BOOK OF ABSTRACTS

19 – 22 October 2014
Hotel Elbflorenz · Dresden · Germany

7th Green Solvents Conference
Advanced Fluids in Science and Application

www.dechema.de/gsfs2014
Lectures
Old Solvents – New Solutions

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Solvents have played a central role in Green Chemistry since its inception, particularly because, once used, solvents can contribute so much to the waste from a process. Furthermore, many conventional solvents are toxic have potentially high environmental impact. Therefore it is not surprising that this series of Dechema conferences has made a significant impact on how Green Chemists view the use of solvents ever since the first conference in Bruchsal in 2002.

The great strength of Green Chemistry is that it represents a partnership between industry and researchers in academia, focussed on delivering cleaner, environmentally more acceptable processes for making chemicals and materials. The closeness of this partnership means that academic researchers need to be sensitive to changes in the global chemical industry. Recently, there has been an increasing awareness of sustainability in chemical processes but, at the same time, the availability of low cost shale gas has transformed the commercial attraction of conventional hydrocarbon feedstocks, especially in the United States.

Although this series of conference has often focussed on the so-called “neoteric solvents”, particularly supercritical fluids and ionic liquids, the aim of this lecture is to suggest that we should not overlook the possibilities of using more traditional solvents in new ways. I shall do this by giving some recent examples of work from our laboratory showing how conventional solvents can be manipulated to simplify separation of products and recycle of catalysts.

I thank the EPSRC, Lucite, INVISTA, Sanofi, the EU SYNFLOW project and the University of Nottingham for supporting our research. I am particularly grateful to my colleague Professor Mike George for countless years of fruitful collaboration and scientific partnership in research. Finally, I thank all of our students, postdocs and collaborators who have contributed to the research described in the lecture, and all of our technicians whose skills have contributed so much to the success of the experiments.
The history of ionic liquids (ILs) effectively started in 1914, when the physical properties of ethylammonium nitrate ([CH₃CH₂NH₃⁺][NO₃⁻], m.p. 13-14 °C) were first reported. ILs are generally defined as salts composed of discrete cations and anions with melting points below 100 °C, and many are liquid at ambient temperature. IL research has grown rapidly over the past decade due to the realization that these materials have many unique properties such as negligible vapor pressure and outstanding solvation potential. Ionic liquids have been further emphasized by the fact that their physical and chemical properties can be finely tuned by varying both the cation and anion.

Our research has focused on accurately measuring vapor-liquid equilibria (VLE) and vapor-liquid-liquid equilibria (VLLE) and using thermodynamic models to understand the phase behavior of binary gas mixtures in ILs. This presentation will focus on the importance of characterizing the global phase behavior of gases in ionic liquids and how this can provide insight into new applications. Solubility measurements of several gases in ILs will be discussed and important experimental details regarding VLE measurements using a gravimetric microbalance and VLLE measurements using a mass-volume technique will be highlighted. VLE data have been successfully correlated with a modified Redlich-Kwong equation of state (EOS), and in certain cases (e.g. hydrofluorocarbons) the EOS predicts partial immiscibilities (LLE) with lower critical solution temperatures (LCSTs) in the fluorocarbon-rich side solutions. We have also found that gases such as CO₂ can exhibit different solubility behaviors in ILs (i.e. physical and chemical absorption) and that these behaviors can be analyzed with the EOS using a simple association model and excess thermodynamic functions.

Knowledge of gas and IL phase behavior has led to several practical applications including separation of azeotropic gas mixtures, removal of CO₂ from flue gas and new fluid pairs for absorption cooling. These along with other interesting examples from the literature will be discussed.
Due to their beneficial ecobalance,\(^1\) CO\(_2\)-based polyethercarbonate polyols attract increasing interest of the industry as an alternative to conventional polyether and polyester polyols, which are currently used for manufacturing polyurethanes. The properties of the polyols, such as molecular weight, CO\(_2\)-content and functionality have significant influence on elasticity, rigidity, curing rate and thermal stability of the polyurethane products.\(^2\)

The properties of the polyurethane product can be tuned by adjusting the molecular structure of the polyols. In this study, we aim to synthesise and study polyethercarbonate polyols varying in architecture and functionality (Figure 1).

![Graphical representation of polyethercarbonate polyol architectures and functionalities (f).](image)

During the synthesis of such polyethercarbonate polyols with different architecture, we identified surprising effects of the CO\(_2\)-expanded reaction medium on the rate and selectivity of the double metal cyanide (DMC) catalysed reaction between the reagents CO\(_2\) and epoxides. Closer investigation of the properties of the polyols revealed astounding structure-property relationships between the molecular architecture and physico-chemical parameters such as viscosity, diffusion-coefficients, thermal stability and the reactivity of the terminal OH-groups. Besides the very good accessibility of the terminal end-groups in symmetric polyols, giving rise to high curing rates in polymer applications, there are also surprisingly differences in viscosity in dependence of the architecture, which can be linked to the diffusion rate of the molecular entities.

Aqueous Formaldehyde for Homogeneous H₂ Production

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An intensively studied fuel molecule is H₂ owing its energy content which is interesting for new energy storage systems based on molecular compounds like methanol or formic acid.⁹¹,² Interestsingly, formaldehyde (FA) has never been studied for H₂ storage, although the H₂ content is high and it forms a stable diol in aq. solution. Similar para-FA is also suitable for molecular H₂-storage as these molecules can be easily and selectively dehydrogenated forming pure H₂ and CO₂.³ A novel water-stable molecular catalyst under base-free conditions is capable to produce H₂ at low temperature. Isotope-labelling experiments (²H, ¹³C and ¹⁸O) confirm that the H₂ released originates from both, H₂O (H₂¹⁸O or D₂O) and H₂CO (²H and ¹³C-labelled), and the isotopes are confirmed in the gaseous (online) and liquid products (in situ) as well as in the catalyst (isolated and in situ). A theoretical efficiency of 8.4 wt% of H₂ considering 1 eq. H₂O and H₂CO is possible, this is higher than for formic acid (4.4 wt%), even when technical FA (H₂-cont.: 5.0 wt%) is used. This catalytic decomposition of H₂CO can be envisioned for simultaneous H₂ production and decontamination of wastewater with FA impurities – a waste to value approach.

References
Sponge-Like Ionic Liquids: Switchable green solvents for biocatalysis and extraction

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Sponge-Like Ionic liquids (SLILs) are hydrophobic ILs based on cations with long alkyl side-chains, e.g. octadecyltrimethylammonium bis(trifluoromethylsulfonyl)imide, ([C18tma][NTf2]), which behaves as sponge-like systems by switching from liquid to solid phase with temperature. Based on this new property, the SLILs have been used to develop straightforward and clean approaches for extraction and synthesis of nearly pure compounds of added value (e.g. geranyl acetate, anisyl acetate, biodiesel, etc).

As liquid phases, the SLILs are able for dissolving (soaking) hydrophobic compounds at temperatures compatible with enzyme catalysis (e.g. vegetable oil and methanol mixtures are monophasic in [C18mim][NTf2] at 50°C). The resulting monophasic systems showed an excellent suitability for carrying out lipase-catalyzed esterification and transesterification reactions. For example, the lipase-catalyzed methanolysis of triolein in [C18mim][NTf2] at 60°C results in fast and efficient biodiesel synthesis, i.e. up to 100% yield in 8 h at 60°C, with exceptional enzyme stability (up to 1370 d half-life time at 60°C). As another example, Novozym 435-catalyzed the direct esterification between an aliphatic carboxylic acid (acetic, propionic, butyric or valeric) and a flavour alcohol (isoamyl alcohol, nerol, citronellol or geraniol) in the [C16tma][NTf2] SLIL, obtaining near to 100 product yield (up to 0.757 g/mL product concentration) for 4 h at 50°C. For the case of the anisyl acetate fragrance, a 100% esterification product yield was obtained for 1 h at 50°C under microwave assistance.

As solid phases by cooling the reaction mixture under room temperature, the system can be fractionated by releasing (wringing) products from the SLIL using iterative centrifugations, which resulted in two phases: a solid SLIL phase and a liquid phase containing synthetic products (flavour esters, biodiesel, etc), being facilitated by using centrifugal filters (see Fig. 1). For the biodiesel production case, the addition of water into the liquid reaction mixture resulted in a three phase system after the centrifugation/separation step, i.e. solid SLIL (bottom), aqueous phase containing glycerol (middle), and pure biodiesel phase (top phase, see Fig. 1), demonstrating the suitability of this green approach for producing biodiesel of easy scaling-up.

References.

Acknowledgements. Work partially supported by MINECO, Spain (Ref: CTQ2011-28903), and SENECA Foundation, Spain (Ref: 08616/PI/08) grants
Enabling Technologies for Organic Synthesis- New Opportunities with Flow Reactors and Inductive Heating

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Recently, magnetic nanoparticles\(^1\) have gained considerable interest in different areas of chemistry. On the other hand, meso and micro reactors have found widespread interest in organic synthesis as an enabling technology to perform reactions more efficiently.\(^2\) But, there is still a quest for efficiently heating mesofluidic devices.

In order to combine the interesting features of such nanoparticles with flow synthesis we showed for the first time, that those particles can efficiently and very rapidly be heated by an inductive magnetic field.\(^3\) When serving as fixed bed material composed of an iron oxide core and a silica shell inside a flow reactor the reactant stream can be rapidly heated to well above 300°C. The particle architecture allowed us to immobilize catalytic species on the nanoparticle surface and e.g. perform palladium catalysed transformations.\(^4\)

The report presents the latest applications in this newly emerging field, covering organic reactions, reactor and system design as well as heterogeneous catalysis. It will provide a critical view on scopes and limitations of inductively heatable nanoparticles as fixed bed material.

Literature

Solvent free synthesis of $\gamma$-valerolactone and its use as a green reaction media for catalysis

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Due to its outstanding physical and chemical properties, $\gamma$-valerolactone (GVL) can be considered as a sustainable liquid and used for the production of both energy and carbon-based chemicals [1]. Since the most effective protocol to manufacture GVL is the selective hydrogenation of levulinic acid (LA), we have developed a recyclable sulfonated-tertiary and bidentate phosphines-modified Ru catalyst systems that can quantitatively convert LA, which was obtained by dehydration of fructose to GVL under solvent and additive free conditions (Scheme 1) [2].

Recently it was also revealed, that GVL and its ionic liquid (IL) derivatives can be used as a "green" reaction media for catalytic transformations [3]. We have demonstrated the successful utilization of GVL based ILs as catalyst phase for selective hydrogenation of olefins having various functional groups in the presence of [Rh(cod)$_2$][BF$_4$]/RP(C$_6$H$_4$-m-SO$_3$Na)$_2$ ($R =$ Me, Pr, Bu, Cp) catalyst [3b].

Our contribution will show the catalyst design and development for production of GVL including synthesis of its optically active form. The characterization (vapor pressure, viscosity, thermal stability) and application of GVL based ILs as alternative solvents for catalytic transformation e.g. hydrogenation and transfer hydrogenation, hydroformylation, metathesis etc will be presented as well.

Possibilities for valorization of biomass resources in supercritical methanol and other bio-derived solvents

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This contribution outlines recent efforts in our laboratories addressing the effective utilization of carbon–neutral and renewable lignocellulosic biomass or derived platform chemicals without the formation of intractable side products. The valorization of highly functionalized biopolymers requires new catalytic approaches. Moreover, the solid nature of biomass feedstocks necessitates careful selection of reaction media. In this regard, supercritical solvents may play a crucial role.\[1\]

First, briefly, a catalytic system will be presented, whereby cellulose[2], organosolv lignin[3], and even lignocellulose[2] are transformed into organic liquids. The reaction medium is supercritical methanol (sc-MeOH), while the catalyst is a copper-doped porous metal oxide (PMO). This catalyst serves multiple purposes, catalyzing substrate hydrogenolysis[4], hydrogenation and methanol reforming. Notably, the reducing equivalents needed for the diverse reductions are derived by the reforming of the solvent, which thereby serves as a “liquid syngas”. The one-pot conversion of biomass in this system is quantitative, giving little or no biochar residual.

Further, the tunable and selective conversion of 5-hydroxymethyl-furfural will be discussed using a Cu-doped PMO and other types of catalysts in ethanol at various reaction temperatures with added H\textsubscript{2} gas.\[5\] At milder reaction temperatures 2,5-furan-dimethanol can be obtained in up to 97% isolated yield. Notably this transformation can also be performed in a continuous setup where 1.5 g HMF is converted using 0.3 g catalyst. Higher reaction temperatures (220 °C) favour selective deoxygenation to 2,5-dimethylfuran (DMF) and 2,5-dimethyltetrahydrofuran (DMTHF) with a combined yield as high as 81%. Notably, high product yields are maintained at substrate concentration up to 10 w% and low catalyst loading. The reaction intermediates formed at different temperatures are identified. This provides mechanistic insight into the nature of reduction pathways and possible competing ring opening processes, which influence product selectivity.

Finally, the use of Cu-PMO catalyst in the upgrading of sugar fractions of pyrolysis oils will be presented.\[6\] The advantage of the reported methodology is, that it enables the clean conversion of the complex set of substrates present in the sugar fraction to aliphatic mono-alcohols (50.8%), diols (21.6%), esters (16.1%), ethers (8.6%) and furanics (2.8%). Similar product suite is obtained by converting concentrated, 15 wt% sugar fractions in scEthanol, however catalyst stability needs to be addressed in this case. These product mixtures with improved H/C ratios, would be significantly better suited for direct co-feeding into methanol to hydrocarbon processes utilizing zeolites.

Immobilization of Pd-NHC complexes on inorganic supports
Activity and reusability in C-C coupling reactions

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Recent reports have described the successful use of para-alkoxy-functionalised N-heterocyclic carbenes as ligands in Pd-catalyzed cross-coupling reactions.\(^1\)\(^,\)\(^2\) In this work we describe a very general and straightforward procedure for the attachment of Pd-NHC complexes onto the surface of MCM-41, γ-Al\(_2\)O\(_3\) and TiO\(_2\). Alkoxy functionalization at the aryl para positions of the imidazolium preligands is used as a handle to introduce triethoxysilyl groups, suitable for condensation with hydroxyl groups present on the surface of the inorganic solids. Characterization of the solid-supported Pd complexes of these ligands was followed by the study of their catalytic performance in Suzuki-Miyaura, Heck and Sonogashira couplings. Recyclability studies are also presented here.

Catalytic activation of carbohydrates in deep eutectic solvents
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Introduction of carbohydrates in chemical processes has dramatically changed the way how to design a catalytic process. Among the different strategies that are under investigation, the search of alternative solvents for the catalytic conversion of carbohydrates has become of growing interest. In this context, the so-called “deep eutectic solvents” (DES) are now receiving a great deal of attention. DESs are obtained by simply mixing two components that are generally safe and biodegradable and capable of auto-associating together, often through hydrogen bond interaction, to form a liquid phase.¹ Hydrogen bond donors such as carbohydrates, renewably-sourced carboxylic acids, polyols are generally used in combination with a hydrogen bond acceptor, often choline chloride.

In this keynote, we wish to discuss the remarkable potential of DESs for the catalytic conversion of carbohydrates to furanic derivatives. Beside their ecological benefit, we wish to demonstrate that DESs offer advantages that no other solvent can provide such as (1) conversion of highly concentrated solution of carbohydrates (up to 80 wt%), (2) assistance of acid catalyst and (3) synergistic effect with water. For instance, in the presence of safe and abundant metal chlorides such as AlCl₃ or FeCl₃, best systems were capable of converting glucose and even cellulose to 5-hydroxymethylfurfural with 70% and 50% yield, respectively, which is in a similar range than yields obtained with classical systems comprising of an imidazolium-based ionic liquid containing a chromium salt. Stabilization of furanic derivatives in and by DES as well as extraction issues will be also discussed. Finally, possible heterogeneization of DESs on a solid acid catalyst will be demonstrated as a feasible concept to facilitate the conversion of carbohydrates in low boiling point organic solvents. Whereas carbohydrates are not soluble in such organic solvents, we will pointed out that the coating of an acid solid catalyst by a DES allowed facilitating a better interaction carbohydrate/solid catalyst resulting in a significant catalyst activity enhancement of nearly 10 times as compared to non-coated catalyst.

Polyolefin Oligomers as Recyclable Solvents for Thermomorphic, Latent Biphasic, and Pseudo-Biphasic Reactions

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The work to be discussed in this presentation describes systems where polyolefin oligomers serve as nontoxic, nonvolatile hydrocarbon solvents, as phase anchors for homogeneous catalysts, and as anti-leaching agents for polyolefin oligomer-bound species including polyolefin-bound catalysts. In such systems, polyolefins that are low viscosity oils at room temperature or as melts at temperatures <100 °C serve as recyclable replacements for low molecular weight hydrocarbon solvents. For example, a polyethylene or polypropylene oligomer can replace hexane or heptane. In mixed solvent systems that have thermomorphic or latent biphasic properties, such solvent replacements serve as a recyclable nonvolatile alternative to heptane for recycling homogeneous catalysts. In other cases, such solvents can be used as cosolvents in batch type homogeneous reactions where a catalysts that is phase selectively soluble in heptane is used under pseudobiphasic conditions. Examples of reactions under thermomorphic, latent biphasic, or pseudo-biphasic conditions include ring closing metathesis, cross coupling chemistry, photoredox catalysis, allylic substitution chemistry, and cyclopropanation and O-H insertion chemistry, and polymerization chemistry. Finally, opportunities where polyolefin solvents recover catalysts or catalyst-ligand complexes as dispersions in in an unreactive solid polyolefin wax matrix at the end of the reaction will be discussed. In these cases, the solid polyolefin solvent as a wax protects the recovered catalyst or ligand from polar solvents and reagents.
Decomposition of Perfluorinated Ionic Liquid Anions Using Subcritical and Supercritical Water

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Ionic liquids (ILs) have been widely investigated for green chemistry applications. Furthermore, there has been increasing interest in electrochemical applications of ILs, mainly as electrolytes safer than organic solvents [1]. In particular, perfluorinated IL anions are being introduced in many electrochemical devices owing to their non-flammability, high thermal stability, wide electrochemical windows, high ion conductivity, and low viscosity.

Wider use of ILs will require that waste treatment be established. Incineration is one method for decomposing these chemicals. However, incineration requires high temperatures to break the strong C–F bonds, and hydrogen fluoride gas is formed, which can seriously damage the firebrick of an incinerator. In addition, these anions do not biodegrade under either aerobic or anaerobic conditions [2], which indicates that conventional microbial degradation process is not applicable for treatment of waste ILs. If perfluorinated IL anions could be decomposed to F⁻ by means of environmentally benign techniques, the well-established protocol for the treatment of F⁻ ions could be used, whereby Ca²⁺ is added to the system to form CaF₂, which is a raw material for hydrofluoric acid. Thus, the development of such a method would allow for the recycling of fluorine, the global demand for which is increasing.

In the present work, we investigated the decomposition of two typical perfluorinated IL anions, [(CF₃SO₂)₂N]⁻ and [(C₄F₉SO₂)₂N]⁻, in subcritical and supercritical water in the presence of oxidizing agent or reducing agent. We detail an effective methodology for the IL anions to F⁻ ions [3].

References
The use of biomass as a source of fuel is on the sharp increase. In parallel with this expansion, new chemical processes and technologies are required to improve efficiency, sustainability, and profitability. This paper explores three potential roles for ionic liquids in biorefineries that generate alcohols; as an extractant, reaction medium, and catalytic reagent.

Underpinning the potential of ionic liquids in this area is: 1. the ability of ionic liquids to solubilize polyols; 2. the facility to functionalise ionic liquids and tune properties; 3. the low volatility of ionic liquids.

Of particular focus is the potential for ionic liquids to facilitate combined biocatalytic and chemocatalytic routes from impure biomass to isolated value added chemicals;¹⁻⁴ and the potential of ionic liquids to be heterogenised in gels providing recyclable catalytic systems.⁵,⁶

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Self-Assembly and Immobilization of organic-inorganic hybrid CeO$_2$
Nanocrystals synthesized in supercritical hydrothermal condition

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CeO$_2$ nanocrystals (NCs) are of interest for oxygen storage materials. Especially, cubic shape CeO$_2$ nanocrystals, where (001) surfaces are exposed, exhibit higher oxygen storage capacity owing to their high chemical activity.

In this talk, synthesis of CeO$_2$ NCs in supercritical water will be a first topic to be mentioned. In order to disperse NCs at high concentrations for self-assembly on the substrate, those were modified with fatty acid during synthesis of NCs to produce organic-inorganic hybrid NCs. In supercritical water medium, high-density of self-assembled monolayer of fatty acid was formed on the surfaces of metal oxide core. Besides, {001} facets were selectively terminated with fatty acid because of high-affinity, yielding cubic shape CeO$_2$ NCs.

Then, reassembly of hybrid NCs during solvent annealing after self-assembly on the substrate at room temperature is discussed. Atomic force microscope (AFM) observation revealed that, after the solvent anneal in tetrahydrofuran (THF) at 40-80°C for 5-15h, hybrid NCs adsorbed on the substrate were rearranged to be more highly-ordered structures, where {001} facets of well-aligned NCs were attached to the surface. Grazing incident small-angle X-ray scattering (GISAXS) also revealed highly-ordered nanocrystalline structures macroscopically. However, when THF annealing had applied to the nanocrystalline monolayer, where the chemical bonds were established between hybrid NCs and the modified substrate by using local ligand exchange, no rearrangement had occurred during solvent annealing owing to immobilization.

Figure: AFM and GISAXS images of reassembled multi/monolayer after THF annealing.
Ionic Liquids as novel quenching medium for heat treatment of alloys

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Ionic liquids (ILs) have been tested for a wide range of applications. In a very few cases they have been able to substitute a volatile organic solvent. But during the last years they have been used more than a functional material to achieve a certain goal. Due to the large variation of anions and cations possible ILs can be specifically designed for every conceivable application.

In the heat treatment of metal alloys large amounts of a quenching medium are usually necessary to cool down the parts in the shortest possible time to obtain the desired amount of crystallinity and therefore hardness. On the other hand the cooling has to be gentle and uniform in order to avoid different temperatures in the parts leading to distortion. For quenching of metals mostly water as evaporating liquid is used. A major problem accompanying its use is the formation of an insulating vapor film on the surface of the part, which results in a slowing of the quenching. This special effect is the so called Leidenfrost-phenomenon. During the quenching process the vapor film breaks at different times and positions, which may lead to distortion of the part and residual stresses. To circumvent the drawbacks of evaporating liquids, various ionic liquids were investigated. Their advantage of the low melting point, in many cases below room temperature, and their extremely low vapor pressure, as well as their high thermal stability during short-term temperature stress makes them ideal quenching media [1].

The following results are presented:
• different ionic liquids are investigated as quenching media for heat treatment of metallic components, showing nearly no Leidenfrost-Effect [2, 3]
• ILs are able to provide a fast and homogeneous cooling
• varying compositions and bath temperatures ([EMIm][NTf₂],[EMIm][EtSO₄], with EtOH/ H₂O, at 30/60/85°C)
• stability of ionic liquids was detected by DSC, TGA [4], NMR, IR and elementary analysis

In addition to the quenching effect, investigations on short time and long-time thermal stability, costs, work safety and component cleaning of different ILs as quenching media were conducted.

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Solvent-controlled reactivity and selectivity profiles in carbon dioxide conversion catalysis

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In this contribution we will discuss the influence of (green) solvents on the reactivity and selectivity features of various organic transformations that involve carbon dioxide as a carbon reagent. The use of amino-triphenolate metal complexes has found to be critical to create success with challenging conversions of sterically congested oxirane substrates, internal epoxides and oxetanes into their cyclic organic carbonates.¹ ² The type of solvent was found to be crucial in a number of cases enabling improved reactivity (increasing TOF/h values) and controlling chemo-selective conversion of the oxirane derivatives (cyclic versus poly-carbonate formation).³

Of further importance is the development of a new organocatalyst system that shows unprecedented turnover frequencies (reactivity),⁴ and the vital role of the type of solvent to accommodate particular activation profiles creating more powerful catalysts for CO₂ conversion.

References:
The importance of proper solvent selection for synthetic efficiency in the pharmaceutical industry

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The impact of solvents on the environment, in terms of overall environmental footprint has long been understood. However, until recently, limited significant changes have occurred in the low volume industries and pharmaceutical industry especially. Research in this area has greatly accelerated in the last few years, whether in the form of process intensification and the reduction of solvents used, or the better selection and development of sustainable alternatives, which should soon more dramatically improve our environmental scorecard.

Our efforts in the field will be illustrated by a number of applied examples using sustainable alternatives, optimal syntheses and process designs, and future promising leads such as utilization of surfactants.
A new class of liquid materials with a very high metal content, Liquid Coordination Complexes (LCCs), has been recently developed by our group. It was demonstrated that the reaction of molar excess of $\text{MCl}_3$ (M = Al or Ga) with a donor (including $\text{O}^-$, $\text{S}^-$, $\text{P}^-$ or $\text{N}^-$-donors) under solventless conditions often yields mobile liquids (Fig. 1, left). Multi-technique spectroscopic studies demonstrated that under such conditions the donor molecule causes both homolytic and heterolytic cleavage of the ‘$\text{M}_2\text{Cl}_6$’ unit, which leads to the formation of LCCs containing neutral, cationic and anionic species, remaining in a dynamic equilibrium with each other (Fig. 1, right).

Like chlorometallate ionic liquids, LCCs have good thermal stability, wide liquidus range (>200 °C), conduct electricity and may be strong Lewis acids. However, unlike in chlorometallates, the metal coordination can be fine-tuned by varying the donor molecule. Furthermore, the need for an expensive organic cation is eliminated; LCCs are prepared in a one-step process, at nearly-ambient temperatures, from off-the-shelf donor molecules and common metal halides. Less expensive and easier to prepare than ionic liquids, they are a promising addition to the Green Solvents toolbox.

Here, we present the multi-technique spectroscopic studies that have led to the elucidation of LCCs speciation, followed by preliminary experiments demonstrating their applications in Lewis acidic catalysis.

Bifunctional nanoparticle-SILP catalysts (NPs@SILP) for the selective deoxygenation of biomass substrates

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We present the design of a bifunctional catalyst involving the stabilization of metal NPs on a supported ionic liquid phase (SILP) for the deoxygenation of biomass substrates. Our catalyst design involved the immobilization of an acid-functionalized ionic liquid on SiO$_2$ to provide an acid catalyst and a stabilization medium for ruthenium nanoparticles (Ru NPs). Integration of an acid and metal catalyst onto a support allow for a single catalyst to carry out the dehydration, hydrogenation and hydrogenolysis reactions required to deoxygenate biomass. Our bifunctional catalysts (RuNPs@SILPs) possess high catalytic activity, selectivity and recyclability in the deoxygenation of tetrahydrofuran substrates, derived from furfural and 5-hydroxymethylfurfural, to 1-octanol and 1-nonanol, respectively. Furthermore, RuNPs@SILPs provide a tunable catalytic system that allow access to tetrahydrofuran, alcohol and ether value-added chemicals from a single starting material.

References:
Sorbitol dehydration into isosorbide is an interesting option for the development of renewables both as chemical building blocks or energy carrier. ZnCl₂ hydrate seems to be an attractive solvent for this reaction.

A molecular modelling study was carried out to develop a better understanding of this complex reaction in the molten salt medium. Catalysis of sorbitol dehydration by ZnCl₂ most likely starts with complexation of the sugar alcohol functions to Zn, followed by an internal SN₂ mechanism of a secondary alcohol function attacking a primary alcohol function with the Zn-complex acting as a favourable leaving group. The dehydration reactions to 1,4- and 3,6-anhydrosorbitol show a very similar activation barrier in good accordance with experimental results. The same holds for the formation of isosorbide from 1,4- and 3,6-anhydrosorbitol, albeit with a slightly higher activation barrier. The relative level of the activation barriers reflects the increased strain in the sorbitol skeleton in the corresponding transition states. ZnCl₂ turns the dehydration reaction from an endothermic one to an exothermic one by forming a strong complex with the released water. Finally, the ZnCl₂–H₂O system has been compared with HCl–H₂O, which could have been an alternative; it, however, turned out not to be the case.
Switchable Hydrophilicity Solvents and Switchable Water

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Since the invention of switchable solvents in 2004, the author’s group and collaborators have been developing the concept\(^1\) to ensure that such solvents can be practical, inexpensive, and as environmentally benign as possible. While the original solvents were switchable-polarity solvents, meaning that their polarity underwent a significant change when the solvent switch was triggered, two other classes of switchable solvents are currently the focus of research in the group.

“Switchable-hydrophilicity solvents” normally form a biphasic mixture when mixed with water but, when exposed to \(\mathrm{CO}_2\), these solvents become very hydrophilic and completely miscible with water (Figure 1).

“Switchable water” is an aqueous solution of a polyamine. In the absence of \(\mathrm{CO}_2\) it has a very low ionic strength. However, after \(\mathrm{CO}_2\) is introduced, the polyamine changes to a salt, raising the ionic strength. That change in ionic strength dramatically changes the properties of the water and its performance in many applications.

The presentation will include the development and applications of these two classes of solvents, with an emphasis on molecular design to minimize environmental impact.

![Figure 1](image_url)

**Fig. 1.** a) Switchable-hydrophilicity solvents normally form a biphasic mixture when mixed with water, but in the presence of \(\mathrm{CO}_2\) the two liquid phases merge into one. Removal of the \(\mathrm{CO}_2\) reverses the process. b) Switchable water solutions have low ionic strength in the absence of \(\mathrm{CO}_2\) but high ionic strength in the presence of \(\mathrm{CO}_2\).

Selective oxidation of amines to nitriles in the presence of ruthenium-terpyridyl complex immobilized on ILs / SILP

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Oxidations in presence of ILs have been reported using both homogeneous organometallic complex catalysts and heterogeneous catalysts.¹ However, despite the successes the use of pure ILs as reaction media can lead to product separation difficulties. To overcome this issue, Wasserscheid and co-workers² proposed the heterogeneization of the ILs as a supported ionic liquid phase (SILP). Accordingly, thin ionic liquid layers are deposed on solid supports.

This study reports the immobilization of the ruthenium complex Ru₂Cl₄(az-tpy)₂ via SILP methodology using different ionic liquids and SiO₂ as support. In this way resulted a heterogeneous catalyst more efficient than the homogeneous one in methanol. The oxidation of long chain linear primary amines to corresponding nitriles followed a “green” route using a cheap and easy to handle oxidant (oxygen or air). The conversion was found to be strongly influenced by the alkyl chain length of the amine substrate and the choice of oxidant. No condensation reaction was observed between the starting amines and the selectivity to nitrile was 100%. An effect of the O₂+N₂ composition was also demonstrated for the oxidation of all the substrates using SILP catalysts. Moving from a composition of 20 atm N₂ - 5 atm O₂ to 5 atm N₂ - 20 atm O₂ led to enhancements in the conversion (n-alkylamines). With benzylamine the change in the N₂/O₂ led to a small decrease in the amine conversion but increased the selectivity to the corresponding nitrile by a factor of almost 3. This behaviour was associated with a combination of increasing oxygen pressure and a poisoning effect of nitrogen binding to the ruthenium centre. To understand the effect of N₂ on the catalyst system, FTIR spectra were collected under N₂. Compared with the spectra obtained when the SILP catalyst was purged with helium, all the catalysts (those exposed to air and those purged with nitrogen) showed a weak band located at 2006 cm⁻¹. The absence of this band in the presence of helium may suggest that this is due to N₂ binding at the ruthenium centre confirming its poisoning effect.

Polyol-mediated Synthesis of Nanoscale Elements: In, Cu, Re, Se, Te, C-dots

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Synthesis in high-boiling, multivalent alcohols (so called polyol synthesis) in between is a widely used approach for obtaining high-quality nanomaterials [1]. In general, polyols allow controlling particle nucleation and growth as well as particle agglomeration. Moreover, readily crystalline compounds can be obtained without any powder post-sintering.

Here, we present the polyol-mediated synthesis of nanoscale elements, including In, Cu, Re, Se, Te, and carbon dots (C-dots) (Figure 1). Properties and potential applications of the as-prepared nanomaterials range from catalysis (Cu, Re) [2], nanoparticulate precursors for CIGS thin-film solar cells (In, Cu, Se) [3] to emissive multicolored C-dots [4]. The latter are highly interesting for optical imaging, optoelectronic devices and catalysis.

This presentation summarizes synthesis conditions and material properties.

Figure 1. Various element nanoparticles obtained via polyol-mediated synthesis.


The Immobilized Metal Containing Ionic Liquids in the Catalysis of Radical Processes

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Metal-complex catalysts were prepared by the immobilization on silica of the ionic liquids; the immobilized cations are follows.

Metal containing anions ($\text{CuCl}_4^{2-}, \text{CuCl}_3^-, \text{MoO}_3^{2-}, \text{WO}_4^{2-}$) were incorporated either by anionic exchange or by chemical adsorption.

The composition and the structure of the complexes were determined by the elemental analysis, $^{13}$C NMR-MAS, XPS, EPR-, UV DR spectroscopy. These catalysts are highly active in environmentally important radical processes. We found Cu$^{2+}$ containing systems to be efficient in liquid-phase oxidation of thiols with air oxygen, leading to the formation of disulfides [1]. Compositions on the basis of molybdenum and vanadium display high activity in the sulfides oxidation in hydrocarbon media. The activity of these systems is much higher, than the activity of analogous homogeneous complexes.

Complexes of ionic liquids with univalent copper are efficient catalysts for Sandmeier reaction. For the first time arylchlorides were obtained with catalytic yields, exceeding these yields for any previously known catalysts.

Acknowledgment: The work was financially supported by Darville Enterprises Limited.

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Design and optimization of ILs – based solvents for gas separation

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Gas separation was regarded as an important operation to remove harmful and toxic gas emissions from waste gas to resolve the environmental problems, and separate impurities from gas mixtures to improve the quality of gas to satisfy the requirement of gas products. As emerged promising alternatives, ionic liquids (ILs) have great potential to be applies in gas purification and separation processes due to their remarkable properties.

In this work, an application-oriented framework was proposed to develop new processes for gas separation with ILs, which focused on the following aspects: 1) the structure-property relationship of ILs is studied with molecular dynamics (MD) simulation and the quantum mechanics (QM). The interaction force between the gas and IL is studied to understand the separation mechanism and to design promising ILs; 2) new thermodynamic model of the ionic fragment contribution-corresponding states (FCCS) were developed to predicate the physicochemical properties of ILs, and the contribution values of ionic fragment are estimated with QM method; 3) the bubble behavior, such as bubble size distribution, gas holdup, Sauter diameter were investigated, and then the mass transfer properties were measured and predicted.

Based on the above framework, several task specific ILs are designed and optimized for CO₂ capture, SO₂ capture and NH₃ recovery. The absorption capture capacity, the selectivity to other gases as well as the physicochemical and transfer properties are measured. The pilot plants are established to test the new solvents and optimize the operational parameters. Afterwards, the candidate structures of the new process are designed and simulated using the rigorous thermodynamic/kinetic models. With the multi-objective method, the whole process is optimized to minimize its energy consumption and maximize the green degree of the process. Then, the techno-economic-environmental performance of the new process is assessed and the industrial feasibility is obtained.
Continuous flow ethylene methoxycarbonylation by supported ionic liquid phase (SILP) catalyst

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Polymethyl methacrylate (PMMA) is a highly world demanded transparent thermoplastic polymer with many useful applications such as alternative to glass, medical technologies, etc.[1] One of the routes to prepare PMMA includes the use CO, ethylene and methanol as raw materials to give methylpropanoate (MP) as key material in the production of PMMA in a reaction known as ethylene methoxycarbonylation. Typically, the methoxycarbonylation of ethylene is carried out homogeneously in the presence of Pd-phosphine complex catalysts and a strong Brønsted mineral acid.[2] Due to the problems associated to the use of an strong acid at industrial level the searching for an alternative is still a challenge. In this sense, we have published recently a work where Brønsted acidic ionic liquids are used as both alternative to the mineral acid and reaction media yielding a biphasic system affording excellent results being the only backdraw the high amount of ionic liquid required to generate the biphasic system and the diffusion problems associated to it.[3] An elegant alternative to overcome these problems is the use of the supported ionic liquid phase technology (SILP). The SILP technology consists in an ionic liquid (IL) film immobilize on a porous solid material and a homogeneous catalyst dissolved in a supported IL layer. The resulting IL catalyst film is only a few manometers thick minimizing mass transport resistance from the gas into the liquid phase. SILP catalysis has potential for efficient catalyst recycling and it makes possible the application of homogeneous catalysis in fixed-bed reactor 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). A screening of the influence of different reactions parameters such as, IL loading, nature of the support, metal loading, temperature, GHSV (h⁻¹) etc., in both catalyst activity and selectivity has been performed.


Pharmaceutical and fine chemical industry employs more and more enantioselective catalysts for concise and economical drug synthesis. Up to date, 70% of all registered active pharmaceutical ingredients (APIs) are chiral molecules. Particularly asymmetric hydrogenation has been launched into drug development and manufacture.

Herein, we will shortly describe the problems inhibiting the successful implementation of enantioselective catalysis into today’s pharmaceutical production. And highlight the importance of the application of more benign solvent systems, with a special focus on asymmetric catalysis in aqueous solvent systems.

DexLeChem and its competencies will be presented, introducing its viability for the pharmaceutical industry. To illustrate a recent advance for the application of aqueous catalysis, the successful asymmetric hydrogenation of ketones with commercially available BINAP-type ruthenium complexes will be presented (Figure 1). Working in aqueous media enables organic-solvent free reactions, that result the same activity and selectivity as obtained for the identical reaction in organic solvents. Catalysis in water not only provides a much “greener” reaction but also offers the advantage of catalyst re-using.

![BINAP ligand](image)

(Figure 1) BINAP ligand

Dipolar aprotic solvents are widely used because of their good solvency performance and low reactivity. Members of this class of solvents include N,N-dimethyl formamide (DMF), N,N-dimethyl acetamide (DMAc), N-methyl pyrrolidone (NMP) and dimethyl sulfoxide (DMSO). While these solvents have been used for many years in numerous applications, several of them have been classified as reprotoxic. This has caused NMP for instance to be put on the list of substances of very high concern (SVHC), leading to more stringent labeling of products containing (residual) NMP, restricted use in many applications and overall scrutiny by the industry and the society.

The current research presents experimental data for a new alternative to NMP. Kinetic data were measured for several test reactions such as the Menschutkin reactions (typical SN2 reaction) and the catalytic Heck and Suzuki reactions. The obtained experimental data were then compared to other solvents and linked to calculated and measured solvency parameters. Additionally the use of the solvent to dissolve agrochemical active substances and its use in coatings, inks and electronics is demonstrated.
Aquatic biomass in general and microalgae in particular are attracting attention as fast-growing renewable feedstocks for fuels and chemicals. The conversion of aquatic biomass to renewable fuels and chemicals can be facilitated by performing the necessary thermochemical processes in the aqueous phase, either below or above the critical temperature of water. Many of the necessary thermochemical processes require heterogeneous catalysts to proceed at appreciable rates. Previous work has shown, however, that catalyst stability, catalytic kinetics, and catalytic reaction pathways can differ in hydrothermal media vs. the liquid organic solvents or vapor phase systems more traditionally used for hydrocarbon processing.

This presentation will focus on recent research related to hydrothermal catalytic processing of algal biomass and its model compounds and hydrothermally derived degradation products. We will demonstrate the efficacy of heterogeneous catalysts for improving biocrude yields from hydrothermal liquefaction of algae and fuel gas yields from hydrothermal gasification and for upgrading algae biocrudes into materials that more closely resemble petroleum crude oils. We will also discuss catalyst deactivation and reactor engineering strategies that can be employed to mitigate deactivation when working with algal biomass and biocrudes. Work with simpler model compounds (e.g., fatty acids, N- and O-containing organic compounds) reveals the governing reaction pathways and kinetics and provides insight into how these differ in hydrothermal systems vs. liquid organic solvents. Finally, this presentation will discuss work in catalyst discovery aimed at developing new catalytic materials that are active, stable, and selective in near- and supercritical water.
Carbazole functionalized ionic liquids for studying dehydrogenation of a liquid organic hydrogen carrier by XPS

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The low vapor pressure of ionic liquids (ILs) allows addressing fundamental mechanistic questions by surface science methods that were originally developed for solids. In particular, X-ray photoelectron spectroscopy (XPS) is a powerful method for studying molecular enrichment and orientation effects at the IL – vacuum and the IL – solid interface.[1] Even classical organic reactions in the liquid phase and gas-liquid reactions can be investigated using XPS under ultra-high vacuum (UHV) conditions by incorporation of otherwise volatile reactants as functional groups in ILs.[2-4]

In the context of liquid organic hydrogen carriers (LOHC) chemistry, we were able to follow under UHV conditions thermal dehydrogenation of dodecahydrocarbazole that was covalently linked to an imidazolium cation in the absence and the presence of platinum as catalytically active IL support.[5] Both, XPS and gas phase mass spectrometry revealed that the release of hydrogen occurs stepwise. The first step is the dehydrogenation at the central pyrrole ring of carbazole and occurs around 480 K, which is close to temperatures for conventional catalyzed dehydrogenation of neat carbazole under ambient pressure. In contrast, on gold as an inert support, the corresponding dehydrogenation step of the functionalized IL occurs at much higher temperature (530 K).

Micellar multiphase systems are innovative solvent systems which can be applied to increase the reaction rates of reactions in liquid/liquid systems. Furthermore, these systems fulfil many principles of the “green chemistry” e.g. using water as a solvent. Additionally, micellar multiphase systems are able to combine the advantages of heterogeneous and homogenous catalysis; high reaction rates and selectivities at mild conditions can be combined with a simplified separation. The highest reaction rates and the fastest separation were achieved when a three phase system was created (aqueous phase, organic phase and a microemulsion phase). But with the occurrence of a new phase and the presence of interfacial active molecules an additional mass transfer resistance arises, which again affects the reaction rate. To understand the mechanisms of reactions in micellar multiphase systems in detail the occurring transport processes can not be neglected.

To analyse the transport phenomena in micellar multiphase reaction systems the hydroformylation of 1-dodecene was used as an example reaction. A dependency between the stirrer frequency and the reaction rate was observed; hence transport phenomena have to be taken into consideration. To quantify the influences of mass transfer on the reaction rates it is necessary to gain a fundamental knowledge of the dispersion conditions as well as the occurring interfacial phenomena. For the determination of the dispersion conditions endoscopic and conductive measurements have been carried out. The characteristics of the interfaces were quantified by the determination of the interfacial tension and the interfacial rheology. The gas/liquid mass transfer was determined by observing the mass transfer coefficient of carbon monoxide in the three phase systems at different temperatures. From these results transport mechanisms in micellar multiphase reaction systems were derived.
Ionic Liquids (ILs) are by definition liquids composed exclusively of ions. The large range of possible combinations of cations and anions has led to ionic liquids being described as ‘designer solvents’.¹ This synthetic flexibility comes at the price of it being difficult to find the best ionic liquid for any given application. Further problems arise with the use of such a wide range of ionic liquids outside academic laboratories with each different ionic liquid requiring full REACH registration (or similar outside the European Union) as a unique compound to be used in industry, which is a lengthy and costly process. One approach to circumvent these problems is the formulation of mixtures of ionic liquids.² This has the advantages that the ingredients of these ionic liquid formulations have well defined properties, their syntheses are well known and only the pure components of the formulation are required to be registered under REACH. To realise these advantages it is necessary to understand how ionic liquids behave when mixed.

The mixing of ionic liquids has shown itself to be remarkably close to ideal. This is demonstrated through examples of changes in a range of physical properties. I will also show spectroscopic results that indicate the underlying structural behaviour that leads to these observations.

Probing interfacial phenomena of advanced fluids by XPS

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It was not until 2005 that the rather obvious compatibility of ionic liquids with ultra high vacuum (UHV)-based spectroscopies was fully realized. Since that time, an ever-increasing portfolio of UHV based techniques have been applied to the study of both pure ionic liquids, ionic liquid mixtures and solutions thereof.1-6 UHV techniques give tremendous insight into many aspects of ionic liquid properties and the role that they can play in chemical reactions and processes.7

Since 2005 we have developed a series of robust spectroscopic protocols that allow the direct comparison of spectroscopic data, and more critically allows the investigation of subtle changes in binding energy that result from chemistry within the sample itself.7 The application of rigorous charge referencing protocols reveals subtle variations in the observed binding energies of photoemissions corresponding to elements located in charge carrier moieties. This data suggests partial charge transfer between the charged components of a given liquid, i.e. anion-cation interactions, particularly when the anion component is highly coordinating or strongly basic. This lecture will explore the impact that ion selection can have upon the fluid in terms of the electronic environment in which chemistry can proceed. Initially we will review anion selection, and then move on to explore first experiments on cation selection, particularly with respect to both nitrogen and phosphorus based systems. Conformational constraint within the cation will be evaluated particularly regarding open chain quaternary ammonium species and pyrolidinium based analogues. The lecture will close with a comparison of XP data captured with both Al Kα and Ag Lα sources, opening new opportunities for investigation of both the near surface and indeed bulk of liquid samples.

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Chem In Ed 2012, 51, 2610.
The recovery of metals from spent supported metal catalysts is both a challenge and a necessity regarding the increasing prices of especially noble metals. The extraction of the metal components into supercritical fluids, e.g., supercritical CO₂, represents a novel approach that enables the recovery of the metals at mild conditions (353 K, 15 MPa) and without digestion or destruction of the whole catalyst material [1]. The standard hydro- and pyrometallurgical recycling procedures involve huge amounts of mineral acids (aqua regia) or very high temperatures up to 1600 °C [2]. Furthermore, there is the possibility to extract the metals separately and sequentially by choosing proper oxidizing and complexing agents [3].

In this study, the extractability of palladium and copper into supercritical CO₂ after oxidation and complexation will be presented. Therefore, the influence of different oxidizing and complexing agents as well as different nanoporous support materials was investigated.

**Experimental and Results**

Catalysts were first prepared by wet impregnation of porous γ-alumina, silica, zirconia and carbon with metal loadings of 2 wt.-% Pd, 2 wt.-% Cu or both. The extractions were carried out for 2 h in a batch autoclave (300 mL) at 353 K and 15 MPa. Acetylacetone (AA), hexafluoro acetylacetone (hfac), tributyl phosphate (TBP), diisooctyl thiophosphinic acid (DiOTPA) were used as extraction agents and hydrogen peroxide and a nitric acid-TBP adduct as oxidizing agents.

Results show that it is possible to extract both copper and palladium from the nanoporous supports by supercritical fluid oxidative extraction (SFOE). The extraction efficiency of the metals strongly depends on the applied complexing agent. This is related, *inter alia*, to the complex formation equilibrium, the solubility of the metal complex and the adsorption equilibrium of the metal complex on the support material. Also, the CO₂ pressure and temperature of SFOE are shown to be decisive.

**References**


Chemists have to face evolving constraints to provide well adapted solutions to consumers. Increasing performance and regulatory issues are strong drivers toward alternative formulations. In solvent formulations, some ‘top’ solvents widely used for their high solvency efficiency needs to be replaced. Those exhibit specific properties, which makes them difficult to replace. At the same time, the spectrum of eligible solvents or blends thereof is broad, and the solution might depend on the targeted application. So finding an iso-performance and greener alternative to solvency issues is a huge challenge.

In this context, in the last few years Solvay has developed new safer solvents based on ester amide functions. In addition, to maximize chances to succeed, Solvay has developed a rational methodology based on a smart combination of Hansen solubility parameters theory, design of experiment, and high throughput experiments. Hansen theory helps targeting required physical properties, DoE enables optimizing the statistics in the choice of blends, and HTP allows testing of a large number of solutions, which can be unreachable in a classical way of formulating.

Those chemical structures and the new methodology will be discussed in this paper in the frame of the crop protection market, by showing examples for actives ingredients or mixtures of active ingredients, for which a greener alternative was identified. These solutions then enable manufacturers to formulate crop protection products that are even more efficient at overcoming resistance phenomena.
Ionic Liquid–Liquid Chromatography (ILLC™)
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Ionic liquid-liquid separations, in which at least one phase is an ionic liquid, represents a new philosophy for the separation of organic, inorganic and bio-based materials, using the principles of modern countercurrent chromatography. A custom-designed instrument has been developed and constructed specifically to work with ionic liquids, and has been demonstrated on the 0.1-10 g scale. Separations which have been demonstrated include transition metal salts, arenes, alkenes, alkanes, bio-oils and sugars.
Enabling the integrated biorefinery: CO₂ as a solvent and reaction medium

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Current chemical and energy industries are heavily reliant on fossil fuels, an unsustainable feedstock that contributes to economic and political vulnerability. Biomass, a renewable resource, has potential to fulfill the energy and chemical needs of society while minimizing environmental impact and increasing sustainability. To achieve viable and sustainable utilization of biomass for fuels and valuable co-products, a biorefinery approach is proposed. Analogous to petroleum refining for a wide spectrum of products, biorefining maximizes utilization of all biomass fractions, reducing economic and environmental barriers to large-scale fuel production. Accordingly, integrated biorefineries present a feasible way to increase the economic viability of the biofuel industry by valorizing the other biomass components as bulk and fine chemicals (e.g., polymers, fiber composites and pharmaceuticals).

Compressed carbon dioxide – subcritical, supercritical, and CO₂ expanded liquids – has the potential to enable a sustainable biorefinery by enhancing extractions (including fractionation and refinement) and reactions. Numerous examples exist for the direct application of CO₂ in biorefinery-type operations with two particular examples highlighted. The first relates to the extraction of lipid and enrichment of key chain lengths from algal biomass. The second details the use of carbon dioxide to expand methanol to selectively and efficiently transesterify triglycerides to fatty acid methyl esters. While there remain questions related to fundamental system behavior as well as industrial scale operations, carbon dioxide shows significant potential to serve as an enabling green solvent in biorefinery settings.
Hydrothermal Methods for the Decarboxylation of Amino Acid Derived Imidazolium compounds: Towards Sustainable Ionic Liquids

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Imidazolium-based ionic liquids (ILs) have recently received great attention and, due to their unique properties such as negligible vapor pressure and high thermal and chemical stabilities, they are often considered safer and easier to handle than traditional molecular solvents. Moreover, ILs can be tuned for specific reactions and have been anticipated as very important in the context of biomass processing, being able to dissolve cellulose and wood. However, they still suffer from long and energy-intensive syntheses and elaborate purification procedures, which are both non-sustainable and expensive. Recently, we have introduced a simple and efficient one-pot protocol to generate functionalized zwitterionic imidazolium building blocks via a modified Debus-Radziszewski reaction from amino acids and carbohydrate-derivable dicarbonyl fragments. These compounds function as sustainable building blocks for the synthesis of a variety of compounds, including carbon materials, ligands, and polymers. More interestingly, these multifunctional building blocks can be converted in good yields into ionic liquids via acidic hydrothermal decarboxylation in flow. Solvents prepared in this way were successfully applied to metal catalyzed reactions and the dissolution of cellulose. Representative examples will be presented.


Continuous metathesis of cocoa butter triglyceride

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Continuous ethenolysis of a food-waste triglyceride, cocoa butter, to 1-decene was successfully achieved in an AF-2400 tube-in-tube flow reactor using a heterogeneous [RuCl2(iBu-phobane)2(3-phenylindenyl)] catalyst. Following identification of the appropriate catalyst under batch conditions, translation was made into flow processing whereby a number of parameters could be explored for optimisation.

Notably, process optimisation was expedited by being conducted in low-volume meso scale flow equipment where alterations of pressure, temperature and reaction time (residence time) are easily achieved.

schematic of the flow equipment used for the valorisation of waste cocoa butter.
Supported Ionic Liquid Phase (SILP) materials in hydroformylation catalysis

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Dr. Dyballa, Prof. Franke, Dr. Hahn, Evonik Industries AG, Marl, Germany;
Prof. Wasserscheid, Friedrich Alexander Universität, Erlangen-Nürnberg, Germany

In the chemical industry hydroformylation of alkenes is the most important homogeneously catalyzed reaction. In 2008 the production of oxo-products exceeded ten million metric tons.\[1\] About 70 percent of the consumed alkenes were represented by short chain alkenes. Supported Ionic Liquid Phase materials are an innovative concept for hydroformylation reactions which allows the immobilization of homogeneous catalysts on a heterogeneous support. The SILP concept combines the traditional benefits of homogenous catalysis with those of heterogeneous catalysis. The SILP concept consists of three major building blocks, namely the support, the ionic liquid and the transition metal complexes dissolved in the ionic liquid. It is ideally suited for continuous gas phase processes due to the near-zero vapor pressure of the ionic liquid and long-term stability.

This novel technology combines the benefits of increasing the efficiency and conservation of natural resources: e.g. reduction of unit operations for separation of solvents. In addition the ability of ionic liquids to selectively dissolve starting materials in the supported liquid film could be utilized. The special characteristics of the ionic liquids shall result in a more selective conversion of complex feeds.

In this talk we will give an overview of the insides of SILP materials we gained so far: In cooperation with Prof. Wasserscheid we showed that SILP catalysts with sensitive bisphosphite ligands remained stable over 800 h time on stream.\[2\] For a prospective technical application, SILP materials were also tested in the upgrading of highly diluted technical C4 streams.\[3\] Within the BMBF project HY-SILP (in cooperation with professors Claus and Wasserscheid) we were able to develop – amongst others – a deeper understanding of the processes occurring on SILP materials.\[4\]