hence, we investigated the effect of aforementioned parameters on the activity of the catalysts and the stability of the enzyme (i.e. half-life time). The measurement of the enzyme stability was performed in a continuous stirred tank reactor under temperature and water activity controlled conditions. The results show a significant influence of parameters, particularly of the water activity on the activity and stability of the (bio-) catalysts.

Enzymatic glucose ester production in ionic liquid solvent

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The choice of solvent for the enzymatic synthesis of sugar esters is very difficult, because one reactant is polar (sugar), the other is nonpolar (fatty acid) and the resulting product is amphiphilic (sugar ester) [1]. In addition, most enzymes are quickly inactivated under hydrophilic organic solvents which are able to dissolve high concentration of both sugars and fatty acids [2].

ILs containing [BF₄] and [PF₆] anions can be used as an alternative reaction media for biotransformation of sugars, but the solubility of sugars in these ILs is very low. The production of glucose palmitate was investigated and according to the preliminary results in different ILs, Bmim[PF₆] ionic liquid and Novozyme 435 enzyme were used. Statistical design of the experiment to study the influence of the reaction conditions on the ester yield after 48 h was performed using the two-level full factorial design with four process variables: temperature, glucose and palmitic acid concentration and water content. The highest concentration of ester produced in the investigated variable range was 0.205 mmol g⁻¹ of ionic liquid at the following experimental conditions: 70 °C, equimolar concentration of glucose and palmitic acid of 0.5 mmol g⁻¹ and 0.5 % of water.


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Electrorefining of Na in NaFSI-TEATFSI Mixture Ionic Liquids

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Recently, sodium-sulfur secondary battery (Na-S battery) have been widely used for load leveling of electric power, emergency power supply for interruption in factory, and storage device of power generation by natural energy. Large amount of the used batteries will be discarded in near future. In inside of the battery, metallic sodium and sodium polysulfide were formed during a charge and discharge process. It is important from a viewpoint of material recycling to use metallic sodium effectively. We have proposed sodium electrorefining using an ionic liquids\(^1\). In our previous study, we used a NaTFSI (sodium-bis(trifluoromethanesulfonyl)imide)-TEATFSI (tetraethylammonium-bis(trifluoromethanesulfonyl)imide) mixture ionic liquids as an electrolyte. In this study, to improve an electrical conductivity, we used NaFSI (sodium-bis(fluorosulfonyl)imide)-TEATFSI mixture ionic liquids as electrolyte.

NaFSI (Mitsubishi materials) and TEATFSI (Iolitec) were mixed with various molar ratios. For investigation of the optimal ratio as the electrolyte, the melting point and electrical conductivity were measured. The melting points of the ionic liquids were measured by DSC (DSC823, Rigaku, scan rate: 10 Kmin\(^{-1}\)). The electrical conductivity was calculated from the resistance value at high frequencies region in AC impedance measurement. During the AC impedance measurement, temperature of the liquids was kept 160 °C. The maximum conductivity is attained to 53 mScm\(^{-1}\) at 20 mol% NaFSI-TEATFSI. From the result, we assumed that 20 mol% NaTFSI melt was a suitable concentration. Then a voltammogram was measured to determine the current density in electrorefining. From the results of the voltammogram, current density of 20 mAcm\(^{-2}\) was selected for electrorefining of Na. Finally, the electrorefining between liquid Na anode and Fe cathode was carried out in the ionic liquids electrolyte for 10 hours at 160 °C.

Reference

Effect of Additive Concentration for Al Electroplating in AlCl₃-EMIC Ionic Liquids
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To form the bright Al electroplating layer on Cu substrate, effects of additive concentration in electrolyte were investigated in an ionic liquid of 1-ethyl-3-methylimidazolium chloride and aluminum chloride (EMIC- AlCl₃) at 333 K. An ionic liquids of 80 ml prepared by mixing 67 mol %AlCl₃ with 33mol% EMIC, was used as electrolyte (Koei Chemical). The chemical of 1, 10-phenanthroline (PT: Wako Chemical) as an additive was added to the ionic liquids with concentration of 0.002 M and 0.02 M. Cu plate and Al plate were used as cathode and anode, respectively.

The electroplating of Al was carried out in the AlCl₃-EMIC ionic liquids containing PT by pulse electrolysis at 25 mA cm⁻² and 0.83 Hz with duty ratio of 0.83. In the electroplating, applied electricity was 14.4 C cm⁻². Here, the duty ratio \( \frac{t_{on}}{t_{total}} \) is defined as the ratio of the duration of on-time for the cathodic current \( t_{on} \) and the sum of the durations of the on- and off-times \( t_{total} \).

The surfaces of Al formed at pulse current electroplating in the electrolyte containing 0.002 M and 0.02 M PT were white and grey, respectively. In the grey surface formed at 0.02 M PT, outer part of electroplating surface became bright. The SEM images of electroplating surface in the additive concentration of 0.002 M and 0.02 M PT are shown in Fig. 1. Figure 1 (a) shows rough surface of Al electroplating formed at 0.002 M PT and Fig. 1 (b) shows smooth surface formed at 0.02 M PT. From the results, it was found that the grain size of Al electrodeposits become uniformly smaller by adding of 0.02 M PT.

Fig. 1 SEM images of electroplating surface formed at 25 mA cm⁻² in AlCl₃-EMIC ionic liquids containing (a) 0.002 M PT and (b) 0.02 M PT at 333 K.
This work focusses on making novel amphiphilic ionic liquids and determining their physical properties. Figure 1 shows the three components to the design of the anion; the fluorinated alkyl chain is linked to the alkyl sulfonate chain via an ether link.

In general, fluoroalkanes are colourless compounds with high densities; weak intermolecular forces tend to give low viscosities when compared to alkanes of a similar boiling point. Fluorocarbons are mostly noted for their hydrophobic properties and are not usually miscible with most organic solvents. Conversely, the other side of the molecule is a sulfonated alkane. This should be water soluble and have a very flexible backbone; whereas the fluoroalkane should be innately inflexible in its behaviour; the ether link acts as a bridge between the two regions.

Figure 2 shows the four regions which are available for modification; there are no restrictions on the cation. The fluorinated chain was modified in two ways; the length of the chain can be increased where \( n \) (Figure 1) can be anything from two to ten; the “\( R \)” group can either be another fluorine or hydrogen.

It is expected that changing the \( R \) group will have a much smaller effect on the physical properties than additional fluorines in the chain, increasing the fluorinated chain length should tip the balance of physical properties in favour of the hydrophobic rather than hydrophilic.
From Salty Predators and Creators to Surface Modifiers: Ionic Liquids as Reducing Agents Towards Nanoparticle Catalysts

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In recent years, ionic liquids (ILs) have proven their versatility in synthetic and catalytic applications, provoking ever-growing interest in both academic and industrial research. One particularly intriguing field is the synthesis of nanoscale metal catalysts of controlled size and shape, namely metal(0) nanoparticles (M-NPs).[1-2] Herein we present a conceptual approach for the synthesis of metal and metal oxide NP catalysts immobilized in IL media. The ILs act in these particular cases not only as solvent, stabilizing and protecting agent for the formed NPs, but selected ions are suitable to act as very mild reducing agents.[3-7] We found tailor-made systems, where the right combination of cations and/or anions of the ILs are capable to reduce certain metal complexes or metal salts as NP precursors. In particular cases even common ILs derived from imidazolium (BMIM.NTf$_2$ or BMIM.OAc$_2$) are capable to act as mild reducing agents. The advantage of this approach is that external reducing agents as additives such as hydrogen, hydrazine or borohydrides are obsolete. Moreover, the reducing process is slow which implies that the local metal(0) concentration is kept low, avoiding a fast particle growth leading to undesired large particles, but allowing the synthesis of small particles. The metal and metal oxide nanoparticles are readily obtained embedded in the ionic liquid without further excessive purification. Therefore, the NP catalysts can be directly used for hydrogenation of arenes, C-C as well as hetero multiple-bonds, C-C bond cleavage and C-N coupling reactions.[3, 5-6, 8,9] The incorporation of functional groups into the IL-moiety allows the modification of the metal surface with ligands, thus controlling the (chemo)selectivity for example in hydrogenation reactions.[4, 6, 9, 10]

Catalytic Hydrogen Production using Water and Formaldehyde as Hydrogen Source

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For findings towards new energy storage systems, an intensively studied fuel molecule is $\text{H}_2$ owing its energy content, and the possibility to store it in form of hydridic and protic hydrogen.[1,2] Here we show that water in presence of (para)formaldehyde (FA) is suitable for molecular hydrogen-storage as these molecules can be easily and selectively dehydrogenated forming pure $\text{H}_2$ and $\text{CO}_2$.\[3\] The reaction runs on air using a water-stable molecular catalyst under base-free conditions. Both molecules, $\text{H}_2\text{O}$ and $\text{H}_2\text{CO}$, act equally as source of $\text{H}_2$. Isotope-labelling experiments ($^2\text{H}$, $^{13}\text{C}$ and $^{18}\text{O}$) confirm that the $\text{H}_2$ released originates from both, $\text{H}_2\text{O}$ ($\text{H}_2^{18}\text{O}$ or $\text{D}_2\text{O}$) and $\text{H}_2\text{CO}$ ($^2\text{H}$ and $^{13}\text{C}$-labelled). Isotope-label complexes and gaseous products could be assigned by means of NMR, ESI-MS and continuous gas-phase MS. A theoretical efficiency of 8.4 wt% of $\text{H}_2$ considering 1 eq. $\text{H}_2\text{O}$ and $\text{H}_2\text{CO}$ is possible, this is higher than for formic acid (4.4 wt%), even when technical aq. $\text{H}_2\text{CO}$ is used, the solution has a min. efficiency of 5.0 wt%. This catalytic decomposition of $\text{H}_2\text{CO}$ can be envisioned as novel approach for simultaneous $\text{H}_2$ production and decontamination treatment of wastewater with formaldehyde impurities – a waste to value approach.

\[ \text{HO(CH}_2\text{O})_n\text{H}_{\text{H}_2\text{O}}^{\text{H}^+} \]

6.7 wt% $\text{H}_2$ per unit

8.7 wt% $\text{H}_2$

8.4 wt% $\text{H}_2$

4.4 wt% $\text{H}_2$

References


Mechanistic insight into the catalytic dehydrogenation of alcohols and the effect of water

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Established methods for the oxidation of alcohols into its corresponding carboxyl acids usually demand strong and toxic oxidants along with many additives, or the use of stoichiometric oxygen supplying reactants or even the presence of pure pressurized oxygen.[1] Alternatively to these reactions, it is desirable to use a clean, environmentally friendly reaction pathway, without the necessity of aggressive and toxic oxidants and by avoiding chemical waste products. Recently, it has been shown that alcohols are directly converted into carboxylic acid salts using water as oxygen source.[2] In our current studies, we focus on the experimental mechanistic aspects for this transformation. It was possible to characterize and isolate in situ formed ruthenium complexes during the alcohol dehydrogenation in absence and presence of water (Figure 1). The ruthenium precursor [Ru] and the formed intermediates were characterized by NMR-, IR- and LIFDI-MS techniques (LIFDI: liquid injection field desorption ionization).[3-4] Besides the liquid phase analysis, we also performed online MS analysis of the gaseous phase during the dehydrogenation and decarbonylation reactions.

Figure 1. Snapshot of the initial formation of the catalytic active specie the [Ru(MePNP)H2(CO)].

References
We have recently shown that polyhedral oligomeric silsesquioxanes (POSS) with various side groups can be solubilized in environmentally benign and nontoxic supercritical carbon dioxide (scCO₂) at 308-323 K below 300 bar. POSS are hybrid materials with side groups attached to each silicon atom on the cage-like structure. They are most commonly used as nanofillers in polymers to improve properties such as flame retardancy, oxidation resistance, mechanical strength, thermal resistance, and bioactivity. POSS bonded with methyl, isobutyl, iso-octyl, methacryl, and trifluoropropyl groups are among the materials studied for their solubility in scCO₂. Except the one with methyl side groups, all the POSS exhibited homogenous solutions with scCO₂, showing that the type of side groups determine the solubility of the components in the supercritical fluid. The liquid-vapor and solid-vapor phase equilibrium curves of POSS-CO₂ systems were formed with the dew and cloud point measurements respectively.

Being soluble in environmentally benign scCO₂, POSS-CO₂ systems can be used in the design of greener material processing applications. We are currently using POSS in the formation of porous thin biofilms for biomedical applications, where scCO₂ is applied to foam PLLA thin films with about 200 micron thickness. The process parameters including temperature, pressure, depressurization rate, and POSS-additive concentration affect the microstructure of the polymer. Initial results also show that CO₂-philic POSS can contribute to generation of more uniform and interconnected pore structures in porous PLLA thin films obtained with scCO₂ at moderate temperatures and pressures.
Immobilized metal complexes with ionic liquids as catalysts for halogenation of alkanes with polyhalogenmethanes

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Design and synthesis of novel heterogeneous catalytic systems based on immobilized on the surface of the mineral carrier the transition metal complexes with ionic liquids has conducted. They showed high efficiency in the processes of radical halogenation of alkanes with polyhalogenmethanes.

Fair activity in the radical-chain interaction of CCl₄ with alkanes of the mononuclear copper complexes containing catalysts has been established [1]. The efficiency of the analogous catalytic systems has been shown in the bromination of hydrocarbons in the case of the reaction of tetrabromomethane with decane at relatively mild condition – 130-140°C. Bromodecanes are produced with high yield in the both cases of applying as catalyst the copper (I) bromide complex or the copper (II) chloride complex with grafted on the silica gel either imidazolium or tetraalkylammonium halogenide with the similar gegenion. The addition of donor additive (alcohol, preferable n-PrOH) to the catalytic reaction leads to substantial positive yield effect. At that the formation of the products is described by the extremal dependences on the temperature and the concentration of the alcohol. The study of bromine-containing catalyst by MALDI method showed that on the surface of the carrier are each a mononuclear catalytic form and polynuclear copper clusters. Both catalytic forms display similar high activity in the bromination reaction.

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References
Hydroaminomethylations of fatty esters in thermomorphic solvent systems to different bifunctional molecules

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Fats and oils are easily available renewable resources. Functionalized fats are used for production of materials e.g. surfactants or polymers.[1] The chemical conversion of unsaturated fatty acid esters with carbon monoxide plays an important role in functionalization of fatty compounds.[2]

Recycling of homogenous catalyst is a quest to be fulfilled for an economic and ecologic process. Functionalized fats are non-polar products which can be separated by employing organic solvents.[3] Thermomorphic solvent systems are merging reaction and extraction by using solvent mixtures with temperature depending miscibility gaps.

In this contribution the hydroaminomethylation of diethylamine, proline and 3-methylaminopropionitrile of oleic acid methyl esters were optimized and transferred to thermomorphic solvent systems in order to achieve convenient catalyst recycling (Scheme 1).

Scheme 1: Hydroaminomethylation of oleic methyl ester with various amines

This afforded very low metal leaching values in the product phases during all three reactions. Furthermore, it was possible to recycle the catalyst phases in several runs which were accomplished by ongoing catalyst activity.

Ionogels: functional materials for ion transport, sensing, and catalysis

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Ionogels are interesting because they combine the macroscopic properties of a material such as stiffness with “microscopic” properties such as catalytic activity. In many cases high surface areas or the functionalization of existing surfaces is useful or even mandatory for proper function of a material. The group has been active in the development of proton and ion-conductive iongels and in the development of iongels for sensing. While there are now many protocols available for producing ionogels as such, including ionogels with catalytic, sensing, diagnostic, tailored transport, or luminescent capability, the overwhelming fraction of ionogels is a bulk-like material with very low surface area.

A cheap and well-established way of generating moderate surface areas is electrospinning. We will present new data on the electrospinning of ionogels, on the adaptability of the process and on first attempts to transform the electrospun materials into functional materials either by incorporating a functional (that is, metal-containing) ionic liquid or by further chemical transformation of the electrospun ionogel fiber mats.

The presentation will focus on ionogels for ion transport with potential applications in the energy fields, ionogels with pH sensing capability and some new data on the fabrication of higher surface area ionogels that could enhance many properties of ionogels.
Tandem catalyst systems for the chemical fixation of CO$_2$ with epoxides to cyclic carbonates

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The use of synergistic catalysts in combination with ionic liquids leads to exceptional reactive systems for the conversion of CO$_2$ with epoxides to cyclic carbonates. Herein, we present the combination of niobium(V)chloride (NbCl$_5$) with a series of imidazolium bromides as tandem catalytic system for the chemical fixation of CO$_2$.\[1\] The Lewis-acidic NbCl$_5$ activates the epoxide and the imidazolium bromide acts as a nucleophile for the subsequent ring-opening of the pre-coordinated epoxide. The impact of varying substitution patterns at the imidazolium ring, resulting in steric and electronic changes, as well as differing solubility in the substrate, was investigated. The following optimization of the cation structure leads to a highly reactive tandem catalyst system for the production of propylene carbonate at very mild reaction conditions.\[1\] The combination of pentaerythritol with ionic liquids illustrates an alternative synergistic catalyst system.\[2\] The epoxide is activated through hydrogen-bonding to the alcohol, which facilitates the ring-opening by the halide. Therefore, the system demonstrates an organocatalytic approach comparable to NbCl$_5$. As the catalyst system is non-toxic, easily recyclable, widely applicable and shows excellent yields, it enables the fixation of CO$_2$ to a variety of cyclic carbonates in an especially sustainable manner.\[2\]


Tailor-made imidazolium bromides for the synthesis of propylene carbonate under mild reaction conditions

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The cycloaddition of carbon dioxide (CO₂) and propylene oxide (PO) to propylene carbonate (PC) by ionic compounds is highlighted in some recent reviews.[1,2] Especially, organocatalytic systems are of interest to avoid the use of metal-containing catalysts. Herein, we present a catalyst screening which demonstrates the influence of different substituents at the imidazolium ring on the reactivity. Thereby, it could be shown that on the one hand, the acidity has a great influence on the catalytic activity due to activation of the epoxide through hydrogen-bonding.[3] On the other hand, the degree of ion pairing has a high impact on the halide nucleophilicity, thus the catalytic activity. Besides ion pairing, the solubility of the catalyst in PO and PC is important to obtain good conversions. Based upon these results, a tailor-made ionic liquid was used as recyclable catalyst with excellent conversions and selectivities under mild reaction conditions.[3] Furthermore, novel functionalized imidazolium bromides for the conversion of CO₂ and PO were synthesized and used as catalyst. For an efficient activation of the epoxide through hydrogen bonding, the imidazolium moiety was functionalized with hydroxyl groups. Therefore, higher reaction rates are obtained compared to our previous study.[3] The reaction is carried out without solvent in a temperature range below 100 °C and pressurized with less than 10 bar CO₂ to make the process energetically friendly.

We are developing biodegradable, non-toxic extraction media based on inexpensive sugars and organic acids. The melts are able to dissolve metal salts and metal oxides with high efficiency and selectivity.

Typically, extraction procedures and hydrometallurgical processes are used for the recovery of metals as secondary raw materials from substance mixtures. However, the complexing agents for the extraction of metals (e.g. cyanides) are often environmentally hazardous and require high effort for disposal.\cite{1} Recently, low melting mixtures – also called “deep eutectic solvents” (DESs) – and ionic liquids (ILs) that consist of natural compounds and are non-toxic, mostly inexpensive and completely bio-degradable, were developed.\cite{2,3} DESs as well as ILs can be used as solvents with a polarity in the range of DMF or water. Moreover, DESs have the advantages of a facile preparation and usage of readily available starting materials that makes their handling as extraction media more practical. We are studying the extraction properties of DESs, to provide a rational basis for possible applications, for example the extraction sewage sludge ashes as secondary raw materials.

Metal salt solutions with different DESs.


Dimethyl Phosphate based Ionic Liquids: Synthesis, Characterization and Application

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A series of dimethylphosphate based ionic liquids (ILs), prepared by an one-pot process from trimethylphosphate and suitable nucleophiles (alkylimidazoles, tertiary alkyl amines, alkylpyrazole and trialkyl phosphines) is presented. The cation core and the variable alkyl chain length impact the physico-chemical properties of the resulting salts. The principal features of these new ILs (such as melting points/glass transitions, thermal stability, density, viscosity) as well as their polarity, determined using both solvatochromic probes and physical measurements, will be discussed considering the main structural peculiarities.

Data about the ability of these ionic liquids to dissolve important biopolymers (cellulose, lignin and so on) and their application in extraction and synthesis processes will be also reported and discussed.
New Chiral Ionic Liquids for surface polymerization processes

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Chiral ionic liquids (CILs) have received considerable attention as enantioselective catalysts and as media for asymmetric syntheses or extraction processes. The aim of this work was to design and synthesize novel chiral ionic liquids starting from natural or synthetic chiral alcohols, and to investigate their ability to form highly ordered liquid surfaces useful in selected surface processes such as the oxidative polymerization of melanine-like precursors. 1R-Nopol, (S)-(−)-β-citronellol, (1R,2S,5R)-(−)-menthol and (S)-1-(naphthalen-2-yl)ethan-1-ol were selected among the natural chiral alcohols, while synthetic enantiopure alcohols were prepared through simple procedures starting from (R)-propylene oxide. In order to minimize the interactions between the chiral moiety and the positively charged imidazolium ring, an appropriate spacer was inserted between the nitrogen atom and the stereogenic centre. When anions such as bistriflimide, tetrafluoroborate and mesylate were employed, the resulting chiral salts melt at or near room temperature (always below 100 °C) allowing their use in oxidative coupling reactions involving thermolabile substrates.

Each CIL, generally obtained in high yield, was fully characterized.

The principal physico-chemical properties of these new chiral media and their application in surface polymerization processes will be discussed in this communication.
Metal organic frameworks (MOFs) are a versatile class of coordination polymers, consisting of metal atoms or clusters connected by multifunctional organic linkers. A distinctive advantage over classical porous materials like Zeolites or activated carbon is the size uniformity and tuneability of the pores as well as the high surface area. These features make MOFs ideal media for gas separation and storage. Also, their use in catalysis is promoted by the easy introduction of active centers through linker modification or inclusion of coordinatively unsaturated metal atoms.

In the recent years, ionothermal synthesis of MOFs in ionic liquids was established. It was shown by various groups that preorganization in ILs as well as structural variations of the cation directly affect the final MOF structure [1,2].

In our work we not only utilize ILs as solvent for MOF synthesis but also as reactant. Either ion can be integrated as organic linker, which in theory allows even stronger influencing and should enable new low temperature synthesis routes for MOFs.

Proof of concept was achieved by the reaction of [EMIM][Hbdc] (hydrogen therephthalate) with an alumina precursor in DMF (see scheme 1).

![Scheme 1: Reaction conditions for the formation of the [EMIM][Hbdc] MOF.](image)

The produced Mil- 53 MOF is directly obtained in its ht- phase, while normal synthesis from H₂bdc leads to a mixture of ht- and as- phases.

We herein report the synthesis and characterization of a series of novel functionalized imidazolium and therephthalate based ionic liquids, using their hydroxides as precursors. A neat way to produce these halogen free hydroxide ILs via Donnan Dialysis will also be presented.

References:
Benign catalytic oxidation of levulinic acid to succinic acid in water over magnetically Ru\textsuperscript{III}/WCNT

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With a total market of more than 400,000,000 USD/year, succinic acid (SA) and its salts serves as building blocks for numerous chemical intermediates and end products for bulk and fine chemicals, food and pharmaceutical industries. The fermentation processes are not fully selective towards the formation of SA. It is therefore desired to provide a suitable thermo-chemical pathway for the production of SA from biomass, which can operate under highly concentrated aqueous biomass conditions, at relatively low temperatures. Based on these considerations, we focused our efforts on the preparation of Ru(III) based catalysts coordinatively bound to functionalized WCNT previously modified with magnetite (Ru/MWCNT) able to efficiently transform the LA into SA (Figure 1).

Results and discussion

In the presence of Ru/MWCNT catalysts, the oxidation of LA takes place with a total conversion and 100% selectivity in SA, with molecular oxygen under mild experimental conditions and without the need of a base in the reaction medium (Figure 2). Moreover, the catalyst can be efficiently recovered and recycled at least four times without significant lose of the catalytic performances. The proposed strategy constitutes an excellent example of a green catalytic oxidation using molecular oxygen as oxidant, water as solvent and a stable nanomagnetic recyclable catalyst.

Acknowledgements: Authors kindly acknowledge UEFISCDI for the financial support (project PN-II-PCCA-2011-3.2-1367, Nr. 31/2012).
Checking the Greenness of Glycerol-Derived Solvents: Ecotoxicity Studies of Glycerol Ethers

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Glycerol and glycerol derivatives are gaining an increasing interest as sustainable solvents. In particular, alkyl glycerol ethers present the advantages of chemical stability, low volatility, and easy modulation of physico-chemical properties through changes in the substitution pattern. However, toxicity and ecotoxicity studies on these kinds of compounds—an essential requirement to claim the greenness of these solvents—are scarce. In this communication we present a study on the acute ecotoxicity of several glycerol derivatives in order to check their potential greenness using Vibrio fischeri as bioindicator. The chemicals have been selected with the aim of analyse the effect of the length and position of the substituents.

Some results are shown in Table 1. Ecotoxicity increases as the length of the radical does. However, an extra substituent in position 2, makes the toxicity lower than the corresponding analogous. Most of the compounds tested can be classified as harmless, according to the Passino and Smith classification, with V. fischeri toxicities lower than those of commonest organic solvents and, in some cases, even lower than that of a well-established green solvent as ethyl acetate. Only in the case of compounds with longer linear radicals, chemicals can be considered toxic for the environment. Further toxicity studies of this family of potential green solvents are ongoing.

Table 1. Toxicity of several glycerol ethers to V. fischeri

<table>
<thead>
<tr>
<th>R¹</th>
<th>R²</th>
<th>R³</th>
<th>Solvent code</th>
<th>EC50 (mg/L)</th>
<th>P&amp;S Class.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Me</td>
<td>H</td>
<td>H</td>
<td>1-0-0</td>
<td>45,121 ± 424</td>
<td>H</td>
</tr>
<tr>
<td>Et</td>
<td>H</td>
<td>H</td>
<td>2-0-0</td>
<td>3,983 ± 178</td>
<td>H</td>
</tr>
<tr>
<td>^nBu</td>
<td>H</td>
<td>H</td>
<td>4-0-0</td>
<td>978 ± 68</td>
<td>P</td>
</tr>
<tr>
<td>Me</td>
<td>H</td>
<td>Me</td>
<td>1-0-1</td>
<td>13,060 ± 88</td>
<td>H</td>
</tr>
<tr>
<td>Me</td>
<td>Me</td>
<td>Me</td>
<td>1-1-1</td>
<td>25,712 ± 126</td>
<td>H</td>
</tr>
<tr>
<td>^nBu</td>
<td>H</td>
<td>^nBu</td>
<td>4-0-4</td>
<td>11 ± 1</td>
<td>M</td>
</tr>
<tr>
<td>^nBu</td>
<td>Me</td>
<td>^nBu</td>
<td>4-1-4</td>
<td>55 ± 7</td>
<td>M</td>
</tr>
</tbody>
</table>

*a: Harmless; P: Practically harmless; M: Moderately toxic

How can a carbene be active in an ionic liquid?

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In the last few years the inherent availability of N-heterocyclic carbenes (NHCs) in imidazolium-based ionic liquids (ILs) with basic anions (e.g. acetate) has been proven to be relevant in many applications, uniting the beneficial solvent properties of ILs and the versatile chemistry of NHCs in e.g. CO$_2$ absorption, metal-oxide surface functionalization, organocatalytic processes. For all these applications it is highly important to have the NHC as an active species in the IL, so that the preferred reaction can occur. However, the NHC is a strong hydrogen bond acceptor, while the imidazolium cation is a strong hydrogen bond donor, and these matching characters should precipitate in a strongly bound, inactive species.

Thus, to understand the NHC’s observed activity, and to possibly further improve the application of external or inherent NHCs in ILs, we investigated the solvation of 1-ethyl-3-methylimidazol-2-ylidene in 1-ethyl-3-methylimidazolium acetate by ab initio molecular dynamics simulations. We show that although the carbene can indeed form strong hydrogen bonds with the ring hydrogen atoms of the imidazolium ring, they are outperformed by the strong interplay of these hydrogen atoms with the basic anion. Therefore, the NHC is pushed away from these interaction sites, to establish significantly weaker hydrogen bonds with the alkyl sidechains of the imidazolium cation, leaving the carbene available for the desirable reactions; inferring that the activity of even external NHCs is influenced the basicity of the IL’s anion.

After having seen the reasons of NHC activity in this IL, in the second part of the presentation the possibility of forming carbene complexes with the UO$_2^{2+}$ cation in imidazolium acetate ILs as solvents and carbene sources will be discussed. According to the classical and ab initio molecular dynamics simulations, only four acetate anions are bound to the solute cation, preferably in a monodentate manner. Since the uranyl cation is generally coordinated by 5-6 bonds with its ligands, the acetate anions leave free space for the available carbenes to coordinate. Static DFT calculations show that the formation of the U-C bonds is energetically favourable, so the corresponding NHC complexes can be expected to form by simply dissolving the metal salt in the IL. Also, this approach can help improving the extraction steps that are applied for nuclear waste management.
Among the different applications of ionic liquids (ILs), the gas absorption and separation processes caught the interest of scientists during the last decade. For the improvement of these processes the in-depth understanding of the solvent's structure around the solute and the corresponding solute-solvent interactions are required. Recently the physisorbed CO$_2$ in different classical aprotic ionic liquids was studied. So far the characteristics of CO$_2$ absorption in protic ionic liquids (PILs) – which can be easily synthesized via neutralization of Brønsted acid and base – or in ILs with amino acid anion have remain uncovered from the microscopic point of view. Interestingly, there are many open questions concerning CO$_2$ absorption in these ionic liquids. For example, how does CO$_2$ enter the ionic liquid and yet keeps the system volume almost unchanged? Does the structure of ionic liquids change when CO$_2$ dissolves? What are the dominant types of interactions between the solute and the solvent? To answer these points, we studied the CO$_2$ absorption by ab initio molecular dynamics simulations in the PIL ethylammonium nitrate and amino acid IL 1-ethyl-3-methylimidazolium glycinate. The entire structure of both ILs remains similar with the pure liquids. Our data indicates that CO$_2$ induces an energy loss due to entering the liquids via extending the already existing small voids, which is fully compensated by a specific attractive interaction of CO$_2$ with the ions of ILs. The dominance of the non-polar groups in the solvation shell of CO$_2$ was determined in PIL, whereas the reversible chemical absorption of CO$_2$ with amine group was observed in amino acid IL.
Large pore acid-modified mesostructured SBA-15 for biodiesel synthesis from acid oil: Process optimization and reaction kinetics

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Jigisha K. Parikh, Chemical Engineering Department, Sardar Vallabhbhai National Institute of Technology, Ichchhanath, Surat – 395 007, Gujarat, India;
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Abstract
Biodiesel synthesis from acid oil (AO) containing high free fatty acids (FFA) over pore expanded sulfonic acid functionalized mesostructured SBA-15 has been studied. Reaction parameters affecting the FAME yield were optimized using Taguchi design. 99% FFA conversion was obtained under optimum conditions viz. at 100 °C with 4 wt.% catalyst amount and 1:15 oil to methanol ratio after 8 h. Kinetic study revealed that the reaction followed pseudo first order kinetic law. The fuel properties of synthesized biodiesel were found in accordance with national and international biodiesel standard limits.

Keywords
Biodiesel, acid oil, solid acid catalysts, SBA-15, Taguchi method
Comparison of Solvents for Extraction of Bio-oil from Algae

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The limitation of using microalgae as a biofuel feedstock lies in the need to develop better downstream processing technologies for dewatering, extracting and fractionating the bio-oils. Current extraction methods use flammable and/or chlorinated solvents such as n-hexane or a mixture of chloroform/methanol, which must be separated from the bio-oil using distillation. Moreover, the simultaneous extraction of undesirable polar lipids (e.g. phospholipids) and pigments interferes with the subsequent transesterification process, indicating a need for a solvent which is selective for neutral lipids. An ideal solvent for lipid extraction would be inexpensive, non-toxic, and lipid specific to minimize the co-extraction of non-lipid constituents, and be more selective towards desirable neutral (mono-, di-, and tri-acylglycerols) lipid and free fatty acid fractions.

We will compare liquid CO₂, methanol, CO₂-expanded methanol, supercritical CO₂, and CO₂-triggered switchable solvents for the extraction of bio-oil from algae. The presentation will include yield, selectivity, and considerations of practicality and environmental impact of each option.
Removal of picric acid using ionic liquid supported cloud point extraction: evaluation of thermodynamics parameters

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Cloud point extraction (CPE) was carried out to extract picric acid from aqueous solution using non-ionic surfactant Triton X-100 (TX-100) containing [TEA(BF₄)] ionic liquid (IL) as an additive. The effect of different operating parameters such as concentration of surfactant, picric acid and IL, temperature, time, pH on extraction of picric acid has been studied in order to establish optimum conditions. The extraction of picric acid increases with temperature, time, surfactant concentration and IL concentration.

In the recent years, large number of inorganic salts have been practiced as an additive to enhance the CPE efficiency of non-ionic surfactants [1,2]. However, literature review revealed that very few reports are available for the use of ILs as an additive with non-ionic surfactants in CPE for metal separation [3,4] but no report is available for the removal of picric acid. Because of unique physical and chemical properties of IL, it was thought of interest to use it as an additive in the above mentioned study.

The effects of temperature and concentration of surfactant on various thermodynamic parameters, like change in Gibbs-free energy ($\Delta G^0$), change in enthalpy ($\Delta H^0$), and change in entropy ($\Delta S^0$) was observed. Negative values of $\Delta G^0$ dictate the solubilization was spontaneous phenomena. The positive values of $\Delta H^0$ dictate the endothermic nature of the solubilization process.

References

Biodegradable polymers may be characterized by their decomposition into small non-toxic molecules under physiological conditions. Advanced applications are found in the biomedical sector, e.g. for tissue engineering, drug delivery systems or suture materials. These applications require medical grade polymers obtained via a clean synthetic route. To replace potentially toxic solvents supercritical carbon dioxide may be considered as reaction medium. Moreover, frequently used tin-organic catalysts may compromise applications in the biomedical sector. Thus, alternate catalyst systems are needed. Besides using different metal-organic catalysts enzymatic reactions are highly attractive. Utilizing enzymes not only avoids the use of toxic catalysts, in addition, reactions may be carried out at lower temperatures, which reduces or even avoids thermal decomposition of the polymer already during polymerization.

In this contribution we report on reactions performed at pressures up to 1500 bar in the presence of scCO$_2$ using *Candida antarctica* as catalyst. Polymers with well-defined molecular weights were obtained. As the mechanical strength and resorption time strongly depend upon the molecular weight of the material, excellent control of polymer architecture is crucial for specific medical applications\[^1\]. In addition, the decomposition time is strongly affected by the chemical structure of the material and the synthetic route. Therefore, different monomers, such as diglycolide and $\varepsilon$-caprolactone were used. It is shown that the polymerization is strongly affected by the material employed for immobilization of the enzyme.

Stronger high performance Nd-Fe-B- magnets by electroplating dysprosium from ionic liquids and subsequent grain boundary diffusion

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Driven by an increasing interest in hybrid electric vehicles and wind power generators Nd-Fe-B sintered magnets have found wide application due to the highest maximal energy product \((BH)_{\text{max}}\) of any known magnet. The high temperature coefficient of Nd-Fe-B sintered magnets causes a rapid decrease in coercitivity \(H_c\) within typical operating conditions of up to 200°C also resulting in a decrease of the \((BH)_{\text{max}}\). This problem can be resolved by further increase of \(H_c\). This has been achieved by alloying heavy rare earth elements (HREE) such as Dy or Tb, as the substitution of light rare earth elements (LREE) in the magnetic Nd\(_2\)Fe\(_{14}\)B-grains by HREEs increases the magnetocrystalline anisotropy and consequently the coercitivity [1].

The grain boundary diffusion process, a well known process uses HREE coatings which are allowed to diffuse into the bulk material during a heat treatment above the melting temperature of the Nd-rich phases instead of alloying with the bulk material. So far various types of diffusion sources for the HREEs have been reported ranging from HRE vapour phase [2] to HRE containing pastes [3], and metallic coatings prepared by sputtering [4]. In a novel process to enhance the coercitivity, dysprosium has been electroplated onto Cu-coated Nd-Fe-B sintered magnets as the initial step in the grain-boundary diffusion process. The electrochemistry of dysprosium bis(trifluoromethylsulfonyl)imide in the air- and water-stable 1-butyl-3-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide ionic liquid was studied by cyclic voltammetry, chronoamperometry and the electrochemical quartz crystal microbalance (EQCM). X-ray photoelectron spectroscopy and energy dispersive x-ray was used to verify electroplating of metallic Dy. After a conventional treatment at 900 and 400 °C the coercitivities increased up to 20.4% for 2.6 µm thick deposited layers.

On the application of novel solvents for lignocellulosic biomass delignification

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Current industrial processes are still dominated by the use of common organic solvents at optimised operating conditions. These solvents however, often exhibit high volatility, flammability, toxicity and limited selectivity. Novel, task-specific, ‘green’ designer solvents, such as ionic liquids (ILs), low transition temperature mixtures (LTTMs) and deep eutectic solvents (DESs) can overcome these limitations[1–4].

Designer solvents can improve the traditionally energy consuming and environmentally challenging pretreatment processes for lignocellulosic biomass [5]. ILs have proven to selectively extract lignin from biomass at mild conditions [6–8]. In this work, LTTMs and DESs are examined for the first time for the delignification of biomass at low temperatures. In contrast to most ILs, LTTMs do not require complicated synthesis routes. They can be easily prepared by mixing solid hydrogen bond donors and acceptors without the need for further purification [3], [4].

The LTTMs studied were able to selectively dissolve lignin over cellulose, implying a high delignification selectivity [9]. However, first results show that low lignin accessibility in the biomass limits the extraction performance. (Fig. 1) Currently, the extraction conditions and solvent composition are tuned to increase lignin accessibility and drive the amount of extracted lignin towards the maximum lignin solubility. In that case, LTTMs will offer a new, cheap and environmentally benign lignocellulosic biomass treatment.

References
The green synthesis of γ-valerolactone (GVL), using homogeneous and heterogeneous catalyst system

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The catalytic hydrogenation of levulinic acid (LA) to γ-valerolactone (GVL), is a key step in the conversion of biomass to platform chemicals. The LA can be converted to GVL using either homogeneous,¹ or heterogeneous² catalyst systems. Recently, several application of GVL have been explored e.g. production of alkanes and alkenes,³,⁴ etc. Although, the catalytic reductions of LA to GVL is well studied the enantioselective hydrogenation resulting in the formation of (R)-GVL or (S)-GVL has not been reported yet. The chiral GVL can be used as an optically active building block or as chiral green solvent.

Under homogeneous and solvent free conditions, a Ru-based catalyst systems were tested in the presence of various water soluble tertiary phosphines. Due to the easy separation of the catalyst, the reduction of LA we also performed under heterogeneous conditions, in H-Cube® tubular flow reactor.

Details of the reaction conditions, the effect of ligand structure on the activity, the optimization of the reaction conditions will be presented.

Water Soluble Phosphonium Salts as Supramolecular Synthons

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The formation of polymers of transition metals and organic molecules (metal-organic frameworks, MOFs), is intensively studied in today’s chemistry. Coordination of Ag⁺-ions with organic ligands containing multiple N-, O- and P-donor atoms are frequently used for synthesis of such polymers.

The P-analog of urotropine, the water soluble phosphine, 1,3,5-triaza-7-phospha-adamantane (pta) can be also suitable for this purpose. Prior to our work it was generally accepted, that phosphonium salts of pta can be formed only by indirect synthesis, however, our studies revealed that this phoshpine easily reacts with activated olefins in water under mild conditions. We prepared a library of phosphonium salts by reacting pta with unsaturated dicarboxylic acids (fumaric, maleic, itaconic, glutarconic, mesaconic, and citraconic acid). These phosphonium salts were characterized by elemental analysis and ¹H-, ³¹P-, ¹³C-NMR spectroscopies. The molecular structures of the compounds in solid-state were determined by single crystal X-ray diffraction.

In the above phosphonium salts the N-atoms of pta together with the O-donor atoms of the dicarboxylic acids are suitable for the formation of metal-organic frameworks. Accordingly, the reaction of AgCF₃SO₃ in aqueous solution with the phosphonium salt prepared by the reaction of glutarconic acid and pta yielded a coordination polymer what was characterized by single-crystal X-ray diffraction.

Acknowledgements

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Light olefins are mainly produced by steam cracking or catalytic cracking of crude oil fractions. These processes lead to a mixture of various compounds with the desired alkenes being used as intermediates for the synthesis of polymers, other petrochemical products or gasoline additives. Due to the growing demand of olefins and the availability of new gas resources the dehydrogenation of alkanes has become more important in recent years, as it enables the targeted production of required olefins [1].

Conversion of alkanes to alkenes is limited by thermodynamic equilibrium, so the dehydrogenation is carried out at elevated temperatures. In technical processes supported heterogeneous catalysts like Pt/Sn or Cr₂O₃ on Al₂O₃ are applied. The main problem of these systems is catalyst deactivation caused by coking [1].

A possible way to overcome this issue is the modification of conventional catalysts with molten salts also referred as supported molten salt catalysis (SMS-catalysis). These catalysts are basically structured like SCILL (solid catalyst with ionic liquid layer) [2] systems but with higher melting salts instead of ionic liquids, which mostly are thermally unstable above 200 °C. SMS-catalysts already showed good results in methanol steam reforming [3], so we were interested to find out whether comparable positive effects also exist for the dehydrogenation of n-butane (similar to alkali doped dehydrogenation catalysts [4]).

Thus we modified precious metal catalysts with alkali hydroxides, carbonates and chlorides and mixtures thereof. Catalytic experiments were performed in a continuous gas-phase plant with fixed-bed reactor at T = 450 to 550 °C and at atmospheric pressure. The SMS-catalysts were evaluated by means of activity, stability and selectivity with particular attention to deactivation caused by coking and catalyst regeneration.

References:

Customized Ionic-Liquid - Solvent Mixtures for Application as Reaction- or Extraction-Media

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The profound knowledge attained during an extensive study on the liquid-liquid (LLE) phase behavior of mixtures of different 1-alkyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)amides (C<sub>x</sub>mimNTf<sub>2</sub>; 1 ≤ x ≤ 14) with n-alkyl alcohols (C<sub>n</sub>OH; 1 ≤ n ≤ 20) allows for a selection of suitable liquid mixtures for different applications. Initially, our work was mainly focused on the characterization of the LLEs over a wide temperature range (225 – 423 K) at ambient pressure by applying the cloud point method. Partial miscibility with upper critical solution temperatures (UCST) is observed increasing with the chain lengths of the alcohols and decreasing with the length of the side chain of the cation. The systematic trends of the phase behavior and the results of the numerical analysis (UCST, critical composition, width and diameter of the phase diagrams, validity of the rectilinear diameter) are discussed in detail together with an empirical relationship which allows for the description or estimate of UCSTs for the IL-alcohol family. This concept enables the selection of suitable customized mixtures as task specific reaction or separation media, respectively. In this context, the concept of corresponding states, which provides a more general view on discrete phase diagrams in thermodynamics and yields one single master-curve for more than 65 single systems, can be used as a tool to support the selection of systems for specific applications.
Ionic liquids (ILs) are salts that have a melting point below 100 °C. One of the most interesting characteristics of ILs is their dual nature with respect to their solvating properties for polar and nonpolar compounds. The combination of their particular properties and the possibility of their tuning by the adequate combination of the cation and/or the anion allows the design of these solvents to present selective solubilities for particular components in mixtures. These characteristics make ionic liquids as a good alternative solvents for extraction purposes and potential green solvents of industrial interest. [1]

Tetraoctylammonium oleate and methyltrioctylammonium oleate are evaluated in this work as extractant solvents for the separation of acetic acid from water. Compared to conventional separation methods (e.g., distillation, adsorption, precipitation) it is expected that ionic liquids can be used to separate acetic acid from diluted aqueous media using much less energy and generating less wastes. [2] The liquid-liquid phase behavior (LLE) of the ternary system comprising of water, acetic acid and the ionic liquids used for this investigation was determined at several temperatures at atmospheric pressure. The results obtained so far were used to evaluate the influence of the cation on the LLE data. Additionally, it will contribute to the development and optimization of an extraction route for recovery of acetic acid from fermentation broths.

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One of the major interests in ionic liquids is their use in “green” chemistry. Their negligible vapor pressure minimizes the risk of atmospheric contamination and reduces associated health concerns. They can also reduce the amount of solvent or catalyst in chemical reactions. [1, 2] Apart from the use of ionic liquids as bulk solvents, also SILP (supported ionic liquid phase catalyst) and SCILL (solid catalyst with ionic liquid layer) technologies have been developed and show very interesting potential for various reactions, such as hydroformylation [3] or hydrogenation [4].

One major problem in using conventional ionic liquids carrying organic cations is their limited thermal stability. For many systems, long-term applications are limited to temperatures below 150 °C. By using alkali ions instead, we are able to extend catalysis in molten salts towards higher temperatures. In addition, the substitution of imidazolium-based ionic liquids by alkali-based molten salts opens room for using such liquids also for reactions under basic conditions.

In our contribution we present Pd-catalyzed Suzuki-coupling reactions in molten cesium bis(trifluoromethylsulfonyl)imide systems and discuss the general features of such molten salt system for base-promoted catalytic reactions.

References
Solution calorimetry as an experimental approach to evaluate the solvation power of ionic liquids for cellobiose dissolution

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Herein, we demonstrate Solution Calorimetry as an experimental approach to assess the driving forces of cellobiose dissolution in ionic liquids (ILs). The solution enthalpies for the dilution of cellobiose (CB) solution (10 wt% in DMSO) in binary mixtures composed of [BMIM][Cl] (1-butyl-3-methylimidazolium chloride) and DMSO (dimethyl sulfoxide) were determined (Figure 1).

Interestingly, two distinct regimes are observed for the dependence of solution enthalpy with ionic liquid molar fraction. This feature suggests a transition state for [BMIM][Cl]-DMSO solutions, as it was proposed by Niazi and co-workers1 for [BMIM][Cl]-H2O binary solvent mixtures. Within this, one can understand the behavior displayed in Figure 1 as the following: in the first regime, the cellobiose solvation occurs in a solution of [BMIM][Cl] solvate by DMSO, requiring the breaking up of ion-dipole interactions between DMSO and [BMIM][Cl] ionic species. Thereby, the solvation of cellobiose occurs predominantly through formation of H-bonds with DMSO. The ions strongly bind with the hydroxyl groups of cellobiose as the concentration of IL is increased. Those interactions are claimed to be more exergonic than DMSO-CB or [BMIM][Cl]-DMSO interactions. In fact the solution enthalpy decreases rapidly from $\chi_{[BMIM][Cl]}$ higher than 0.12, becoming an exothermic contribution at $\chi_{[BMIM][Cl]}$ above 0.3.

Overall, solution calorimetry is shown herein as a powerful tool to assess the solvation power of ionic liquids for cellobiose dissolution. From this concept, aspects such as the effect of different substituents in the imidazolium cation, different anions, and different cosolvents (including the antagonistic effect of water) were evaluated systematically to understand their influence on cellulose dissolution.

Coupling Reactions in Microemulsion Systems

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Coupling reactions, e.g. Heck or Suzuki, are usually carried out in organic solvents to have a good solubility of all reactants. Based on the principles of “Green Chemistry” to exchange organic solvents by aqueous media, the organic reactions can be performed in microemulsion systems instead. If a heterogeneous catalyst is applied, the microemulsion system is only used for a better solubilisation of the hydrophobic reactants in water, but in case of homogenously dissolved catalyst complexes, it allows for catalyst recovery via phase separation. Thus, we can overcome one of the major drawbacks in homogenous catalysis: the separation of catalyst and product after reaction. The last case requires the exact knowledge of the phase behaviour of the micellar system.

In this contribution, we will show examples for coupling reactions, e.g. the synthesis of an important Boscalide precursor via Suzuki coupling (Figure 1), with dissolved and sol-gel supported noble metal catalyst complexes, carried out in different microemulsion systems.

![Figure 1: Synthesis of a Boscalide precursor via Suzuki coupling reaction](image)

We will discuss the efficiency of the sol-gel supported catalysts (e.g. mass-transport limitation vs. recyclability) and show that the homogenously dissolved catalyst complex can be recycled many times with negligible leaching into the product phase, if the phase behaviour is well known.
Physical properties for mixtures of 1-ethyl-3-methyl imidazolium octyl sulfate with heavy water at temperatures between 273-298 K

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The knowledge of physical properties of ionic liquids and its mixtures with solvents is necessary to develop industrial process and to design new ionic liquids for a specific purpose by changing their formulation [1]. In addition, they are essential for the development and checking of theoretical models and numerical simulations.

In a previous paper we presented for the first time an ionic rigid gel obtained from aqueous binary mixtures of 1-ethyl-3-methyl imidazolium octyl sulfate (EMIM-OS) [2]. We report electrical conductivity for liquid and gel state for different concentrations and we note that there are no jumps in the trend of that property when the phase change occurs. With the aim of elucidate the mechanism of charge transport in such mixtures in this paper we present measurements of electrical conductivity for mixtures of the ionic liquid EMIM-OS with deuterated water, which also creates ionic gel states. We also measured density and viscosity for those mixtures in the same temperature range and compared results with those obtained for fresh water mixtures.


A comparative study of conventional and synergistic systems for solvent extraction and separation of lanthanoids: chloroform or ionic liquid as innovative organic phase

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Mixed ligand chelate extractions of trivalent lanthanoids (La, Nd, Eu, Ho and Lu) with 3-methyl-1-phenyl-4-(4-phenylbenzoyl)-pyrazol-5-one, HL and 5,11,17,23-tetra-tert-butyl-25,26,27,28-tetrakis-(dimethylphosphinoylmethoxy)calix[4] arene (S) as synergist were carried out in chloride medium at μ=0.1 and CHCl₃ as organic phase. The composition of the extracted species was established as LnL₃•HL with HL as a single extractant, and as LnL₃•S. The parameters of the extraction process were determined. The values of the equilibrium constants were calculated. The addition of S to the system Ln/HL/CHCl₃ leads to a very large increase of the values of $K_{L,S}$ in comparison with those of $K_L$ (4-5 orders of magnitude) and produces rather large synergistic effect. The separation factors between metals were evaluated. A liquid-liquid extraction of La(III) ions using HL and S as complexing compounds alone and their mixture was performed in an ionic liquid(IL), 1-methyl-1,3-butylimidazolium-bis(trifluoromethanesulfonyl)imide in order to establish and examine the synergistic effect. The mixture HL−S shows similar extraction mechanism towards La(III) ion using [C₄C₁₋im][Tf₂N] and CHCl₃ as diluents. The influence of S on the extraction process is discussed. The comparison of the two systems, classical (a molecular diluent) and modern (IL) (drawbacks/phenomenological character), was done.

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Subheading
A comparative study of conventional ans synergistic systems for solvent extraction
Absorption and Oxidation of NO in Flue-Gasses by Ionic Liquids

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Emission of acidic gasses such as NO\textsubscript{x}, SO\textsubscript{x} and CO\textsubscript{x} from combustion processes is a major concern in relation to atmospheric pollution and climate changes. Therefore, these gases have to be effectively removed from flue gases [1,2]. Presently, this is mainly achieved in large stationary installations such as power plant by relatively energy intensive and resource demanding technologies via selective catalytic reduction (SCR) of NO\textsubscript{x} with ammonia, by gypsum formation after SO\textsubscript{2} wet-scrubbing while organic amines may be used as absorbents in CO\textsubscript{2} scrubbers [3]. NO\textsubscript{x} removal by ammonia-SCR is widely used and has proven to be very efficient. However, the technology requires access to large quantities of ammonia and is thus less suited for implementation in, for example, the maritime industry.

In this work, we demonstrate how ionic liquids (ILs) can be tuned by design to perform as selective, high-capacity absorbents of environmentally problematic flue gases. Particularly, it is demonstrated how NO can be absorbed and surprisingly also catalytically converted to nitric acid (HNO\textsubscript{3}) by ILs [4]. The reaction mechanism and kinetics has been examined and elucidated by in-situ Attenuated Total Reflection-Fourier Transformed Infrared (ATR-FTIR) spectroscopy. Furthermore, industrially relevant solid absorber formulations in the form of Supported Ionic Liquid Phase (SILP) materials were found to show remarkable reversibility, with no measurable loss in capacity after 50-100 absorption-desorption cycles.

A Novel Approach to the Synthesis of Chiral Reversible Ionic Liquids from Available Biomass Starting Materials

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In the last few years, the concept of reversible ionic liquids (RevILs) has emerged to overcome classical problems and limitations associated to the use of conventional ionic liquids, while preserving their advantageous properties.[1] RevILs are able to switch between an ionic liquid phase and a molecular liquid phase as a result of a reversible reaction with CO$_2$. Moreover, they can also be used as temporary linkers to change physicochemical properties of some active molecules.

Herein, we report an environmentally friendly methodology to access to a new family of chiral RevILs from CO$_2$ and natural amino acids. A platform of chiral amines was synthesized and characterized. The chiral amines will be then transformed into the expected chiral RevILs by action of CO$_2$ (Scheme 1). As far as we know, very few examples have been reported so far. This reversible equilibrium could be turned to the molecular liquid phase by heating or bubbling argon in the mixture reaction, allowing thus easier product purification.

![Scheme 1. Synthesis of chiral RevILs](image)

These new RevILs will be use as solvent and/or catalyst in several organic reactions and as a reversible linker for glycochemistry. The results of this study will be presented in this communication.

Synthesis of supported Catalysts by Chemical Fluid Deposition

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Our study focuses on the synthesis of supported metal nanocatalysts using the chemical fluid deposition (CFD) approach\(^{[1,\ 2]}\). Here, a suitable metal complex is dissolved in a supercritical fluid (SCF, typically scCO\(_2\)) and reduced to metallic ensembles by addition of molecular hydrogen. Depending on the reaction conditions, supported metal aggregates of nanoscale can be obtained.

\[ \text{SBA-15} \xrightarrow{\text{impregnation}} \text{Pd and Pt} \xrightarrow{\text{scCO}_2} \xrightarrow{\text{H}_2} \text{Pd/Pt\text{nano}@SBA-15} \]

**Figure 1.** Synthesis of SBA-15 supported bimetallic Pd/ Pt nanoparticles by CFD.

By applying this methodology, a variety of mono- and bimetallic supported Palladium and Platinum based nanoparticles have been synthesized using different support materials, metal loadings and solvents. According to TEM investigations, uniform nanoparticles can be deposited on mesoporous SBA-15. The substitution of the SCF by conventional solvents under otherwise identical reaction conditions resulted in a deposition behavior which is either comparable to the one in scCO\(_2\) (as in the case of \(n\)-pentane) or entirely different (as observed for toluene and THF). So, our study identifies scCO\(_2\) and \(n\)-pentane as good candidates in the deposition process – not only from a material science point of view but also in terms of catalytic activity: Almost full conversion and \(\gamma\)-valerolactone selectivities of 99% were obtained in the hydrogenation of LA with our best catalysts from both production protocols.

**References:**


Chemical fixation of CO$_2$ to quinazoline-2,4(1H, 3H)-diones in water promoted by choline hydroxide

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Efficient conversion of CO$_2$ to high value-added chemicals with cheap and non-toxic catalysts in water is a very attractive topic in green chemistry. Being the pharmaceutical intermediates and biologically active additives, quinazoline-2,4(1H,3H)-diones are an important class of pharmaceutical intermediates and have a wide range of applications. In this work, choline hydroxide was first used to catalyzed the formation of quinazoline-2,4(1H,3H)-dione from CO$_2$ and 2-aminobenzonitrile. It was found that this abundant, natural, environmentally benign and cheap material could promote the reactions of CO$_2$ and 2-aminobenzonitrile very efficiently in water. Under the optimized reaction conditions, the satisfactory isolated yield could be obtained (92%, Figure 1). Further study indicated that the catalytic system was also very efficient for reactions of CO$_2$ with transformation of other substituted 2-aminobenzonitriles. In this case, the organic solvents are replaced by water and the catalyst choline hydroxide is very cheap and easy to obtain. We believe that this efficient, green, cheap catalyst has potential application for synthesizing quinazoline-2,4(1H,3H)-diones from CO$_2$ and 2-aminobenzonitriles.

![Graph](image.png)

**Figure 1.** The dependence of the isolated yield of quinazoline 2,4(1H,3H)-dione on the reaction time at 2.0 MPa and 90 °C.
Efficient conversion of glucose to 5-hydroxymethylfurfural in DBU-based ionic liquids

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Efficient conversion of glucose to 5-hydroxymethylfurfural (HMF), an important platform molecular for fuels and chemicals, is a promising topic in green chemistry. In this work, several new DBU-based (DBU=1,8-diazabicyclo[5.4.0]undec-7-ene) ionic liquids (ILs) with benzene sulfonate anion were synthesized and used as the solvents for the dehydration of glucose to HMF. It was found that all the ILs were excellent solvents for dehydration of glucose to form HMF using CrCl₃ as the catalyst and Et-DBUBS generated the best result. Under the optimized reaction conditions, the yield of HMF from glucose could reach 83.4% (Figure 1), which was considerably higher than the values reported up to date in the literature. The Et-DBUBS/CrCl₃ system could be reused at least five times without considerable reduction in the efficiency. Further study indicated that the catalytic system was also very efficient for transformation of fructose, inulin, and cellobiose to HMF.

![Figure 1. Effect of reaction time on dehydration of glucose to the HMF in ILs/CrCl₃ catalytic system at 110 °C.](image-url)
Method to form activated carbon from waste wood using partial oxidation in high-temperature water.

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In a wastewater management facility, activated carbon (AC) is used to remove colored compounds at a final stage of the process. Currently, feedstocks of AC are typically coal or coconut shell, which are produced from fossil resources or from area-limited biomass. To produce AC from resources available in many areas, waste wood is appropriate because most of it is used as fuel for biomass boilers. To make AC from wood, the most common activation method is chemical activation and it has two big problems: (1) requirement of a large amount of energy and (2) treatment of acid gas that requires a large amount of water. For developing a green process for AC production from wood, reduction in the input energy and in the amount of chemicals is required. The specific surface area can be increased by hydrolysis of tar at hydrothermal conditions [1] and absorption capacity of colored compounds can be improved because of the increase of surface hydrophilic function groups by the hydrolysis [2].

In this study, wood-AC was made from pyrolyzed char of waste wood by a batch reactor at hydrothermal conditions. To know the effect of pretreatment, oxidant addition and reaction temperature on the activation, burn-off and specific surface area of carbon were investigated. In addition, adsorption capacity of colored compounds of hydrothermally treated carbon was also evaluated by methylene blue adsorption. By adding oxidant at the pretreatment step and applying hydrothermal treatment, the adsorption capacity of the wood-AC increased and it was found that its capacity was one third of commercial AC. Adsorption capacity of the wood-AC could be correlated by burn-off but not by specific surface area. The reason for the increase in the adsorption capacity of the is probably due to added functional groups formed on the surface of the carbon by oxidant and hydrothermal treatment.

References
Extraction of single ring phenolic compounds from lignin pyrolysis oil using a supercritical fluid method

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A supercritical fluid method has been developed for the effective partitioning of single-ring phenolic compounds from lignin microwave-pyrolysis oil. The method is superior to normal supercritical fluid extraction in terms of selectivity and superior to extraction using switchable solvents in terms of having lower complexity and number of process steps.

Additional text

Due to rapid depletion of fossil fuel resources and increased demand, alternative renewable energy sources have gained attention. Lignin pyrolysis oil is one of the most promising as it is obtained from abundant, economical lignin renewable feedstock. However, separation or purification were challenging in transforming this low combustible mixture to valuable fuel. We present a facile green technique which involves modified supercritical CO₂ extraction to separate valuable single ring phenolic compounds.
Highly Enantioselective Tandem Enzyme-Organocatalyst Crossed Aldol Reactions with Acetaldehyde in Deep-Eutectic-Solvents

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Graphical Abstract

The development of novel integrated tandem enzyme-organocatalytic concepts is one of the current frontiers of the sustainable chemistry. Herein we report a highly enantioselective approach in Deep-Eutectic-Solvents (DES) as reaction media. DES, e.g. combining choline chloride and glycerol, have emerged as promising bio-based and cost-effective reaction media. We focus on the enzymatically in situ acetaldehyde production combined with highly enantioselective crossed aldehyde-aldehyde C-C bond formation organocatalysis. This leads to an integrative concept with straightforward product recovery and promising catalysts recycling, enabling the synthesis of highly valuable optically active building blocks under mild reaction conditions.
Polyesters are applied in many different fields of material science. For instance, polybutylene succinate (1) is used as a biodegradable packaging material. Substitution of the 1,4-butandiol by oligoacetal units derived from formaldehyde would lead to a potentially more sustainable polyacetal ester (2), since both building blocks, succinic acid and formaldehyde, can be obtained from sustainable resources.

Trioxane is a commonly used formaldehyde source for the production of polymers such as polyoxymethylene (POM). Using in situ-IR spectroscopy, we demonstrated that trioxane is inserted into anhydrides via a ring opening insertion mechanism to form oligoacetal dicarboxylates (Figure 1).

This opens the route to build polyester structures from trioxane and cyclic anhydrides (Scheme 1). The resulting polyacetal esters are a new class of polyesters with unprecedented properties.

Thus, a detailed mechanistic understanding of the reaction between acetic anhydride and trioxane provided the fundament for the development of the new polyesters from potentially sustainable feedstocks.

The Preparation of Novel Catalysts for Lignocellulosic Biomass Valorization

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In the last decades, the research and technological development in the field of biomass have been increasing with the ultimate aim of providing a sustainable source of energy and chemicals for a greener world because biomass represents an abundant carbon-neutral renewable resource and its enhanced use would address several challenges.

While several methods have been published regarding transforming cellulose to more valuable chemicals such as glucose, sorbitol and 5-hydroxymethylfurfural (HMF), there is still no viable process for converting lignin into chemicals, even though some industrial sectors produce massive amounts of lignin as a by-product (Gosselink et al. 2004). Due to being converted to various valuable chemicals as illustrated in Figure 1, HMF is one of the most important platform molecules and it can also be utilized as a fuel precursor.

![Figure 1. A selection of monomers derived from 5-hydroxymethylfurfural (HMF)](image)

The novel catalysts of various metal salts onto different molecular sieves are promising for the valorization of lignocellulosic biomass in order to obtain the valuable platform molecule HMF. Alternative methods (synthesis for metal nanoparticles, desilication...etc.) have been utilized for the preparation of catalysts. The characterization techniques such as XRD, UV-VIS, FT-IR, BET, and SEM are carried out.
COSMO-RS-based solvent selection for a reaction to 5-hydroxymethylfurfural utilizing an integrated extraction

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In the development of new extraction processes the selection of solvents is an essential step. Today this solvent selection is often still based on heuristics alone. At the same time predictive methods such as COSMO-RS, allow for the computation of solvent properties important for extraction, such as partition coefficients. In addition the partition coefficient calculations are highly efficient: Utilizing a normal desktop computer\(^1\), several thousand possible solvents can be evaluated within a day. Thus these methods can be used in support of experimental work, augmenting proven heuristics. COSMO-RS was used to search for solvents (brown phase) for the extraction of 5-hydroxymethylfurfural (HMF) from water (blue phase), in which fructose reacts to HMF. HMF has to be extracted in situ from the aqueous phase to prevent further reaction to levulinic acid (LA) and formic acid (FA). To ensure a large solvent search space the entire COSMO-RS databank of more than 8000 solvents was used in the screening. About 3000 possible solvents were identified in an initial screening step. Aiming for a subsequent transformation of HMF after extraction, e.g. via oxidation or hydrogenation, the solvent set can be confined yielding a set of promising solvents, which was examined in more detail experimentally and computationally. The experiments showed that COSMO-RS predicted the solvent ranking correctly.

Due to the maturity of the system, most of the identified solvents were already known from literature. Nevertheless, this work highlights the possibilities offered by the approach: For the relatively low computational and manpower cost, interesting solvent suggestions can be obtained, potentially outside the range found through traditional means.

\(^1\) Intel quad core i5-2520M (2.5 GHz), 8 GB RAM, OpenSuSE
Deprotonation as an indicator for ion basicity in electrolytic media for cellulose dissolution

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The conversion of lignocellulose requires a pretreatment which cleaves the composite like structure of biomass for subsequent conversion steps. An innovative pretreatment concept was developed with ionic liquids (ILs) [1]. Some of these liquid salts dissolve cellulose (e.g., chloride-based ILs) and some can even disintegrate wood into fibers (e.g., with acetate or glycinate anions), but these effects are largely limited by water. The anions show differences in the tolerable water content for dissolution or disintegration of biomass. This behavior cannot be explained by established solvent parameters like Kamlet-Taft basicity. Basic anions can, however, lead to the formation of carbenes [2]. These effects of dissolution and disintegration are scarcely understood and have not been explored in the presence of water. Understanding the interaction and basicity of the ions is clearly important for the design of novel pretreatment liquids consisting of multiple cheap ions.

Here, low-field nuclear magnetic resonance spectroscopy (NMR) was used as a tool to directly characterize non-diluted strong electrolytic media. 1-ethyl-3-methylimidazolium chloride (EMIMCl) and the respective ILs with acetate (EMIMAc) and glycinate (EMIMGly) were investigated in mixtures with deuterated water (D₂O) from dilute solutions (40 wt % D₂O) to almost no water content. The peak position and peak area of the C2 proton of the imidazolium were monitored to characterize the interaction with the anion.

The results show that the nature of the anion governs the interaction. For EMIMCl no deuterium exchange is observed whereas for EMIMGly complete exchange of the C2 proton with deuterium takes place. The exchange is almost complete with EMIMAc. This follows the order of the pKₐ of the conjugated acids and supports the non-reactivity of Cl-based ILs [2]. Mixtures of EMIMAc and D₂O show a different rate of proton exchange depending on D₂O concentration. The rate of deprotonation is similar up to a water content of approximately 20 wt %, which coincides with the limiting water content in cellulose dissolution. Above this particular water content, the rate decreases. It can be hypothesized that the deprotonation of hydrogen and the presence of carbene intermediates characterize the ability to decrystallize lignocellulose in mixtures of ions and water.


Continuous Flow Homogeneous Catalysis:  
SILP or PTA? This is the question!

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Implementing homogeneously catalysed reactions into continuous flow systems is of great interest as it can lead to safer and less labour intensive as well as more sustainable and economically advantageous processes. The use of small, flexible, and largely automated continuously operated devices allows for reduced reactor sizes, integrated downstream, and a more efficient use of catalyst as compared to batch processes. The immobilization strategy of the molecularly defined catalyst plays here a pivotal role for guarantying the intrinsic catalyst selectivity and activity as well as for the long term stability and suppression of catalyst leaching.

In this contribution two alternative immobilization methods are investigated and compared: On the one hand the methodology originally developed by Augustine et al.\(^1,2\) based on the use of heteropoly acids like phosphotungstic acid (PTA) as anchoring agents on a solid support like alumina and on the other hand the Supported Ionic Liquid Phases (SILP) in the presence of scCO\(_2\)\(^3,4\). Most importantly, both methods allow the use of off-the-shelf catalysts without any need of ligand modification or functionalization and the immobilization procedure is rapid and straightforward.

A multipurpose setup was constructed comprising two plug flow reactors that can be used alternatively and with the possibility to analyse the product stream directly via online-GC. The continuous-flow asymmetric hydrogenation of a not-volatile vinyl acetamide was investigated to benchmark the two approaches: advantages and drawbacks of these two very promising complementary strategies will be discussed.

Hydroxymethylfurfural production from cellulose via 3-step reaction in ionic liquid-water mixture

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Hydroxymethylfurfural (HMF) is a useful compound that can be derived from cellulose. It is known that formation of HMF from cellulose is a 3-step reaction: (1) hydrolysis of cellulose into glucose, (2) glucose isomerization to fructose and (3) fructose dehydration to HMF. The reactions 1 and 3 are acid reactions and the reaction 2 is a base reaction. To increase the yield of HMF, optimization of each reaction step is effective and efficient. Ionic liquids composed of imidazolium cation and chloride anion are good solvents for cellulose. Previously, cellulose hydrolysis into glucose (step 1) in 1-butyl-3-methylimidazolium chloride ([bmIm][Cl]) was optimized by sequential water addition method in the presence of heterogeneous acid catalyst such as ion exchange resin, zeolites and carbon catalyst [1]. For fructose dehydration into HMF (step 3), the effect of heterogeneous catalysts, temperature and co-solvent was investigated [2][3].

To develop the total process from cellulose into HMF, in this study, step 2 (glucose isomerization) was optimized in the presence of water and the effect of water on step 3 was investigated. In addition, for reuse of ionic liquid, separation of HMF from the ionic liquid-water mixture by ethyl acetate was also studied.

For isomerization of glucose in the presence of 35% or 50% of water in [bmIm][Cl], several magnesium catalysts (magnesium carbonate, magnesium oxide and dolomite) were effective (at glucose conversion: 20%~60%, 20%~30% of fructose was formed). Fructose dehydration is insensitive to the presence of water. Ethyl acetate was effective extraction solvent for HMF recovery from [bmIm][Cl]-water mixture.

References
Utilization of lignocellulosic biomass as a renewable raw material for the production of fine chemicals has become the topic of intense researches mainly boosted by the necessity to reduce our dependency to fossil reserves. Production of fine chemicals from lignocellulosic biomass is however challenging and requires few obstacles to be tackled such as (1) the low accessibility of biomass to (bio)catalysts, (2) the recycling of aqueous effluents and (3) the control of the reaction selectivity.

In this communication, we wish to show that betaïn hydrochloride (BHC), a cheap, biodegradable and safe co-product from the sugar beet industry, can be successfully used in combination with water to produce an ionic acid media capable of promoting the selective production of furfural and levulinic acid from wheat straw in a single reactor. By adjusting the reaction temperature (150°C or 180°C), furfural and levulinic acid can be successfully produced with 65% and 87% yields, respectively. With these results in hand, we will discuss the influence of the amount of wheat straw (1-50 wt%) and the BHC content (5-80 wt%) not only on the reaction selectivity but also on the extraction efficiency of furfural, a serious shortcoming of current processes. Finally, we will demonstrate that BHC is a robust chemical that can be conveniently recovered (> 95 wt%) and recycled at least 5 times without affecting the efficiency of the process. It is our opinion that the recyclability of BHC, the possibility to use up to 20 wt% of wheat straw together with the low cost, biodegradability and low toxicity of BHC dramatically improve the sustainability of this process.
Enantioselective esterification with triglycerides in carbon dioxide

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Our objective was to perform the enantioselective esterification with triglycerides, as cheap and natural reagents in liquid and supercritical carbon dioxide solvent. Dense carbon dioxide is GRAS and environmentally benign solvent and its dissolving power can be easily controlled with pressure and temperature, additionally the diffusion coefficients are by orders of magnitude higher than in liquids [1]. As model compound racemic 1-phenylethanol was selected, as well defined esterification agents triacetin and tributirin were applied. The reaction was catalyzed by commercial Candida antarctica lipase B (CALB) immobilized in macroporous acrylic resin. Experiments were either performed in view cell units or in autoclaves, with possibility of constant pressure and temperature sampling, in 6-21 MPa pressure and 20 – 65 °C temperature ranges. Enantioselectivities, reaction rates and Michealis-Menten constants were determined and compared with results of atmospheric reference experiments in n-hexane or neat.

Both triacetin and tributirin are efficient esterification reagents and the reaction is highly enantioselective (E>1000) in all conditions studied. In dense carbon dioxide reaction rates are higher than in n-hexane under the same conditions except pressure, while neat reactions are the fastest. Slight increase in reaction rates were observed with increasing pressure. Equilibrium enantiomeric excess values (80-92 %) of remaining alcohol slightly depends on pressure, temperature and solvent. Phase equilibrium strongly depends on pressure especially when tributirin is applied, which is very promising for further developments on separation of products.

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Continuous subcritical hydrothermal synthesis with *in situ* surface modification of cerium oxide using L-glutamic acid

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Cerium oxide (CeO$_2$) is an important catalyst, catalyst promoter, and supporter. The catalytic activity significantly depends on the size and morphology of the particles. A noble and green process for the synthesis of metal oxide nanoparticles (NPs) is the supercritical hydrothermal reaction. Beside the fast reaction, an advantage of this method is the *in situ* surface modification of NPs that controls the shape and dimension of CeO$_2$ particles depending on applied organic surfactant such as oleic acid. However, a complex phase behavior of the organic phase, water phase and supercritical water complicates the observation of the surface modification mechanism in detail. By simplifying the reaction system to a single phase synthesis with the introduction of a water-soluble surfactant, kinetic information as well as new CeO$_2$ structures can be obtained. In this work, we studied the effect of L-glutamic acid (Glu) as capping agent on the cerium oxide structure depending on the cerium to modifier ratio and reaction time. The experiments were performed in a lab-scale flow type reactor at 250°C and 25 MPa. The cerium concentration was 0.01 mol L$^{-1}$ and the amino acid concentration was varied from 0 to 0.05 mol L$^{-1}$ to achieve a molar ratio of Ce to Glu of 0, 1:0.5, 1:1, 1:3 and 1:5, respectively. Electron microscopy images in Figure 1 identify the surface modification from octahedral shapes, in the absence of the amino acid, to spherical self-assemblies with increased modifier concentration. As the molar ratio of cerium to Glu and the reaction time rises, the assembly grows to uniform 80 nm particles. The reaction rate of the solid-forming reaction estimated on the basesis of a first order assumption decelerates drastically with increasing amount of Glu. The estimated reaction constant $k$ decreases from 0.0286 s$^{-1}$ (without modifier) to 0.0022 s$^{-1}$ at a molar ratio of Ce to Glu of 1:5. From the results, L-glutamic acid has a high impact on the CeO$_2$ reaction system as it alters the morphology and slows the reaction rate.

![Figure 1: Reaction constant dependency on the L-glutamic acid concentration and the corresponding TEM images of the synthesized particles](image-url)
Li–O₂ batteries, possessing a capacity 5–8 times higher than that of Li-ion batteries, are considered promising candidates for electric vehicles.

We built porous graphite-like carbon layers, and loaded RuO₂ nanoparticles on it in supercritical water. Thanks to supercritical condition, the RuO₂ nanoparticles with an average size of about 2 nm are uniformly distributed on the surface of carbon layers. What’s more, RuO₂ nanoparticles can be filled into the layer spacing although the spacing is only 2 nm.

Overpotentials are decreased decently by RuO₂ catalytic effect. The porous channels and layered structure of the RuO₂/C facilitated the electrolyte immersion and Li⁺ diffusion and provided an effective space for O₂ diffusion and O₂ /Li₂O₂ conversion, which effectively enhanced the electrochemical performance of the Li–O₂ batteries.
Continuous-flow transesterification of organic carbonates with glycerol acetics

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The chemical upgrade of bioglycerol and its derivatives represents one of the most attractive goals of a modern biorefineries.\(^1\) In this context, our research group is active in the investigation of new technologies and products specifically aimed at the transformation and use of glycerol carbonate and light glycerol acetics such as glycerol formal and solketal.\(^2\)

The present work describes the implementation of an original protocol for the continuous-flow (CF) synthesis of organic carbonates via the transesterification of non-toxic dialkyl carbonates with glycerol acetals (Scheme 1)

\[
\text{R}_1: \text{H, CH}_3 \\
\text{R}_2: \text{CH}_3, \text{CH}_2\text{CH}_3, \text{Bn}
\]

Scheme 1: Transesterification of dialkyl carbonates with glycerol acetals

Dialkyl carbonates act not only as green reagents, but also as green solvents/carriers of the process. This aspect along with the accurate control of all reaction parameters (reagent flow, temperature, pressure) made possible by the CF-operating mode, greatly contributes to enhance the overall eco-compatibility of the methodology in terms of E-factor, process intensification, and general safety.\(^3\) An even more remarkable feature of such reactions is that they may take place without any catalyst providing that suitable pressures and temperatures are applied. In most cases, at a given temperature (in the range of 250-350 °C), modest variations of pressure may boost the conversion from 0% to more than 85%, with selectivity >95%. This behaviour suggests that the achievement of supercritical (CF) conditions is the most plausible driving force of the observed thermal reaction. To the best of our knowledge, no such results have been previously reported in the literature, especially for glycerol derived acetals.

References

Biomass processing with ionic liquids: New aspects for fine chemical production

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To date, the isolation of valuable ingredients from (waste) biomass is mainly performed using volatile solvent extraction processes; however this is always associated with the dangers of combustible solvents, human risk and often limited efficiency. There are several aspects of ionic liquids that are advantageous in this context: Apart from their unique solvent properties and potential environmental benefits, the ability of ionic liquids to dissolve biomass can lead to a better and higher yielding access to the valuable ingredient embedded in the biopolymers. [1]

Facing these issues, we present novel strategies towards the isolation of valuable components from different types of biomass, including pharmaceutically actives, essential oils or biomacromolecules, e.g. DNA. [2],[3] We will not only discuss ionic liquids as mere extraction media, but focus on the role of functionalised ionic liquids, e.g. surface-active, Brønsted acidic or basic ionic liquids that provide novel and unique possibilities for fine chemical production. [4]

Iron fluoride: the most efficient catalyst for one-pot synthesis of 4H-pyrimido[2, 1, b]benzothiazoles under solvent free conditions.

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Abstract
A new iron fluoride assisted convenient and efficient strategy for the preparation of 4H-pyrimido[2, 1, b]benzothiazoles derivatives in solvent free media is described. The reactions can be performed at low catalyst loadings with excellent functional group tolerance. The catalyst can be readily recovered and reused for next reaction for at least three runs without any significant impact on the yields of the products. The easy recovery of the catalyst and high yield of the products make the protocol attractive, sustainable, and economic.

\[
\text{R} = \text{Me, H} \quad R_1 = \text{Aromatic, Aliphatic, Heterocyclic} \\
R_2 = \text{H, Me}
\]

FeF\(_3\), 100 °C

Solvent Free

Green media
No Hazardous Organic Solvent,
Simple purification

85-97% Yields
26 Examples
A green and convenient protocol for the synthesis of diarylmethanes via a one-pot, three-component reaction catalyzed by new silica tungstic acid (STA) under solvent free condition

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A cost-effective and eco-friendly synthesis of diarylmethanes derivatives has been developed through the Mannich type Friedel–Crafts addition reaction of tertiary aromatic amine formaldehydes with β-naphthol/ indole using silica supported tungstic acid (STA) as a recyclable heterogeneous acid catalyst in solvent free condition. Here we proposed two schemes using same catalyst. Effect of different solvents and comparison of silica supported tungstic acid with different acid catalysts have also been studied.

![Reaction Scheme]

Solvent free, RT, 20-30 min
Yield=90-96 %
Synthesis of 6-Amino-2,4-dihydropyrano [2, 3-c] pyrazol-5-carbonitriles catalyzed by silica supported tetramethylguanidine under solvent free conditions.

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An efficient, high yielding, and rapid protocol has been developed for the synthesis of diversity oriented 6-Amino-2, 4-dihydropyrano [2, 3-c] pyrazol-5-carbonitriles derivatives via a four component, one-pot cyclocondensation reaction of ethyl acetoacetate, hydrazine hydrate, aldehydes, and malononitrile using silica supported tetramethylguanidine as a heterogeneous catalyst for the first time. The protocol proves to be efficient and environmentally benign in terms of very easy work-up, high yields, and ease of recovery of catalyst. In addition, the present method is superior in terms of green media, the amount of catalyst and reaction time.
In continuous flow reactions, solvents are important components as they are used not only as reaction promoters but also as substrate carriers. However, in some cases solvents, which are often regarded as “inert components”, can react to generate unexpected products.

We describe here some interesting examples where the solvent is also a reagent, and can affect the final outcome of a chemical transformation. Flow systems with online analysis have been used to detect side products that were then specifically targeted to develop new chemical transformations, where the solvents are taking part in the reaction process.

The first example involves original multi-component reactions with tetrahydrofurans and/or carbonates to provide a variety of different compounds that could then be synthesised more selectively then by other routes. A second series of examples, where protic solvents were found to interact with the reaction process, will also be presented.

When combined with continuous flow processes, using solvents as reactants is a way to perform “solvent free” reactions, thus rendering a chemical process more attractive from a Green Chemistry perspective.

We thank the EU project SYNFLOW (7th European Framework Program for Research and Technological Development) for funding.

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In our research we are bringing value to carbon dioxide by studying reactions carried out in its supercritical form (scCO₂). ScCO₂ is considered to be a green solvent, due to its many benefits, for example CO₂ is non-flammable, nontoxic and “chemically inert”.¹ These qualities, in addition to others, make scCO₂ an attractive option as a reaction medium, instead of traditionally used toxic organic solvents. Our research is carried out with a continuous flow reactor, which is also self-optimising. This means that the system is automated and the best reaction conditions are found by an algorithm that searches for the maximum yield of the desired product.² The benefits of optimisation include that it makes a process greener by increasing selectivity and conversion, and by minimising the generation of waste.³ In our system the reaction outcome can be monitored by both online GC² and inline FT-IR.⁴ To begin with, the acid catalysed methylation of 1-butanol with dimethyl carbonate to produce butyl methyl ether was studied. This reaction was carried out with and without scCO₂ as a solvent, and optimised using the previously developed FT-IR method. The advantage of the FT-IR monitoring is that it helps makes the process greener, because the optimum conditions can be found up to ten times quicker than when the reaction is monitored by the GC.⁴ As we were able to show that the FT-IR analysis can be used to optimise reaction conditions when scCO₂ is used as a solvent, we will also be able to try and apply this optimisation method to more complex reactions in scCO₂. We thank the Erasmus Mundus Joint Doctorate SINCHEM (FPA 2013-0037) for funding Emilia Streng’s grant and Prof. Dr. W. Leitner for collaboration.

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Polymer Supported Ionic Liquids: Highly Efficient, Green Recyclable Catalyst for Dehydration of Carbohydrate into 5-Hydroxymethylfurfural

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Ionic liquids (ILs) which are composed of cations and anions constituents and can be tailor to possess a characteristic property. Hence, the term “designer solvents” has been used to establish the prospective for these eco-friendly ionic liquids in chemical processes. Subsequently, these designer solvents are able to dissolve several organic and inorganic complexes, they have often been employed in modern times in several catalytic reactions to enhance reaction rate and selectivity. The polymer supported ionic liquids process reassigning the desired catalytic properties of the ionic liquids to solid catalysts could combine the advantages of ILs with those of heterogeneous support materials and various catalytically functional groups or active species.

In the present study, synthesis of polymer supported imidazolium based ionic liquids was carried out by using Merrifield resin as a support material. Various different anions were installed using metathesis reaction and obtained number of PSILs. These prepared catalysts were characterized by using different spectroscopic and analytical methods, and then were to the dehydration of fructose and sucrose into 5-hydroxymethylfurfural (HMF). As a result, catalytic amount of PSILs achieved 100% conversion of carbohydrate with highly efficient yield of HMF in a very short reaction time in ambient condition. Moreover, effect of catalyst dosage, reaction temperature, reaction time, and co-catalysts were also studied. In addition, recyclablility of PSILs were also considered, results revealed that catalyst can be reused eight times without losing catalytic activity. The present environmentally benign catalytic system for the dehydration of carbohydrates was found to be very convenient and eco-friendly method. This work was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education (Grant number: NRF-2013R1A1A2060638).
NiO$_2$ mediator in catalytic oxidation of 2-propanol on glassy carbon electrode modified with nickel oxides

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The communication aims to present the results of the oxidation of 2-propanol on a glassy carbon electrode modified with nickel oxides [1]. After carrying out the modification of glassy carbon by nickel oxide film by means of the potentiostatic polarization and cyclic voltammetry and after its characterization by the open circuit potential, polarization resistance and electrochemical impedance spectroscopy techniques, the electrochemical sensor was used for determining the concentration of 2-propanol in 0.1 mol L$^{-1}$ NaOH aqueous solution. The oxidation of 2-propanol by cyclic voltammetry shows that the anodic peak is within the stability domain of NiO$_2$. This observation led us to propose a reaction mechanism where nickel dioxide NiO$_2$ acts as electrochemical mediator. This approach explains why the peak current of the reversible system [2] NiOOH/ Ni(OH)$_2$ remains constant. This electrochemical sensor showed a good stability and led to the determination of 2-propanol [3] with a good reproducibility, a fast response time and a sensitivity of 54.42 mA mol$^{-1}$ L.

Fig.1 Voltamperograms recorded during anodic oxidation of 2-propanol.

Fig.2 Calibration curve of 2-propanol

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Optimization of the synthesis of glycerol derivatives solvents

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Nowadays glycerol represents an important platform molecule in biorefinery processes\(^1\). Many glycerol derivatives have interesting properties as solvents\(^2\), but in some cases an optimization of their synthesis should be addressed in order to produce cheap and easily available products. The main purpose of this work is the optimization of the synthesis of ketals and ketals derivatives from glycerol using heterogeneous acid catalysts. Some sulfonated resins, such as Dowex 50WX2 and Amberlyst 15 have been tested together with sulfonated hydrothermal carbon (SHC)\(^3\). The synthesis of glycerol ketals from acetone and butanone have been achieved in high yields. Subsequent esterification of the ketals with acetic acid provided the desired product together with acetins as reaction byproducts. The percentage of acetins was higher when solketal was reacted with acetic acid. Interesting results have been obtained with sulfonated hydrothermal carbon in the tandem reaction of glycerol with butanone and subsequent acetylation.

![Fig. 1 – Synthesis of glycerol ketals and ketal esters.](image1)

![Fig. 2 – Results of the tandem reaction of glycerol with butanone and acetic acid.](image2)

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**References**

Dipolarity versus Polarizability and Acidity versus Basicity of Ionic Liquids as Function of their Molecular Structure

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Catalán’s empirical solvent polarity parameters $SA$ (solvent acidity), $SB$ (solvent basicity), $SP$ (solvent polarizability) and $SdP$ (solvent dipolarity) of 64 ionic liquids have been determined by the solvatochromic method. The parameter $SA$ was solely determined by $\text{Fe}^{II}(1,10\text{-phenanthroline})_2(\text{CN})_2$ ($\text{Fe}$), $SB$ by the homomorph dye pair $3$-(4-amino-3-methylphenyl)-7-phenyl-benzo-[1,2-$b$:$4,5$-$b'$]-difuran-2,6-dione ($\text{ABF}$) and $2,3$-(4-$N,N$-dimethylamino-phenyl)-7-phenyl-benzo-[1,2-$b$:$4,5$-$b'$]-difuran-2,6-dione ($\text{DMe-ABF}$) and the $SP$ and $SdP$ parameters by the homomorph pair $4$-$\text{tert}$-butyl-2-(dicyanomethylene)-5-[4-(diethylamino)benzylidene]-$\Delta^3$-thiazoline ($\text{Th}$) and $2$-(4-$N,N$-dimethylamino)-benzylidene-malononitrile ($\text{BMN}$). The separation of $SP$ and $SdP$ for a set of 64 various ionic liquids has been performed for the first time. Correlation analyses of $SP$ with physiochemical data relating to ionization potentials of anions of ionic liquids show the correctness of the method applied. The found correlations of the Catalán parameters with each other as well as with the alkyl chain length of [C$_x$mim]-typ ionic liquids give new information about interactions within ionic liquids.
Ionic Liquids, key to sustainable energy production?

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The level of CO₂ in the atmosphere is rising dramatically, reaching for the first time in May 2013 the level of 400 ppm in Mauna Loa (Hawaii). Thus a great effort is made to find solutions to reduce greenhouse gas (GHG) emissions and especially its major contributor, CO₂. Instead of treating CO₂ as a waste, it can also be considered as a chemical raw material. For example it can be recycled in the food industry or used as chemical feedstock in the synthesis of chemicals (urea, salicylic acid, cyclic carbonates). This approach is known as carbon capture and utilization (CCU) and it is the most promising and energetically “useful” approach.

Conventional solvents for the capture of CO₂ (amines solutions such as monoethanolamine – MEA, methyldiethanolamine – MDEA, or diethylamine – DEA) allows the sequestration of CO₂ but high energy is needed to recover CO₂ from them and they lack stability over time because of the evaporation of water.

Ionic liquids (ILs) are efficient solvents for the selective removal of CO₂ from flue gas. Conventional, off-the-shelf ILs are limited in use to physisorption, which limits their absorption capacity. Adding a chemical functionality, like amines or alcohols, allows chemisorption of CO₂. By carefully choosing the anion and the cation of the IL, equimolar absorption of CO₂ is possible (instead of a 2:1 for amine solutions).

We synthesized different ILs in the purpose of capturing CO₂ and transforming it in methanol by hydrogenation. For its price, availability and greenness we chose choline as cation and prepared a variety of ILs with anions, such as amino acids and phenol derivatives. All these ILs were tested on their CO₂ absorption capacity. Stability and viscosity were the two main qualities that we looked for in our ILs as this is important for further industrialization.

We obtained up to 20 weight percent CO₂ absorption in our ILs, which is among the highest reported in literature.
Solubility of perrhenate-containing ionic liquids and its influence on catalytic performance in liquid two-phase olefin epoxidation


Recently, imidazolium-based perrhenate-containing ionic liquids (ILs) have been demonstrated to be promising candidates as catalysts for olefin epoxidation with hydrogen peroxide as oxidant and cyclooctene as olefin.\textsuperscript{1} Depending on the length of alkyl substituents at the imidazolium ring, large differences in catalytic activity were observed. Solubility and partitioning effects are supposed to be a key to understanding these differences in catalytic activity since the reaction medium consists of four components (cyclooctene, H\textsubscript{2}O\textsubscript{2}, H\textsubscript{2}O, IL) that constitute two phases (aqueous and organic) at the onset of reaction. Moreover, for choosing an appropriate reactor design in view of a future technical application, identification of the reactive phase is a necessary prerequisite.

To elucidate the influence of solubility on activity and constitution of the reactive phase, three ILs are selected and their solubility in either H\textsubscript{2}O, 50\% H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O or cyclooctene and vice versa is determined at room temperature and reaction temperature (70°C). Contents are measured gravimetrically and via trace N analysis. Also, the partitioning behaviour in ternary mixtures of 50\% H\textsubscript{2}O\textsubscript{2}/H\textsubscript{2}O, cyclooctene and IL is investigated.

Both at room temperature and at 70°C, all ILs investigated show low, yet non-negligible miscibility with pure water. They are not soluble in cyclooctene whereas they readily dissolve small amounts of cyclooctene. H\textsubscript{2}O\textsubscript{2} has a strong miscibility-enhancing effect on the water-IL mixture, an effect that probably stems from those molecular interactions that are also responsible for catalytic activity. Our preliminary results on binary mixtures suggest that the aqueous phase is the reactive phase. Research on ternary mixtures is still ongoing and results are going to be presented as well. The differences with regard to catalytic activity exhibited by the ILs are discussed in the light of solubility and partitioning data.

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The aim of this study is the extraction of Iris pallida rhizomes, with choline-based ionic liquids (ILs). The iris butter obtained from iris rhizomes is one of the most luxurious raw materials for perfume industry (approximately €15000/kg). The attractive violet-like fragrance is due to irones formed by oxidative degradation of iridals during rhizome aging. Steam distillation is a relatively long process to obtain the desired product. The yield is low of the already small amount of only 0.1 up to 0.2 % iris butter in the rhizomes. Other extraction methods like solvent extraction are often associated with flammable and critical solvents. Extraction with biocompatible and biodegradable choline alkanoates allows a simple, efficient and mild isolation of the fragrance compounds from iris rhizomes.

Various aqueous solutions of ILs with choline as cation and butanoate or hexanoate as anions are studied varying the particle size of the rhizomes, the extraction temperature, the solid-liquid ratio and the concentration of each IL solution. The yield of irones is determined via HPLC-UV. Choline hexanoate as extracting agent seems to be nearly as efficient as ethanol. The increasing chain length of ILs influences the extraction yield: the longer the chain length the higher the amount of extracted irones. In addition, a different selectivity between the two ILs is observed: choline hexanoate shows a greater extraction efficiency of nonpolar constituents, while choline butanoate extracts more polar compounds.
Encapsulation of grape pomace extract in modified starch using SFEE process

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Grape pomace presents a high content of phenolic compounds, which are associated with health benefits. The use of polymers to encapsulate the extract can prevent adverse reactions such as oxidation of functional substances. The high-pressure technology is emerging as an alternative process for particle formation and encapsulation in a polymer coating. In this filed, a new promising technology is represented by the use of supercritical fluids in combination with nano-emulsions, the Supercritical Fluid Extraction of Emulsions (SFEE), which presents advantages over these two separated technologies. SFEE consists in extracting the organic solvent from the droplets of an oil-in-water emulsion by using CO₂, obtaining a particle suspension. The focus of this work was to study the SFEE process, focusing to protect/stabilize the grape pomace extract biologically active components. The extract was obtained by soxhlet with ethanol. The crude emulsion was prepared with 12.5 mg_extract/mL, 30 mg/mL of modified starch (Hi Cap 100, National Starch), 85% of water, 15% dichlorometane and Tween-20. The dispersed crude emulsion was fed into a ultrasound mixer and processed over 4 min. The SFEE process used 99.9% pure CO₂ as anti-solvent fluid, and it was employed at 40 °C, 110 and 140bar, 1kgCO₂/h, 1 and 2mL_emulsion/min. The droplet size of emulsion and particle size of suspension was measured using dinamic light scatering (DLS). The suspension obtained was dried in a spray dryer. Dried particles were evaluated by morphology and size, using scanning electronic microscopy (SEM), and by thermal profile throughout differential scanning calorimetry (DSC). DLS showed nanoparticles in suspension. After the drying process, SEM results revealed spherical shaped particles with diameters next to 50μm. DSC analysis showed a slight change in the thermal profile, in comparison with the pure modified starch, suggesting effective encapsulation of the grape pomace extract.
Phase equilibria of grape pomace extract pseudo-quaternary system applied in the selection of SAS process parameters

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Large quantities of grape pomace, poliphenol rich residues, are misspent after wine production. High pressure co-precipitation techniques may be used to preserve the biological activities of grape pomace extracts by avoiding its contact with environmental oxygen and light, preventing oxidation and degradation processes. Phase equilibrium data knowledge is very important for the proper choice of operational parameters of high pressure procedures involving multicomponent systems. Therefore, this work aims to study the phase equilibria behavior of the system: grape pomace extract of Merlot variety + ethyl acetate + carbon dioxide in order to establish operational parameters to be used in future Supercritical Anti-Solvent precipitation assays (SAS). Grape pomace extract was obtained by the soxhlet method with ethanol as solvent and studied in the concentrations of 2, 4 and 6 mg\text{extract/ml} in the feed solution, together with poly(lactic-co-glycolic acid) (10 mg/mL) and ethyl acetate. Static method was employed using carbon dioxide compositions from 83.3 to 97.5%, and temperatures of 35, 40 and 45°C. For 2 mg\text{extract/ml} assays, no presence of solid-liquid-vapor or liquid-liquid equilibrium were observed. Therefore, pressures may be chosen preferably to guarantee a single phase equilibrium to avoid particle freezing and agglomeration that may happen in some cases (above 86.9 bar at 45°C, 83.3 bar at 40°C and 75.5 bar at 35°C), using high fractions of CO\textsubscript{2} to guarantee the anti-solvent effect. For 4 mg\text{extract/ml}, suggested conditions include the use of a CO\textsubscript{2} fraction below 95% to avoid the liquid-liquid transition region that appeared at 40 and 45°C and above 88% to avoid the presence of solids. The complex behavior presented by the diagram for 6 mg\text{extract/ml}, with occurrence of solid-liquid-vapor equilibrium and liquid-liquid equilibrium in most of CO\textsubscript{2} fractions studied suggest that the use of this higher extract concentration should be avoided.
Life in hydrocarbons: membranes and vesicles in non-aqueous systems

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Life on Earth has developed based on cell membranes composed by amphiphilic molecules with a polar head and long hydrocarbon chains; in aqueous systems these are able to assemble in a bi-layer and are therefore suitable to mediate transport of chemical species from one side to the other. The purpose of this work is to mimic aqueous membranes, with the difference that the proposed membranes will be designed to assemble in a lipophilic hydrocarbon environment[2]. These self-assembled membranes are to be formed by “dual” amphiphilic molecules with a non-polar head and one or two polar tails.

We have synthesized different new amphipiles, possessing PEG tails and lipophilic heads, and we have studied aggregate formation using dynamic light scattering (DLS).

Once these membrane structures will be available, they will be further used to mimic trans-membrane transport by insertion in the membrane of tailor-made trans-membrane protein analogs, with appropriate dimensions and structure for solute transport.

Figure 1: Reverse membranes

References:
Selective Hydrogenation of 1,3-Butadiene – Improving the Selectivity to Butene with a Solid Catalyst with Ionic Liquid Layer

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Catalytic hydrogenations are important reactions for refinery processes and the fine chemical industry. During the selective hydrogenation of 1,3-butadiene, the formation of the end product butane is almost inevitable. Using the concept of a Solid Catalyst with Ionic Liquid Layer (SCILL) [1] the selectivity to the desired intermediate butene could be enhanced enormously ($S_{\text{butenes}} > 99\%$) at full conversion. Therefore a conventional hydrogenation eggshell catalyst (0.3 wt.-% Pd on Al$_2$O$_3$) was coated with a thin layer of ionic liquid (IL, 1,3-dimethylimidazolium dimethyl phosphate ([DMIM][DMP])). The pore filling degree $\alpha$ amounts to 0.16 ($\alpha=V_{\text{IL}}/V_{\text{pore,0}}$). The remarkable selectivity cannot entirely be attributed to differences in solubility of both, diolefin and olefins in the IL as shown in earlier studies [2]. We assume that adsorption largely affects the selectivity pattern, as shown in the literature for butadiene hydrogenation on Palladium and Platinum surfaces [3]. With a SCILL-catalyst, the IL has to be considered, and competitive adsorption of IL, butadiene and butene occurs on the metal surface: on the Pd-SCILL-catalyst, butadiene replaces the ionic liquid, adsorbs and reacts to butene. Once butene is formed, the IL drives the olefin of irreversibly resulting in no butane formation. On the Pt-SCILL-catalyst, hydrogenation is inhibited indicating that the ionic liquids prevent the adsorption of both olefins.

Hence, the affinity of [DMIM][DMP] to the support and active metal was investigated. Here, the ionic liquid was dissolved in dichloromethane, mixed and agitated with support/active components. The ionic liquid content in solution was analyzed before and after the experiment. From this data, adsorption isotherms were plotted for various supports and active metals. The IL [DMIM][DMP] shows interaction with the supports and both active metals, Pd and Pt. However, the IL interacts stronger with Pt than Pd. These results are consistent with the hydrogenation of 1,3-butadiene on Pd- and Pt-SCILL-catalysts and support the assumption of competitive adsorption.

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Polyalphaolefin synthesis with Liquid Coordination Complexes

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Liquid coordination complexes (LCCs) are a new class of liquid Lewis acids, synthesised by solventless mixing of an organic donor molecule (phosphines, phosphine oxides, ureas) and an excess of metal halide (AlCl₃ or GaCl₃).¹ The product is a liquid, containing equilibrated cationic, anionic and neutral complexes of the metal. When the molar ratio of metal chloride is greater than \( \chi \chi_{\text{MCI}_3} > 0.5 \), the LCC contains strongly Lewis acidic anions, \([\text{M}_{2}\text{Cl}_7]^-\). Very low cost and ease of preparation make LCCs exciting alternatives to ionic liquids in homogenous Lewis acid catalysis. Polyalphaolefins (PAOs) are high-performance synthetic lubricants used in automotive and industrial applications.² In the industry, they are made via carbocationic oligomerisation of 1-decene, catalysed with a BF₃/n-BuOH system,³ followed by hydrogenation. In this contribution, LCCs were used as safer and economically viable alternative to the BF₃ system. A range of LCCs, based on GaCl₃ or AlCl₃ with a range of ligands have been studied, at different reaction conditions. The key parameters affecting products distribution were identified, facilitating fine-tuning of the products distribution. Oligomers distribution suitable for the PAOs manufacture were obtained. The optimised process was scaled up, the products were distilled into fractions and blended to access marketable PAO grades. The essential properties, such as kinematic viscosities, viscosity index and pour point were found to comply with those required for industrial base oils.

Hydrogen-Bond-Rich Ionic Liquids as Effective Organocatalysts for Diels–Alder Reaction

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The possibility of using a renewable and relatively inexpensive starting material, such as D-glucose, as the target ionic liquid cation precursor was investigated in this study. In addition, chloroalcohols served as a source of hydroxyl groups for the construction of the ionic liquid cation. The resulting ionic liquids were liquids at room temperature because of the presence of the weakly coordinating bistriflimide anion. The physicochemical properties of the studied ionic liquids were determined. The thermogravimetric analysis results revealed that the ionic liquids are thermally stable at temperatures up to 430 °C. The resulting ionic liquids are able to create a large number of hydrogen bonds and were used in the Diels–Alder reaction of cyclopentadiene and diethyl maleate. The first approach used equimolar amounts of the ionic liquid with respect to the amount of dienophile, and showed high activity for the studied ionic liquids. The new D-glucose-based ionic liquids were as active as the metal catalyst with respect to the reaction rates but were significantly more active than the other ionic liquids tested. The endo selectivity was high in all cases (around 13). Similar results were obtained when methyl acrylate was used as the dienophile. Encouraged by the successful outcome of the Diels–Alder reaction with hydrogen-bond-rich ionic liquids, we decided to use catalytic amounts (4 mol% with respect to the dienophile) of the ionic liquids as organocatalysts. With this approach, only the D-glucose-based ionic liquids and the tetraalkylammonium ionic liquid with two –OH groups maintained their high activity. The catalytic system proved to be active in the Diels–Alder reaction of various dienes and dienophiles carried out in the presence of the most active D-glucose-based ionic liquid.

Literature


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Supported ionic liquids phase technology: application in gas phase ethylene methoxycarbonylation

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Supported ionic liquid phase (SILP) technology consists in an ionic liquid (IL) film immobilize on a porous solid material (e.g. silica) and a homogeneous catalyst dissolved in a supported IL layer (Figure 1). SILP is the perfect combination of the benefits of both homogeneous catalysts allowing high activity and selectivity and heterogeneous catalysts due to the large interfacial reaction areas and good product separation. Indeed, SILP catalysis has potential for efficient catalyst recycling and it makes possible the application of homogeneous catalysis in fixed-bed reactor technology. Furthermore, the resulting ionic liquid catalyst film is only a few nanometers thick allowing the complete utilization of both ionic liquid and catalyst since the mass transport resistance from the gas into the liquid phase is minimized compared with the biphasic systems where ILs are employed as reaction media [1]. In addition, the very low vapor pressure of ionic liquids makes these catalytic systems optimum to be used in continuous gas-phase processes minimizing the catalyst deactivation [2].

Figure 1. SILP catalysis technology

In this work, it is reported the application of the SILP catalysis technology to the continuous gas-phase methoxycarbonylation of ethylene for methylpropanoate (MP) production where MP is an essential monomer in the industrial production of the highly world demanded methylmethacrylate (MMA). A screening of the influence of different reactions parameters such as, ionic liquid loading, nature of the support, metal loading, temperature, GHSV (h⁻¹) etc, in both catalyst activity and selectivity has been performed.

Borenium Ionic Liquids: Lewis Superacids

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Boron trifluoride, due to its high Lewis acidity and relatively low price, is an industrially important catalyst. However, its toxicity, corrosiveness and high fluorine content inspire the search for more sustainable alternatives.\(^1\) Lewis acidic ionic liquids have been used in catalysis for the past few decades (Friedel Crafts processes, oligomerisation, isomerisation of hydrocarbons), but their Lewis acidic sites have been, effectively, structurally limited to halometallate anions.\(^2\)

In this contribution, a new class of Lewis acidic ionic liquids is presented. They are prepared in a two-step reaction; the formation of a tetracoordinated boron intermediate/complex as shown in Equation 1, followed by halide abstraction to release the three coordinate borenium cation, \([BX_2L]^+\), following Equation 2.

\[
\begin{align*}
BX_3 + L &\rightarrow [BX_3L] \quad \text{Equation 1} \\
[BX_3L] + MX_3 &\rightarrow [BX_2L][M_nX_{(3n+1)}] \quad \text{Equation 2}
\end{align*}
\]

Lewis acidity of these ionic liquids has been quantified by Gutmann Acceptor Number. Recorded AN values up to 180 are among the highest ever measured, placing these materials among Lewis superacids (Fig. 1). Aspects of the design, synthesis, Lewis acidity measurements and catalytic reactions will be presented.

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A silver ionic liquid for olefin/paraffin separation

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Silver containing liquid membranes show significant technical potential for the separation of olefins and paraffins. Their selectivity towards olefins is based on the selective and reversible $\pi$-complexation of the olefins by the silver cation. Often employed silver salt ionic liquid solutions, e.g. Ag[NTf$_2$] in [EMIM][NTf$_2$]$^{[1]}$, Ag[TfO] in [EMIM][TfO]$^{[1]}$ or Ag[BF$_4$] in [BMIM][BF$_4$]$^{[2]}$, however, have one disadvantage: the dilution of the silver salt and therefore a decrease in the silver carrier concentration.

Here, we present the neat silver ionic liquid [Ag(C$_3$H$_6$)$_y$][NTf$_2$], which offers a possibility to overcome this drawback. [Ag(C$_3$H$_6$)$_y$][NTf$_2$] combines a high silver ion concentration with the positive properties of ionic liquids.$^{[3][4]}$

[Ag(C$_3$H$_6$)$_y$][NTf$_2$] can be synthesized starting from silver(I)oxide and bis(trifluoromethylsulfonyl)imide:

$$\text{Ag}_2\text{O} + \text{H}[\text{NTf}_2] \xrightarrow{\text{H}_2\text{O}} \text{Ag}[\text{NTf}_2] + \text{H}_2\text{O}$$

Solid Ag[NTf$_2$] liquefies in contact with propene, forming the room temperature ionic liquid [Ag(C$_3$H$_6$)$_y$][NTf$_2$]:

$$\text{Ag}[\text{NTf}_2] + x\text{C}_3\text{H}_6 \xrightarrow{} [\text{Ag}(\text{C}_3\text{H}_6)^x][\text{NTf}_2]$$

Besides the physicochemical characterization of [Ag(C$_3$H$_6$)$_y$][NTf$_2$], propene and propane uptake were determined up to 5.5 bar from the pressure drop in a pressurized steel autoclave. Furthermore, quantitative $^1$H NMR and $^1$H NMR diffusion measurements were performed at different partial pressures of propene and propane to predict the ideal membrane selectivity according to the solution-diffusion model.

References
Towards the “green membrane” preparation with non-toxic solvents

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Nowadays, membrane systems represents an environmentally friendly, future-oriented, development and implementation of the traditional separation processes. However, some drawbacks, mainly related to membranes manufacture, still prevent to completely define this technology as green. In fact, commonly used preparation procedures, i.e. non-solvent/temperature induced phase separation methods (NIPS/TIPS, respectively), are based on the use of very toxic solvents, such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methyl-2-pyrrolidone, and phatalates. The replacement of hazardous solvents with non-toxic alternatives, in accordance with the 5th principle of Green Chemistry (“Safer solvents and auxiliaries: the use of auxiliary substances (e.g., solvents, separation agents, etc.) should be made unnecessary wherever possible and innocuous when used“) [1], represents the key factor for the “green membrane” preparation in the near future [2]. The choice of the proper substitute should be focused on its ability to solubilize the selected polymer and evaluating its toxicity for human health. Several solvents, such as methyl and ethyl lactate, ionic liquids, citric acid esters triacetate ester of glycerol, supercritical carbon dioxide etc., should represent valid alternatives to the hazardous, commonly used, diluents and should open new perspectives for the sustainable membrane production [2].

Towards the green biofuels and solvents production by SCWG process

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The aim of the paper is the biomethane production from wet biomasses, such as manure, livestock wastes and/or other types of wastes (from wet agricultural to municipal waste biomasses), through a pressurized anaerobic digestion (PAD) process coupled with membrane upgrading system and supercritical water gasification (SCWG) in order to recovery the energy content in the digestate. In comparison to conventional AD processes, the innovative procedure promotes a more flexible use of biogas through a new technology path. In fact, this technology allows to obtain the biomethane production at low-pressure (5-10 bar) and to use the digestate for power production in steam cycle. Moreover, it leads to biofuels production via supercritical water gasification in order to produce high pressure biomethane (>200 bar) and liquid solvent, such as acetic acid which is usable in the green chemistry. Simulation results based on experimental tests were carried out to understand the main advantage of this approach. Using this new technology is possible to produce biogas to 10-15 bars with >90\% CH\textsubscript{4}-content in a single reactor with minimal methane dissolution and to recover the carbon dioxide solubilized in the digestate stream for the production of liquids and gaseous biofuels. This promising technology is almost zero emission process ensuring a CO\textsubscript{2} recovery of about 0.4-0.5Nm\textsuperscript{3} for each cubic meter of biogas produced that is converted for biofuels production. The overall approach supports the economic sustainability starting from the energy self-sustainment that will utilize power and heat produced through the by-products of the integrated methodology.
The fabrication of RuO$_2$/C in supercritical water for Li-O$_2$ battery

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Li–O$_2$ batteries, possessing a capacity 5–8 times higher than that of Li-ion batteries, are considered promising candidates for electric vehicles.

We built porous graphite-like carbon layers, and loaded RuO$_2$ nanoparticles on it in supercritical water. Thanks to supercritical condition, the RuO$_2$ nanoparticles with an average size of about 2 nm are uniformly distributed on the surface of carbon layers. What’s more, RuO$_2$ nanoparticles can be filled into the layer spacing although the spacing is only 2 nm.

Overpotentials are decreased decently by RuO$_2$ catalytic effect. The porous channels and layered structure of the RuO$_2$/C facilitated the electrolyte immersion and Li$^+$ diffusion and provided an effective space for O$_2$ diffusion and O$_2}$/Li$_2$O$_2$ conversion, which effectively enhanced the electrochemical performance of the Li–O$_2$ batteries.

![Figure 1](image)

Figure 1 The SEM of (a) RUB-15 silicate and TEM image of (b) carbon layers (c) RuO$_2$/C composite
Novel Electrolytes for Supercapacitors

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Supercapacitors (also known as electric double layer capacitors (EDLCs)) provide several exceptional properties like a remarkable high power density, long operational life, the ability to be charged and discharged within seconds, and a reliable performance even at extreme temperatures.\textsuperscript{i, ii}

Common supercapacitor electrolytes are using formulations with organic solvents, which leads to drawbacks like a significant vapour pressure at high temperatures and the risk of flammability. In this regard, new electrolytes based on ionic liquids (ILs) are promising alternatives.\textsuperscript{iii} ILs provide large electrochemical stability (Fig.1 ), which can be directly correlated to the EDLC capacity, high thermal as well as chemical stability and negligible vapour pressure. They are incombustible and liquid over a wide temperature range and can be designed to be biodegradable.\textsuperscript{iv}

Fig.1 Electrochemical Stability of BMPyrr BTA

In this presentation we will report on our recent developments in the field of electrolytes for supercapacitors based on ionic liquids. The focus of the talk will be on the development of new kind of cations and anions as well as on the utilization of eutectic mixtures in order to increase the performance at low temperatures and the safety of EDLCs in general.

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