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Catalytic Deoxygenation of Renewable Chemicals – Structure-Performance Studies

Phillip Malcho



Ph.D. Thesis July 2014 Center for Catalysis and Sustainable Chemistry Department of Chemistry Technical University of Denmark

Preface

The present thesis and the work contained within was performed at the Centre for Sustainable Chemistry and Catalysis, a part of the Department of Chemistry at the Technical University of Denmark, conducted in the period 1st of July 2011 to 31st of June 2014. The project was funded by FTP.

The experimental work in this thesis have been performed by the author, with the exception of ATR-FTIR presented in Chapter 3, which was conducted by Dr. A. J. Kunov-Kruse and Ph.D. Stud. J. Andersen who in turns also provided the technical and operational knowledge regarding the EXAFS measurements.

I would like to express my gratitude to my supervisor Assoc. Prof. Anders Riisager for three years of interesting chemistry within the area of valorization of biomass and for being the frontrunner within the area of ionic liquids in Denmark, his enthusiasm provided a unique spirit to this project. Within this project, a number of people have provided important sparring partners among others: Dr. U. V. Mentzel who provided the spark for the heterogenization of a homogeneous catalyst. Dr. E. J. García-Suárez provided much needed support within homogeneous decarbonylation.

I also owe gratitude to Dr. A. J. Kunov-Kruse for the topical discussions on the de-

hydration of HMF in ionic liquids, we often got rerouted from chemistry to other topics.

On a more personal level Ph. D. Stud. C. Engelbrekt and J. Andersen spent three years listening to me and I to them, for that I will be forever gratefull, the two of you both helped me and brought me down to earth when I flew to high, often by beating me in various games. Without the support of the two of you, this work would never have been concluded. The whole group of present and previous members at CSC are all to thank for the enormous amounts of coping with loud music, whistling and high spirits.

The largest amounts of thanks goes to my parents, throughout my whole life I've been their number one priority. They've supported all of my twists and turns on this road. Without them I would never have succeeded.

Copenhagen September 5, 2014

Phillip Malcho

Summary in English

Generation of chemicals from a viable feedstock is an increasingly interesting field. One of the major issues is the high oxygen ratios in biomass. There are a multitude of ways to remove oxygen from organic molecules. This thesis deals with two topics: The dehydration of glucose into HMF and the decarbonylation of aldehydes both heterogeneous and in ionic liquids.

Chapter 1 provides a walkthrough of areas such as green chemistry, ionic liquids, biomass, dehydration of glucose in ionic liquids and decarbonylation. The topics are all taking into account the current research and is subjectively chosen to provide a broad platform for the following chapters. Furthermore, the objectives for the thesis are listed here.

Chapter 2 deals with the synthetic preparation of the catalysts and the catalytic setups.

Chapter 3 deals with the dehydration of glucose into HMF in ionic liquids. The system was investigated thouroughly via several spectroscopic techniques. This was done in order to obtain novel information in regard to the catalytically active sites. EXAFS results showed that during the catalytic reaction, a species of the form CrCl_4O_2 was formed from CrCl_6 in the solution. These are the predominant chromium containing species in the solution. EPR results showed the presence of a $\text{S}=\frac{1}{2}$ spin system, and the only possible choice is radical formation. Optical absorption spectroscopy showed a change in the ligand field around the chromium.

Chapter 3 also deals with the homogeneous decarbonylation of aldehydes. The investigation of the effects of the ionic liquids in the catalytically active species is investigated in depth and the system $[Rh(dppp)_2]Cl$ in BMImCl was shown to be the most active combination. The reusability of the system showed great potential. The system showed a potential to decarbonylate both aliphatic and aromatic aldehydes.

Finally Chapter 3 looks at the heterogeneous decarbonylation of aldehydes, focussing on a continuous flow setup. The catalytic effect of oxidation state and ligandsphere is investigated. And the effects of temperature, solvent and substrate were under scrutiny. The catalyst decomposition was pictured by the aid of TEM and the formation of nanoparticles explained.

Chapter 4 concerns the summation of the results as well as the future perspectives for the respective applications and scientific developments.

Resumé på dansk

Syntesen af kemikalier fra levedygtige ressourcer er et konstant stigende interesse område. En af de største problemstillinger er det høje oxygen indhold i biomasse. Der er masser af muligheder for fjernelse af oxygen i biomasse. Denne these omhandler to af disse emner: dehydreringen af glukose til HMF og decarbonyleringen af aldehyder med udvidelse af emnet til både heterogen decarbonylering samt anvendelse af ioniske væsker som solvent.

Kapitel 1 giver en gennemgang af områderne grøn kemi, ioniske væsker, biomasse, dehydrering af glukose og decarbonylering. Emnerne er udvalgt så de alle medtager den nyeste forskning og er subjektivt udvalgt så de giver en bred platform for de kommende kapitler. Ydermere opremses målsætningerne for denne these.

Kapitel 2 omhandler den syntetiske fremstilling af katalysatorer og en beskrivelse af de katalytiske forsøg og setup.

Kapitel 3 giver en beskrivelse af dehydreringen af glukose til HMF i ioniske væsker. Systemet blev grundigt undersøgt ved hjælp af en mængde spektroskopiske teknikker. Dette blev gjort for at opnå ny viden om de katalytiske aktive specier i væsken. EXAFS viste at der under reaktionen dannedes forbindelser der kan beskrives som CrCl_4O_2 disse dannedes udfra CrCl_6 i opløsningen. Det blev vist at som reaktionen skrider frem er disse de dominerende forbindelser der er tilstede. EPR resultater viste at der tidligt i reaktionen dannedes noget der kun kan tolkes som værende et $\text{S}=\frac{1}{2}$ system samt at den eneste mulighed for opfyldelse af dette er dannelsen af radikaler. Optisk absorptions spektroskopi viste en generel vækst i absorption der indikerer en ændring i ligandfeltet omkring chrom.

Kapitelet omhandler også den homogene decarbonylering af aldehyder. Effekten af de ioniske væsker på den katalytiske aktivitet blev undersøgt og systemet $[Rh(dppp)_2]Cl$ i [BMIm]Cl viste sig at være den bedste kombination. Systemets genbrugelighed viste store potentialer. Det viste sig muligt at kunne decarbonylere både aromatiske og alifatiske aldehyder.

Sidst men ikke mindst fokuserer kapitlet også på den heterogene decarbonylering af aldehyder, med vægt på kontinuært flow setup. Den katalytiske effekt af oxidationstrin og ligandsfære blev undersøgt. Effekt af temperatur, solvent og substrat blev alle sammen undersøgt. Katalysator nedbrydningen blev karakteriseret ved hjælp af TEM og dannelsen af nanopartikler forklaret.

Kapitel 4 omhandler en opsummering af resultaterne såvel som en perspektivering for de respektive anvendelser og videnskabelige udviklinger.

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Abbreviations and Symbols

Abbreviation	Name		
Abs.	Absolut (i.e. absolut ethanol 99.99%)		
Acac	Acetylacetonato		
AD	Aldehyde decarbonylase		
ATR-FTIR	Attenuated total reflectance fourrier transformed infrared		
BASIL	Biphasic Acid Scavenging using Ionic Liquids		
BET	Brunauer Emmett Teller surface area		
BMIm	1-Butyl-3-Methylimidazolium cation		
ⁿ Bu	n-Butyl		
COD 1,5-cyclocatadiene			
Су	cyclohexyl		
DFT	Density Functional Theory		
DIBK	2,6 dimethyl-4-heptanone, Diisobutylketon		
Diglyme	1-Methoxy-2-(2-methoxyethoxy)ethane		
Dioxane	1,4-Dioxane		
DMSO	Dimethyl sulfoxid		
dppp	1,3-Bis(diphenylphosphino)propane		
DSC	Differential scanning calorimetry		
EDX	energy dispersive X-ray spectroscopy		
EMIm	1-Ethyl-3-Methylimidazolium cation		
EPR	Electron Paramagnetic Resonance		

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Abbreviation	Name	
Et	Ethyl	
ether	Diethylether	
Ex	Excess	
GC-FID	Gas chromatography flame ionization detector	
HMF	5-hydroxymethylfurfural	
HPLC	High-performance liquid chromatography	
HSAB	hard-soft acid base	
ICP-MS	Inductively coupled plasma mass spectroscopy	
IL	Ionic Liquid	
LC_{50}	Leathal Concentration that kills 50% of the	
	population in a specific time range	
Me	Methyl	
MHz	Mega Hertz	
MIBK	4-Methylpentan-2-one, methyl isobutyl ketone	
NMP	N-methyl-2-pyrrolidinone	
NMR	Nuclear magnetic resonance	
OAc	Acetate anion	
OMIm	1-Octyl-3-Methylimidazolium cation	
Pa	Pascal	
Ph	Phenyl	
PPh_3	triphenylphosphine	
TEM	Transmission electron microscopy	
TGA	Thermogravimetric analysis	
TMS	Tetramethylsilane	
TOF	Turn Over Frequency	
TON	Turn Over Number	
UV-vis	Ultraviolet-visible spectroscopy	

Abbreviation	Name
Vol%	Volume percent
Wilkinson's Catalyst	$Rh(PPh_3)_3Cl$
XAS	X-ray Absorption Spectroscopy

Chapter 1

Introduction

The current world economy and chemical industry have been heavily transformed over the last two centuries, the development and use of fossil fuels being the dominant factor in going from a preindustrial chemical industry to the modern situation.[2–7] The use of fossil fuels, however, has had detrimental effects on the CO_2 levels in the atmosphere:



Figure 1.1: A Keeling curve from the Mauna Lao Observatory, provided by the Scripps Institution of Oceanography, UC San Diego.[8]

The levels have surpassed 400 ppm for the first time in the meassurement period, and we have now surpassed the levels previously meassured in icecaps from Vostok.[9] This yields the question: Where do we go from here?

There have been several suggestions, nuclear energy, natural gas and biomass. Nuclear

energy has its drawbacks, with the recent earthquake in Japan being of vital evidence to the importance of safety regarding nuclear energy, not taking into account the safe disposal of toxic waste. Biomass has gotten large portions of attention during the last few years.[10] A new chemical infrastructure can be imagined to proceed via the following two paths: The first path is to produce renewable platform chemicals identical to the current one produced from crude oil, e.g. acetic acid and ethylene from bioethanol. The second path is to build a chemical platform with chemicals less used today but potentially easily obtainable from biomass, e.g. lactic acid or HMF from hexoses.[6, 11, 12] A beneficial effect of biomass is that it would be CO_2 neutral, in the sense that the only CO_2 released from the utilization of biomass would have been uptaken by plants during their growth. The following section deals with biomass in its entity, and the composition of biomass itself.

1.1 Biomass

The usage of lignocellulosic biomass has become a vital entry into this new millennium, Figure 1.2 represents one way in which biomass can used. The circle shows than one of the



Figure 1.2: The use of biomass in the industry, a representative illustration showing the promise of the valorization of biomass.

transformations needed to convert biomass is the conversion of lignocellulosic materials to chemicals and materials via deoxygenation. There are at least three ways to deoxygenate lignucellulosic materials: hydrodeoxygenation[13], dehydration and decarbonylation. The latter two will be discussed in this thesis. Figure 1.3 is based on the hydrolysis of cellulose, showing the magnifications of a plant all the way down to the building blocks of the plant walls, namely cellulose. Cellulose is a polysaccharide, it is a linear strain of glucose units connected via $\beta(1 \rightarrow 4)$ glycosidic bonds.[3, 15] The simplicity of lignocellulosic biomass stops at that, while the structure of hemicellulose consist of a wide variety of pentoses and hexoses bound via various glycosidic bonds. Lignin is different in many ways, lignin is not a carbohydrate based compound, but is comprised of aromatic compounds.[15–18] As seen in Figure 1.4 the structures of lignin interchange between relatively simple polymers,



Figure 1.3: The structure of lignocellulosic biomass.[14]



Figure 1.4: Examples of the chemical structures of the components in plant biomass.

to polymers with a wide variety of repeating aromatic entities.[19] Cellulose is currently produced on a multi ton scale, around $170 - 200 \cdot 10^9$ tons per year, in nature.[17, 20, 21] The production of materials from biomass need to be ethically sustainable, and also comprise of starting materials that are non-edible. Taking into account that the current production of ethanol from 2nd generation biomass generates around 40 kg of waste per 1 kg of ethanol,[17, 20] the amount of waste to product ratio is still to high and further work in this field is necessary.

1.1.1 Alternative Feedstocks

There are alternative feedstock to lignocellulose, some of them are the following:

• Starch

The composition of starch is largely different to the composition of cellulose. Starch is made up of two different polymers named amylase and and amylopectin. Both structures are made of glucose units bound together via glycosidic bonds. Whereas both of them are made up of $\alpha(1 \rightarrow 4)$, amylopection also incorporates $\alpha(1 \rightarrow 6)$.[22] This yields two very different structures, where amylose is a linear polymer, amylopection has several branches, due to the dual bonding mode.

• Sucrose

As a dimeric species, sucrose is probably the simplest form of biomass, consisting of a glucose and a fructose unit. Produced from sugar beets and sugar canes this compound is widely used as a sweetener in food and beverages. The production exceeds $1.0 \cdot 10^8$ tons per year.[22]

• Inulin

Inulin is made up of $\beta(2 \rightarrow 1)$ linked fructose units, and the length of inulin spans between 2 to 60 units. Typically, this polymer is found in artichoke and chicory root. Due to the linkage between the units, the polymer resists hydrolysis in humans. Therefore it is classified as a non-edible source of biomass.[23]

As shown, a multitude of possible starting materials are available and the study of these has been heavily scrutinized over the last decade. Lignocellulosic biomass has been proven to be soluble in certain ionic liquids and this could be the pathway to the utilization of biomass in industry.[24, 25]

The following section deals with ionic liquids and the features that make these solvents unique.

1.2 Ionic Liquids

Since the 1990's the development of neoteric solvents such as ionic liquids has taken flight. There has been several reviews focusing on the vast applications of these new solvents.[26–34] Here I will provide a short and concise description of some of the most important facts about these solvents and their uses.

1.2.1 Definitions of ionic liquids

In the upcoming text the following definition will be used for ionic liquids:

A (room temperature) ionic liquid is an ionic compound which has a melting point below 100° C

As a rule of thumb, most ionic compounds are solid at room temperature, ranging from NaCl to complex transition metal salts. But as early as 1888 and 1924, the first non solid ionic compounds were stumbled upon when [EtNH₃]NO₃ was synthesized.[35–37] A few decades went by before people noticed these oddities and started working to-The beginning of this field was sparked by the need for ionic conductors wards it. at low temperatures.[38] There are, however, other interesting facets about ionic liquids, namely that the difference in ionic strength and bonding mode is different from pure ionic compounds. The interaction in compounds like [BMIm]Cl between the cation and anion, differs from the interactions between cations and anions in regular inorganic salts. [39, 40] This can be seen from the different crystal structures obtained of the ionic liquid [BMIm]Cl, a simple salt of that kind traditionally yields single type crystal, such as is the case with NaCl, $BeCl_2$ etc. but the pseudo covalent character changes the crystallizational properties, and it has been stipulated that the large disorder in the ionic liquid structures is the major reason that they are indeed liquid at room temperature.[39, 40] Throughout the development of the field there has been a large number of combinations of cations and anions. The most common cations and anions are shown in Figure 1.5 and

Figure 1.6. As can be seen, there is a multitude of combinations as the R group can



Figure 1.5: Commonly used cations in ionic liquids. R can be both Alkyl and Aryl groups.



Figure 1.6: Commonly used anions in ionic liquids. R can be both Alkyl and Aryl groups.

be interchanged into almost any possible combinations. This also yields a lot of different obstacles, for instance is it at all possible to predict the physical properties of these liquids, and thereby knowing beforehand if a compound is an IL? There have been some attempts to try to predict densities, trying to understand the polarity and thermo physical properties of these liquids, with the help of computational techniques (DFT) and simple physical calculations based on density and surface tension.[41–43] It has been shown that changing the anion in [BMIm]⁺ salts from OTf⁻ to I⁻ and subsequently to I₉⁻ will change the physical aspects of the IL and that it could be predicted by modelling. With the help of surface tension and density, from shorter chained compounds Deetlefs *et al.* obtained a linear correlation of the chain length and density of the ionic liquid, thereby predicting physical properties within a group of ionic liquids.[41] Another aspect of ionic liquids is their lack of vapor pressure, although some can be distilled at reduced pressure. This stands in sharp contrast to all the organic solvents used in the chemical industry.[26–33]

1.2.2 Toxicity

Even though ionic liquids are being used in labs all across the world, little is known in regards to their toxicology. If these solvents are to be used on industrial scale, then knowledge of environmental and physical impacts of ILs is needed.[44–47] The toxicity of a wide variety of compounds where tested in a recent review by Egorova *et al.* it were shown that commodity ionic liquids was indeed toxic to organic cells with an LC₅₀ of $85 \ \mu \text{mol} \ 1^{-1}([\text{BMIm}]\text{Cl})$ in certain invertebrates.[48] The possible decomposition products with *Cytochrome* P_{450} have been theoretically investigated, and the oxidation products are all toxic to humans.[45] The group of Jastorff used a multidimensional risk analysis where they study the environmental effects of the ionic liquids. They looked at:

• Release

Vapor pressure and water solubility was looked at as aspects of release in to nature. Airborne ionic liquids where neglected as they are practically non-volatile.

• Spatiotemporal range

The study of what happens to a chemical compound over time in a given space. In this case the human body.

• Bioaccumulation

The accumulation of the ionic liquid in cell, membranes and other biological structures.

• Biological Activity

The activity of a given compound or ionic liquid when added to a biological sample.

By evaluating these aspects, it would be possible to determine if a given IL would be suitable for use on a larger scale. Given that the IL presents beneficial effects on a given reaction. Extensive studies have been made on the biodegradability of ionic liquids, on the forefront of this has been the groups of Chiappe and Garcia.[49–52] The focus has been on the development of environmentally benign ionic liquids, with a critical view on the current use of ionic liquids in catalysis.[52]

1.2.3 Ionic liquids and some applications

The application of ionic liquids have exploded over the last decade, not all applications are well thought out, the use of ionic liquids should be limited to areas in which the beneficial effects are evident.[28–31, 53–56] Giving a complete overview of the multitude of applications ionic liquids have had over the last decade is unsurmountable at this point, which is evident from the large number of reviews already published on this topic.[28– 31, 53, 53, 54, 56]

Ionic liquids have received an enormous amount of attention due to the nature of these solvents. One of the most studied reactions is the production of HMF, this will be dealt with in the upcoming chapter as it is a vital part of the thesis. Here I will attempt to describe a few examples in which IL's have been used, with a focus on the reactions in which transition metals partake as the active catalyst. The formation of HMF in ionic liquids will be dealt with in the next section as this area is of vital importance to this thesis. In upcoming sections the topic of decarbonylation will be dealt with, a reaction in which CO has been removed from an organic substrate, where as in the case of hydroformylation a CO entity is added, being of related nature a concise description of hydroformulation is in order.

Hydroformylation

Hydroformylation in its simplest form can be described as:



Figure 1.7: Schematic representation of the hydroformylation reaction.

The group of Chauvin showed that immobilizing the catalyst in an ionic liquid phase by adding sulfunated PPh₃ ligands to the catalyst precursor, thereby ensuring complete solubility in the IL but insolubility in the organic phase was possible. [57] It was shown by the group of Keim *et al.* that upon running a hydroformylation reaction in $[BMIm][PF_6]$ with Methyl-3-pentanoate as a substrate. [58] They showed that in the IL, the catalyst $(Rh(Acac)(CO)_2$ with added phosphine ligand) was reusable in up to 10 cycles. They also showed that the TOF and TON was better than that which was observed in conventional solvents, in this case CH_2Cl_2 and toluene. [58] The regioselectivity in this study was based purely on the ligand of choice and not by the IL used. One of the rate limiting steps in the hydroformylation reaction is the gas solubility of CO and H_2 gases, as well the as alkene solubility. If the IL can't dissolve the gas, then the reaction can not take place. [59] A contributor to the use of IL has been the relatively low solubility of the produced aldehyde/alcohol. [59] It took a few years from the two first reported cases before a systematic investigation of the role of the IL appeared in literature. [60] They depicted the 1-hexene solubility as a function of alkyl length in a $[XMIm][CF_2SO_2]$ as well as showing that the anion played a role two going: $\rm [BF_4]^- < \rm [PF_6]^- < \rm [CF_3CO_2]^-. [60]$ These are just some examples, but they serve as benchmarks, as it was shown that ionic liquids had beneficial effects on catalyst stabilization in case of hydroformylation. A range of other examples can be mentioned and the reader is referred to the excellent review of Haumann.^[59]

BASIL - Biphasic Acid Scavenging using Ionic Liquids

The BASIL process is the first process in which IL's have been used in multi ton scale. And - hopefully - this is only the first example of many to come, in which IL's show their true potential. The reaction proceeds as shown in Figure 1.8. Being that this process is the first industrial use of IL's a brief mentioning of the content and benefits of using it should be made. As seen from the reaction (Figure 1.8) the product of the renowned BASIL



Figure 1.8: Schematic representation of the BASIL reaction. [61, 62]

process is alkoxyphosphines, which can be used in various photochemical processes.[63] The reaction used to run with NEt_3 instead of methylimidazolium. The amine and the imidazol were and are used to scavenge the generated HCl gas from the reaction *in situ*. The separation with the amine requires neutralization and filtration to obtain products which have to be further purified, whereas the imidazol exemplifies itself via the ease of separation, a simple gravitational filtration is all thats needed and the products are cleaner and purer to the full extent expected.[61, 62]

1.3 The Furanoic Platform



Figure 1.9: The furancic platform.[64]

Among the products obtainable from the valorization of biomass, the formation of HMF is one of the most studied reactions,[11] a plethora of variations in catalyst and solvent combinations has been studied, and one of the most promising catalysts has been shown to be $CrCl_3$ in [BMIm]Cl.[65] This is a system which is still under heavy scrutiny; primarily due to the uncertainty regarding the catalyst and its mechanism.[53, 66–69] Recently it has been shown that during the reaction one can se the formation of Cr(II) species when the reaction runs from Cr(III)chloride hexahydrate. This can be interpreted as if the sugar itself reduces the Cr, as it is known that sugars can act as reductants.[70] Our group have shown that if the reaction pathway is monitored by *in situ* UV-vis and *in*
situ ATR-FTIR one can follow both the catalyst as well as the substrate and get detailed information as to how the reaction occurs in the ionic liquid.[1]

It is beyond the scope of this chapter to ensure a thorough walk through within the area of carbohydrates to HMF conversions and these have been reviewed elsewhere.[12, 71] One of the reasons to the usage of hexoses or other sugars in the production of HMF is due to the similarity, albeit singularity, to cellulose and other polymers found in bulk in nature. The assumption is that if it is possible to selectively generate HMF from these monomeric sugars, then the selective cleavage of the glucosidic bonds in cellulose is easily obtained by the acidity of the ionic liquids.[72–74] The glucose isomerization



Figure 1.10: The glucosidic platform.[32]

and dehydration pathway, however, were achieved in 2007 by Zhao et al. during their investigations of various metal centers effects as catalyst.[76] The conclusion were that the CrCl_3^- anion in the [EMIm]Cl were the active species. Aided by the formation of [EMIm][CrCl₃] complexes, which could facilitate the mutarotation of the α -glucopyranose anomer to the β -glucopyranose anomer. This hypothesis was later proposed to be the



Figure 1.11: The proposed mechanism in the production of HMF via $CrCl_3$, modified from [75, 76], X = Cl or imidazolium ligand.

same in case of other metal mediated dehydrations of glucose, as shown in Figure 1.11 on the preceding page.[53, 53, 66–69, 77, 78] Determination of the reaction pathway by utilization of NMR spectroscopy was unsuccessful. The choice of solvent was based on previous studies made by Moreau, who showed that dehydration of fructose was aided by the acidity of methylimidazolium chloride.[79, 80] This combined with the known effect of ionic liquids being able to dissolve glucose and metal halides prompted them to use alkylimidazolium chlorides. Pidko *et al.*[53, 66–69] proposed a possible reaction pathway for the CrCl₂ catalyzed conversion of glucose in [EMIm]Cl by applying DFT calculations combined with X-ray Absorption Spectroscopy (XAS). XAS at the Cr K edge was used to determine the coordination properties of the chromium species. In situ XAS was used as proof for the reaction pathway determined by a theoretical DFT study. Combining results obtained from XAS with the crystal structure of $CrCl_2/[EMIm]Cl[81]$ led to two square-planar $CrCl_4^{2-}$ units. With XAS the coordination sphere around the chromium atom can be determined, where it evolves from coordination of chlorine in the $CrCl_2/[EMIm]Cl$

A DFT study performed by Guan *et al.*[75] on the role of the chromium(III) catalyst in the glucose isomerization in [BMIm]Cl shows a different reaction mechanism. The previously mentioned study of Pidko *et al.* showed that the ionic liquid performed as a spectator, similarly has been showed by Hu *et al.*[78] in their study of glucose isomerization by $SnCl_4$ in [EMIm]BF₄. On the other hand, Zhao *et al.*[76] and Yong *et al.*[82] suggest that the imidazolium entity from the ionic liquid is bonded to the metal center. The imidazolium ligand plays a role since a more bulky ligand would decrease the accessibility of glucose to the metal center assuming a carbene formation between chromium and carbon, thus reducing the catalytic efficiency.

The study by Ståhlberg *et al.*[77] concludes that [BMIm]Cl is more efficient than [EMIm]Cl in the conversion of glucose to HMF, when using a $CrCl_3$ catalyst. The results obtained by Ståhlberg were made parallel to later publications on chromium catalyzed

systems.[65, 68, 83–85] It is required to have ionic liquids containing halides to get reasonable HMF conversion. Changing of the halide anions affects the overall yield; changing of chlorine or bromine to iodine lowers the HMF yield from 70% to 20% for an [EMIm]Cl setup. Clearly the ionic liquid plays an important part in the mechanism of the reaction. The difference based on the anion can possibly be explained by applying hard-soft acid base (HSAB) theory. The large imidazolium cation would most likely prefer to bind to the large iodine in a soft-soft interaction. Bromine and chlorine are hard bases resulting in a weaker interaction, making them a lot more reactive, which results in higher yields of HMF. The alkyl chain also affects the reactivity and the highest efficiency occurred in [EMIm]Cl and [BMIm]Cl whereas [MIm]Cl gives a very low HMF yield.

The choice of catalyst also affects the reactivity. Beginning with anhydrous Cr(III) chloride generally yields lower conversion rates of HMF compared to the hexahydrate form. For Cr this can be explained by the extended tight packed crystal structure of the anhydrous Cr(III) chloride, whereas it is easier to dissolve the hexahydrate. This has also been confirmed by Zhang *et al.*[53] It seems that the key step of the conversion of glucose to HMF is the isomerization of glucose to fructose, since both the ionic liquid[86] and Cr(III) chloride[75] catalyze the dehydration of fructose. A recent study by Bali *et al.*[87] demonstrates that the active species is in fact Cr(III) and not Cr(II), which has been the general understanding in the published literature. However, no proof has been made for the exact determination of the oxidation state. Various catalysts based on Cr have been applied in the glucose conversion, with a focus on Cr(II) and Cr(III) with different ligands. It seems that the conversion depends on the ability to substitute ligands. Weakly bound ligands such as THF increase the HMF yield, whereas strongly coordinating ligands such as ethylenediamine limit the glucose conversion. A change in the first coordination shell is implied.

Mechanism

In recent years the mechanism of the dehydration of glucose has been under heavy scrutiny, and especially the Cr catalyzed reaction is something which has been subjected to a great deal of speculation. Guan *et al.* [75] offered a view into the mechanism by means of DFT, however, they maintained that the ionic liquid interacted with the Cr center, generating possible N-heterocyclic carbene complexes, they supported this hypothesis via the results from Yong et al.. A depiction of the mechanistic cycle can be seen in Figure 1.11 on page 15.[65] Looking into the mechanism yields a possible way to optimize catalyst effectivity as well as yields and performance of the overall process. The mechanism can be envisioned via some elementary steps: the isomerization of glucose to fructose, the three dehydration steps, and finally the decoordination of HMF from the Cr catalyst. The isomerization process occurs via the active species $[\text{EMIm}][\text{CrCl}_x]$, where x = 3or 4, depending on whether it is Cr(II) or Cr(III). In the recent years a plethora of different schemes have been proposed for the dehydration of glucose into HMF. Most of the data presented have been computational studies, and while these might be valuable guidelines, it is important to acknowledge the fact that experimental data is needed to support these calculations in order for them to be confirmed, these examples includes both monometallic, bimetallic, innocent ligands and non-innocent ligands. This prompts for further investigations needed to figure out how the catalyst behaves during the reaction, and how the reaction conditions affects the catalytic system.

The Challenges

Generating HMF is something that can be done easily from the proper starting materials. But among the problems regarding starting materials is the fact that the reaction runs smoothly when starting from fructose, as shown in several reactions. However, the availability of fructose in nature and on industrial scale is greatly limited, which is why research has taken a change of direction, into the usage of glucose and other cellulose model molecules, in order to generate a catalytic system capable of generating HMF from cellulosic biomass.[53, 65, 77, 83, 88, 89] Among the major concerns in the recent development have been the isolation of HMF, this can be divided in to three categories: biphasic processes, single phase processes with product extraction and single phase processes with product distillation. These all present several obstacles when used in large scale quantities.

Removal of HMF from a solution

It has been an ever returning challenge to obtain a pure product from different solvents, among other things due to solubility issues. This is, however, an area in which the utilization of ionic liquids has aided a lot, mainly due to the fact that it is now possible to run biphasic reactions.[90–93] It is also possible to distil HMF at relative low temperatures and low pressures (114 - 116 °C at 1 mbar)[94], the low pressure is strictly necessary to avoid the formation of polymers. Another possibility which presents itself is extraction of the product from the HMF succeeded by evaporation of the solvent used for the extraction. This yields a possibility of an easy separational method, albeit this does not circumvent the use of nonvolatile solvents during production, which is one of the major concerns in this greener and more environmental friendly assessment of the production of HMF in bulk scales.

Precipitation of HMF from a solution

This method promises to be the most advantageous to date. Due to the low melting point (30 - 34 °C), crystallization of HMF at room temperature provides an easy accessible route to products of high purity. It has recently been shown that addition of MIBK to a solution of HMF in [BMIm]Cl could generate crystals of HMF with a purity of more than 99.9%, as measured by HPLC.[77] This is also something that could aid the industrialization of

these materials as both of the solvents can be reused multiple times, thereby generating an economically beneficial reactiona as the ionic liquids are not cheap or abundant materials.

1.4 Decarbonylation

A true decarbonylation reaction is defined as:

A reaction in which a CO molecule is selectively removed.

Therefore it is evident that in order to have a decarbonylative reaction, one needs a carbonyl group in the overall molecule, leaving a plethora of molecules to be investigated namely aldehydes, ketones, carboxylic acids and metal carbonyl compounds. The catalytic decarbonylation of aldehydes has been the main focus of this thesis, and to give a comprehensive walk through of the other groups is beyond the scope of the following work.

A simple representation of a decarbonylation of an aldehyde can be depicted as follows:



Figure 1.12: A general outline of a decarbonylation reaction. R can be both Alkyl and Aryl groups, X can be either H or Halides.

The Beginning

The terminology 'decarbonylation' stems from Tsuji and Ohno in the early 1960's where they used Wilkinson's catalyst[95] in large quantities (28%) as a decarbonylating agent.[96– 99] They showed that the decarbonylation of several species could be obtained by boiling in benzene (b.p. 80 °C), they even postulated a mechanism for the study of these reactions:



Figure 1.13: A general mechanism of a decarbonylation reaction. R can be both Alkyl and Aryl groups, X can be either H or Cl.[97]

A problem with the catalyst and the catalytic system was that the recovery of Wilkinson's catalyst was not possible after the reaction and the generation of rhodium black was observed. Some substrates will generate stable complexes of the type Rh(PPh₃)₂Cl(RCO)X which are isolateable, and can therefore be used as a sort of flash photography of the reaction. All of the carbonyl complexes can be isolated from the reaction mixtures making the proposed reaction mechanism plausible. The group of Tsuji and Ohno were the pioneers in this field and they showed that not only could aldehydes be decarbonylated, but also acid halides and α , β -unsaturated aldehydes which retained their stereo chemistry.[98, 99] The group of Wilkinson also showed similar results as well as that the system is rapidly exchanging one of the equatorial phosphines in the Wilkinson catalyst, thereby generation of the active catalyst as the rate of exchange of the coordinated solvent is faster than the exchange of a phosphine ligand.[100] Working with chiral aldehydes in total synthesis is often a necessity and maintaining the chirality after a decarbonylative reaction is of vital importance. Especially in total synthesis of large natural occurring organomolecules.[101–105] The retention of configuration was showed to be maintained when using Wilkinson's catalyst, even the early results from Tsuji and Ohno were corroborated as it was shown that the change in the optical purity could be attributed to the reaction conditions and not the decarbonylation reaction itself.[100]

Going from non-catalytic to catalytic homogeneous decarbonylation

A major step in generating an active decarbonylation catalyst was obtaining knowledge that the system studied in depth could not be reused since, upon addition of CO to Wilkinson's catalyst, one generates a stable $Rh(PPh_3)_2Cl(CO)$ where the CO can't be eliminated photochemically or thermochemically [106] This spiked some interest since the excellent results obtained promised a general entry into the homogeneous decarbonylation. The mechanistic part of these investigations still heavily relied on the Wilkinson's catalyst.[107–109] The use of this novel information generated a novel reaction pathway into chemicals like hydroxymethylfuran, which can be generated by the decarbonylative dehydration of fructose in NMP.[110] It was suggested that the dehydration occurs giving the typical dehydration product, namely HMF which can be decarbonylated yielding the alcohol.[110] The development of novel ligand systems focused primarily on ligands containing phosphorus. The nature of these ligands make design and tunability a large issue. And there is more than one case in which the ligand has proved to stabilize the intermediary states too much, generating species in which the aldehyde have been partially decarbonylated, but never released. [111–113] The types of ligand systems used are diverse and large. Spanning from small phosphines as PMe₃ to large systems as the tripodal $P(CH_2CH_2PPh_2)_3$. The systems can be modified to both chiral and achiral ligands, mono-, bi-, tri- and even tetra-dentate ligands have been used in the literature some of them are shown in Figure 1.14 on page 25.[111–119] The group of Madsen depicted this in

great detail as they spent a substantial effort in generating the most active ligand:solvent combination for these reactions.[117]

Solvent	Boiling point
Diglyme	162 °C
NMP	$202 \ ^{\circ}\mathrm{C}$
DMSO	189 °C
Mesitylene	$164 ^{\circ}\mathrm{C}$
Heptanol	176 °C
DIBK	168 °C
Ethylhexanoate	$166 \ ^{\circ}\mathrm{C}$

Table 1.1: The various solvents tested by Kreis et al.[117]

They started out by studying the influence of the solvent using a series of solvents: The ligands they tested were all sorts of variations needed to select the most active homogeneous catalysts, as seen all of them are multidentate ligands, shown in Figure 1.14:



Figure 1.14: The ligands tested by Kreis et al. n = 2 - 4.[117]

The screening of the ligands was performed using a standard reaction shown in Figure 1.15:

The results serve as a guideline into the design and usage of the catalyst. They found



Figure 1.15: Standard reaction for the testing of ligands.[117]

that the ligands with a bite angles around 93 - 97 $^{\circ}$ would make the structure of the complex square planar. This coincides with the DPPP ligand. The optimized system runs as the setup in Figure 1.15. One of the disadvantages with the system and the setup itself is that the catalyst has a tendency to deactivate via the formation of rhodium black (nanoparticles in undefined sizes) due to the temperatures being above the decomposition temperature of the complex,[120] and the recycling of the catalyst has yet to be shown in the literature.[117] In recent years, the developments of pincer ligands, boron containing ligands and other non-innocent ligands, have produced an intriguing new possibility of having a metal center which are in a stable oxidation state, and all the redox chemistry is transfered to the ligand system.[121, 122] Ozerov ligands have proven intriguing (an example is shown in Figure 1.16).[123–126] The appearance of such ligands could prove to be the stabilization needed to generate an active metal to ligand combination.



Figure 1.16: An example of an Ozerov ligand.[123–126]

The heavy scrutiny of rhodium has left the other transition metals largely unchal-

lenged and it's only within the last few years that the successful attempts have emerged. The reaction conditions has been examined and one particularly interesting result is the decarbonylation of HMF in dioxane with compressed CO_2 . The catalyst is generated *in situ* by adding [Ir(COD)Cl]₂ and 2 eq. of PPh₃ in the dioxane.[127] The decarbonylation of the HMF could yield an entry into the industrial decarbonylation of biomass generated platform chemicals, recyclability is vital in the case of platform chemicals. And the group of Leitner, who ran the experiments in supercritical CO_2 , also reported that the catalyst was indeed recyclable, as the first example in the homogeneous decarbonylation reactions.[127]

The iridium catalyzed decarbonylation was also investigated via the same measurements as the rhodium. The authors repeated the experiments of Madsen *et al.* and saw full conversion after 24 h using the setup described by Madsen.[117, 128] By moving to iridium the authors saw increased reactivity in regard to monodentate ligands. The system showed that cheap ligands such as PPh_3 and P^nBu_3 could achieve good to excellent results in air. Not having to run the reaction under argon is an obvious plus.[128] A major contributor for the lack of use of these catalytic systems in the industry is the price of the metal and ligand simply is to high for the one time usage.

Mechanistic considerations

Not a lot of work has been done within the mechanistic studies of rhodium based decarbonylation with bidentate ligands. The monodentate decarbonylation has been studied in great detail and some things can be applied as shown by Madsen *et al.* by utilizing Hammett studies, testing the competitive decarbonylation between benzaldehyde and *para* substituted benzaldehydes, both activated and deactivated substrates, as well as DFT calculations they showed:

The reaction occurs in four steps, depicted in Figure 1.17 on the next page:



Figure 1.17: Mechanism supported by Hammett studies and DFT calculations.[129]

1. Coordination

The initial step in the catalytic cycle is the displacement of a ligand. In this case the displacement of a solvent molecule, L. The coordination of the aldehyde then takes place through the oxygen. The rhodium center is kept in its square planar geometry.

2. Oxidative Addition

The oxidative addition of the hydride and the inversion of bonding mode, resulting in rhodium going from oxidation state one to three and changing coordination geometry from square planar to tetragonal pyramidal. The change in coordination also facilitates the upcoming step.

3. Migratory Extrusion

The migrational extrusion of the the carbonyl and the aryl/alkyl substituent. Remaining a rhodium(III) but yet again shifting in coordination mode, into an octahedral. With the alkyl/aryl substituents cis in respect to the hydride.

4. Reductive Elimination

Via a reductive elimination, the organomolecule and the hydride recombine, yielding the desired product. The release of the carbonyl for the metal occurs upon the second cycle, when the coordination of a new moiety of substrate attaches.

Heterogeneous decarbonylation using nanoparticles

The attempt to heterogenize the catalysts for the decarbonylation of aldehydes have been pursued since the first literature proofs of these reactions, one of the reasons to attempt a heterogeneous catalyst would be of greater interest to the industry compared to the homogeneous systems in which separation of product and substrate can be non trivial. Among the more successful attempts is the decarbonylation of furfural in gas-phase to generate furan:



Figure 1.18: Palladium nanoparticle catalyzed decarbonylation of furfural.[130]

The reaction conditions required hydrogen as a carrier gas, enabling hydrogenation of the aldehyde as well as stabilization of the Pd and Pt nanoparticles during the reaction. Even though this suggest a possible longevity of activity, the catalyst deactivated by 85%over the course of 4 h, the reactions ran at elevated temperatures around 300 °C.[130] The palladium on alumina catalyst was further investigated with various amounts of potassium doping showing that the decarbonylation of furfural into furan is possible with up to 10% potassium impurities. This was done in order to test wether or not the reaction and the catalytic systems where resistant to alkali metals. With yields up to 99.5%with 8% potassium present, they showed that alkali poisoning was not a problem.[130] The size of the nanoparticles plays a pivotal role in the catalysis, and as the field of nanotechnology has developed, so has the size control of synthetic nanopraticles. It was shown than upon synthesizing too big nanoparticles the reaction changed and instead of observing decarbonylation, the observed reaction was instead hydrogenation of the aldehyde into the alcohol when using platinum. [131, 132] In recent years, the most promising results within biomass related compounds, have been the decarbonylation with palladium on mesoporous silica. These results have shown that mild conditions can be used when working with chemicals prone to polymerization, such as HMF.[133] The common denominator in the heterogeneous decarbonylation of aldehydes with palladium is the necessity for a hydrogen carrier gas, making the distinction between hydrogenation and decarbonylation vague. The carbonyl functionality in furfural has been shown to be the first moiety to be hydrogenated with typical hydrogenation catalysts.[134]

Biological Decarbonylation

In biological systems alkanes and their derivates are widely encountered. These need to be synthesized from readily available starting materials, and since most of the available feedstock are comprised of carbohydrate derivates or other large macromolecules, it is necessary for living cells to have ways to breakdown molecular entities. Aldehyde decarbonylation has been proven as an intermediary step in the reduction of fatty acids to alkanes:



Figure 1.19: Schematic of the deoxygenation and decarbonylation of fatty acids in alkane biosynthesis, R: Acyl Carrier Protein.[135]

The studies of Schirmer *et al.* showed that especially cyanobacteria produce large quantities of alkanes in the bacteria. All of these have one thing in common namely the decarbonylase enzyme, which contain a active site in which there is a diiron center. But one of the things not known about these *Pisum Sativum* was whether or not the decarboxylation took place in one or two steps. If the decarboxylation followed the proposed mechanism in Figure 1.19 then the detection of CO should be possible. However, it was shown that, using a CO trapping agent (Wilkinson's catalyst was used) which was unre-

sponsive towards CO_2 , the reaction did generate CO.[136, 137] The active site of these decarbonylases is a non-heme iron centers.[135] The catalytic cycle of the *Prochlorococcus*

marinus MIT9313, was investigated by the group of Marsh, and they showed that not all kinds of Cyanobacteria went through a two-step mechanism, but instead yielded formic acid as a direct product.[138] The biosynthesis of alkanes can be summarized as follows:



Figure 1.20: Different Aldehyde Decarbonylases (AD) and their products.[139]

As shown in Figure 1.20, aldehyde decarbonylase is remarkably different in a various organisms, and in all cases produces something that is by all means greatly unhealthy to the host. However, all of these compounds are needed for the fatty layers.

1.5 Objectives

The objectives of this Ph.D. research work can be divided into two parts:

Dehydration of glucose using CrCl₃

Within the last decades the dehydration of glucose, fructose, and other sugars has exploded, but there still remain uncertainties regarding the mechanism, and this thesis aimed to utilize spectroscopic studies to characterize and elucidate the nature of the transition state in the chromium catalyzed dehydration of glucose into HMF. As seen in previous sections, the utilized methods in the literature are primarily EXAFS and DFT. We searched to incorporate simple techniques such as IR and UV-vis as well as corroborate the litereature found states via EXAFS. With this knowledge in hand, we hoped to be able to generate a better understanding of the catalytic setup up and potentially obtain the most active catalyst possible. The points can be summarized as follows:

- Improving the catalytic activity and yields by understanding the chemical nature of the catalysts.
- Characterize the catalytically active site, using *in situ* ATR-FTIR, EPR, UV-vis and EXAFS.

Decarbonylation of aldehydes with a rhodium based catalyst

Current research in the homogeneous decarbonylation has focused on organic transformations, with only one example proving that recyclability is possible as seen in the introduction. The idea was to investigate if the catalytic decarbonylation of aldehydes was possible in IL's. If this proved possible, then the idea was to switch focus to two areas, with an attempt to immobilize the catalyst on a solid support and to investigate if IL's could be used as a recyclable solvent. If these things were possible, then the next step would be testing of the scope of these catalysts, trying to elucidate the catalytic systems lifetime and/or the cause of catalytic decrease in activity. The choice of catalytic system was based on the best results obtained in literature, namely the $[Rh(dppp)_2]Cl$. The goals can be divided into two topical parts, one for the homogeneous decarbonylation in IL's and one for the heterogeneous decarbonylation on a silica support:

Homogenous decarbonylation in IL, with a rhodium based catalyst

- The development of a novel catalytic setup, utilizing ionic liquids to generate a biphasic system.
- Testing the catalytic setup towards a variation of aldehydes, both aromatic and aliphatic in nature.
- To obtain a recyclable homogeneous decarbonylation catalyst.

Heterogeneous decarbonylation with a rhodium based catalyst on silica support

- Immobilize the prime example of a rhodium based homogeneous decarbonylation catalyst via impregnation techniques on solid support.
- Obtain a heterogeneous catalyst that could function in a traditional continuous flow setup.
- Test the catalytic activity towards a range of aldehydes.
- Study the stability of the catalyst towards decomposition.

Chapter 2

Experimental

2.1 General comments

2.1.1 Materials

All chemicals were purchased from Sigma-Aldrich and used without further purification unless otherwise noted. The metal compounds used for catalyst preparation were prepared under an inert atmosphere of Argon (grade 5.0, Air Liquide). Silica-90Å support (BET = 340 m²/g; pore volume = $0.95 \text{ cm}^3 \text{ g}^{-1}$; pore size = 90 Å; particle size 70-230 MESH) was calcined for 4 h at 600 °C, dried *in vacuo* at 110 °C for 24 h and kept under moisture free conditions prior to its use.

2.1.2 Characterization Techniques

Thermal stabilities of the catalysts were determined by thermogravimetric analysis (TGA) on a combined TGA/DSC, Mettler Toledo, STARE System with a GC100 gas controller. The heating rate was 5 °C min⁻¹ from room temperature to 260 °C, where the temperature was kept for 6 h.

The surface areas of the support and the catalysts were derived from the nitrogen ad-

sorption desorption isotherms performed at -196 °C (liquid nitrogen) in a Micromeritics ASAP 2020 pore analyzer. Prior to measurement, the samples were degassed overnight by heating at 200 °C *in vacuo* ($<10^{-4}$ Pa) to ensure a clean surface before adsorption. The structure and morphology of the catalysts were examined by transmission electron microscopy (TEM) on a Tecnai G2 T20 from FEI Company (Oregon, USA) before and after decarbonylation. Prior to analysis the samples were crushed into a fine powder and subsequently supported on plain carbon film coated copper grids purchased from Agar Scientific (Stansted, UK). Elemental analysis was achieved by energy dispersive X-ray spectroscopy (EDX) using an X-Max^N detector from Oxford Instruments (Abingdong, UK).

X-Ray absorption experiments were performed at the I811[140, 141] beam line at the Max IV laboratory at Lunds University, Sweden. Spectra were recorded in fluorescence mode at the Cr K edge. Samples were distributed on a flat sample holder and rotated 45° with respect to the beam. Background correction was performed using WINXAS[142] and the linear combination fit was performed using Athena, a part of the Horae program pack.[143, 144] ATR-IR information was obtained for the glucose conversion reaction using time resolved *in-situ* ATR-FTIR recorded at a Nicolet iS5 Spectrometer with a Specac High-Temperature Golden Gate diamond ATR cell. Spectra were recorded isothermally with 2-80 scans (3-60 s recording times) with 4 cm⁻¹ resolution depending on reaction rates, and ATR corrected with the built-in algorithm in OMNIC 8.2 assuming a sample constant refractive index of 1.5. Background spectra were recorded for each sample to determine unique bands.

The catalytic yield was monitored using a GC-FID using a HP 5890 Series II chromatograph equipped with a SGE BP1 non-polar 100% dimethyl polysiloxane capillary column (50 m x 0.32 mm x 0.25 ml). Standard curves were used to quantify the conversion and product yield. Inductively coupled plasma (ICP-MS) (Perkin Elmer ElAN 6000 spectrometer) was used to evaluate Rhodium leaching from catalysts after use. The filtrates from reaction mixtures were subjected to ICP-MS analysis, and the quantification of Rhodium was made by using a series of Rhodium standards.

2.2 Preparation of the catalyst precursors

2.2.1 Synthesis of $[Rh(COD)Cl]_2[145]$

 $2 \operatorname{RhCl}_{3} \cdot \operatorname{aq} + \operatorname{Ex} \operatorname{COD} + 2 \operatorname{CH}_{3} \operatorname{CH}_{2} \operatorname{OH} \longrightarrow [\operatorname{Rh}(\operatorname{COD})\operatorname{Cl}]_{2} + 2 \operatorname{CH}_{3} \operatorname{CHO} + 4 \operatorname{HCl}(\operatorname{aq})$

A 100 ml schlenk flask with a reflux condenser was charged with 30 ml ethanol - water mixture (5:1) and the solvent bubbled through with argon for 15 minutes. To the solvent 2.00 g of RhCl₃·aq (7.6 mmol) was added, obtaining a red solution. Upon complete solvation, the solution was added to 3.0 ml of COD (22.80 mmol), and heated to reflux. The solution was left at reflux for 18 h, during which the product precipitated as a yellow-orange powder. The mixture was filtered hot and the solid washed with 3 aliquots of pentane (10 ml) and 3 aliquots of methanol-water mixture (1:5, 10 ml). Yield: 1.61g (91 % based on rhodium).

Comments

Calculations of the amount of mol of rhodium was based on the assumption that the species present were of the kind: $RhCl_3 \cdot 3H_2O$.

2.2.2 Synthesis of $[Rh(dppp)_2]Cl[120]$

$$[\operatorname{Rh}(\operatorname{COD})\operatorname{Cl}]_2 + 4 \operatorname{dppp} \longrightarrow 2 [\operatorname{Rh}(\operatorname{dppp})_2]\operatorname{Cl} + 2 \operatorname{COD}$$

A 100 ml schlenk flask was charged with 50 ml anhydrous toluene and 1.72 g of dppp (4.16 mmol). The solution was stirred for 30 min. at ambient temperature. To this was added 1.03 g of $[Rh(COD)Cl]_2$ (2.08 mmol) and the suspension was left stirring overnight.

The precipitated pale yellow powder was filtered off and washed with 3 aliquots (10 ml) of anhydrous toluene and 3 aliquots of ether (10 ml) and dried *in vacuo*. Yield: 1.90 g (95 % based on rhodium).

Comments

The analogous iridium compound was synthesized using the same method, albeit the yield was lower (82 %). The compound presented itself as a pale yellow powder.

2.2.3 Synthesis of $[Ir(COD)Cl]_2[146]$

 $2 \left[IrCl_3 \cdot aq + Ex COD + 2 CH_3 CH_2 OH \longrightarrow \left[Ir(COD)Cl \right]_2 + 2 CH_3 CHO + 4 HCl \right]_2$

A 100 ml schlenk flask with a reflux condenser was charged with 50 ml ethanol - water mixture (2:1) and 5.29 g of COD (48.92 mmol) and the solvent bubbled through with argon for 15 minutes. To the solvent was added 2.00 g of $IrCl_3 \cdot aq$ (5.67 mmol) obtaining a red solution, this was heated to reflux. The solution was left at reflux for 24 h, during which the product precipitated as a orange powder. The mixture was filtered hot and the solid washed with 3 aliquots of methanol (10 ml) and 3 aliquots of Ether, and dried *in vacuo*.

Yield: 1.61g (91 % based on Iridium).

2.2.4 Synthesis of $[Ir(dppp)_2]Cl$

$$[Ir(COD)Cl]_2 + 4 \text{ dppp} \longrightarrow 2 [Ir(dppp)_2]Cl + 2 \text{ COD}$$

A 100 ml schlenk flask was charged with 50 ml anhydrous toluene and 1.72 g of dppp (4.16 mmol). The solution was stirred for 30 min. at ambient temperature. To this was added 1.03 g of $[Rh(COD)Cl]_2$ (2.08 mmol) and the suspension was left overnight. The precipitated pale yellow powder was filtered off and washed with 3 aliquots (10 ml) of

anhydrous toluene and 3 aliquots of ether (10 ml) and dried *in vacuo*. Yield: 1.90 g (82 % based on iridium).

Comments

Calculations of the amount of mol of iridium was based on the assumption that the species present were of the kind: $IrCl_3 \cdot 3H_2O$.

2.2.5 Supported Catalysts - wet impregnation

A general approach to the supported catalysts

A 10 ml flask was charged with 1.5 ml CH_2Cl_2 and 1.5 ml of abs. ethanol, to this is added a calculated amount of metal compound (between 10 to 50 mg) to obtain the desired metal loading. The solution was stirred for 15 min. to ensure complete solvation, where after 1.0 g of silica-90 support was added and the suspension stirred for 1 h. After which the solvent was removed *in vacuo* at 70 °C for a period of 30 min. to obtain the supported catalyst. The catalyst was kept under inert atmosphere until its use.

Comments

The various compounds used for impregnation were: [Rh(dppp)₂]Cl, [Ir(dppp)₂]Cl, RhCl₃·3H₂O and [Rh(COD)Cl]₂.

2.3 Catalytic Tests

Dehydration of glucose in [BMIm]Cl

To 1.00 g [BMIm]Cl (5.73 mmol) was added 14.8 mg $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ or 6.8 mg CrCl_2 (0.056 mmol) where after the mixture was stirred for 15 min. to ensure complete solvation. To the purple solution was then added 100 mg D-glucose (0.56 mmol) and the system stirred at room temperature for 15 min. In order to obtain time resolved samples, the solution was heated to 80 $^{\circ}$ C for the duration needed and the solution flash frozen on an acetone/dry-ice bath.

Homogeneous Decarbonylation Experimental Procedure

A 10 ml flask was charged with 1.0 ml of IL or solvent and the desired amount of $[Rh(dppp)_2]Cl$ was subsequently added to obtain a chosen metal loading. The solution was then stirred for 30 min. to ensure complete solvation. 55 μ l of mesitylene was added and the mixture stirred for 1 h at 165 °C with a reflux condensator preventing evaporation of the mesitylene. Then, the substrate was added and the mixture was allowed to stir for the desired reaction time. Upon reaction completion 3 ml of deionized water and 3 ml of ether were added the the ionic liquid mixture. The ethereal phase was decanted off, dried with magnesium sulfate and analyzed by GC-FID. Standard curves using mesitylene as an internal standard were used to quantify the product yield.

Heterogeneous Decarbonylation Experimental Procedure

In a typical experiment, 300 mg of catalyst was placed between two quartz wool plugs in a stainless steel, fixed-bed reactor with an inner diameter of 7 mm. The selected substrate was introduced to the reactor by a HPLC pump (Mikrolab) diluted to 50 vol% in 2-propanol or n-pentane at a flow rate of 0.05 ml min⁻¹. The reactor was heated by an electrical furnace (Horst) at the desired reaction temperature measured through a thermocouple positioned inside the oven close to the catalyst bed. Helium (grade 5.0, Air Liquide Denmark) was applied as a carrier gas with a flow rate of 10 ml min⁻¹ controlled with mass flow controllers (Brooks), and the reaction pressure was 1 bar in all experiments. The product mixture was condensed directly below the reactor in a condenser kept at 0 °C. The setup can be seen in Figure 2.1.



Figure 2.1: A schematic depiction of the heterogeneous continuous flow setup. P is an over pressure valve. Chart made by Ph. D. Stud. Emily C. Nordvang

Chapter 3

Results

Due to the nature of the thesis, the results and discussion part have been divided into two parts. The first part dealing with the conversion of glucose into 5-hydroxymethylfurfural and the second part concerning the selective decarbonylation of aldehydes both heterogeneous and homogeneous.

3.1 From Glucose to 5-Hydroxymethylfurfural

The dehydration of glucose has been extensively studied, and the plethora of results have yielded active catalysts and solvent combinations that are optimum for the reaction. In our group, the focus has been on the dehydration of hexoses in ionic liquids.[77, 147–149] The mechanism of this reaction is something that has yet to be unravelled. In order to investigate the reaction coordinates, a series of techniques were used to see if some brief information could be obtained. We used time ressolved EXAFS, EPR, IR, Mass Spectrometry and UV-vis (optical absorption spectroscopy). The IR experiments and data treatment has been performed in collaboration with Dr. A. J. Kunov-Kruse and Ph.D. Stud. J. Andersen.

3.1.1 ATR-FTIR of the glucose dehydration in [BMIm]Cl with chromium catalysts

ATR-FTIR spectroscopy was conducted in order to visualize the conversion of glucose and the formation of HMF. Two different setups were used to monitor the reaction. A single batch reactor and a thin film setup. Both setups are depicted in Figure 3.1 on the facing page the major difference is the possibility for a clean athmosphere in the thin film setup, by utilizing dry nitrogen one can run the reaction in absence of water. Both setups are thouroughly discribed in the thesis of Dr. A. J. Kunov-Kruse.[1] A brief explanation is however required:

The micro reactor is a 25 micro liter custom made glass cap loaded with reaction mixture before installing on the ATR top plate. Approximately 15 mg of reaction mixture was quickly loaded into a the glass reactor at room temperature, together with a small Teflon coated magnet rod (5x2 mm). The reactor was applied on top of the preheated diamond ATR-plate and magnetically stirred by a home built device placed around the reactor to supply horizontal magnetic stirring.

In the thin film experiments a thin ionic liquid film was dispersed on the diamond and a metal cap was then quickly put on top of the sample to seal it from the ambient atmosphere. Then a dry nitrogen flow was applied.

During the course of the reaction, disappearance of the C^6-O^6 stretch and the O–H bend in the area 1000 – 1140 cm⁻¹ can be seen. The appearance of the C=O from HMF at 1670 cm⁻¹ and the steady increase over time as seen in Figure 3.2 on the next page. The dehydration of glucose in a microreactor showed a significant dependency on temperature, the higher the temperature the faster the conversion, as expected.

In all the cases, there is a large difference in the rate depending on temperature. Even more interesting is the evidence that water pressumably hinders the reaction, by comparing the thin film experiment run under inert atmosphere with the micro batch reactor experiments, it is visible that the water in the reaction is inhibiting the dehydration



Figure 3.1: Experimental setups used for the *in situ* ATR-FTIR reaction monitoring. The left hand-side shows a schematic drawing of the micro reactor setup and the right-hand side shows a schematic setup of the thin-film setup.[1]



Figure 3.2: Representative in situ ATR-FTIR spectra of 9.1 wt% glucose in [BMIm]Cl at 110 °C during the catalytic dehydration with $CrCl_3 \cdot 6 H_2O.[1]$



Figure 3.3: Time resolved ATR-FTIR study of the dehydration of glucose in [BMIm]Cl with Cr(III)Cl₃, in a batch reactor.



Figure 3.4: Time resolved ATR-FTIR study of the dehydration of glucose in [BMIm]Cl with $Cr(III)Cl_3$, in a thin film under anhydrous conditions.



Figure 3.5: Time resolved ATR-FTIR study of the dehydration of glucose in [BMIm]Cl with $Cr(II)Cl_2$, in a thin film under anhydrous conditions.

of the glucose. We observed that upon removing the water, in the thin film setup with a stream of dry nitrogen, the rate of the reaction got significantly faster. The difference in reactivity can only be interpreted as if the coordination of water inhibits the catalyst. The activation energies are roughly the same, as shown by the paralel slope of the lines, around 102 in all cases, giving a E_a of 102 kJ mol⁻¹ for the HMF formation as seen in Figure 3.6 on the following page. This shows that the difference in activity cannot be attributed to the staring materials but solely to an intermediate or deactivational product.[150]

As seen in Figure 3.5, the initial rate for the Cr(II) catalyzed was slower, but compared to Cr(III) which never reached completion, the Cr(II) actually reached a 100% conversion. The discrepency can be caused by several things, first and foremost the difference in oxidation state, the coordination environment, sensibility etc. following the information obained by myself, Dr. Kunov-Kruse and Ph. D. Stud. Andersen an attempt of clarifying the intermediary states was made by other techniques, including EXAFS, UV-vis and EPR.[150]



Figure 3.6: Arrhenius plot of the apparent reaction rate of the various catalyzed reactions monitored by ATR-FTIR.

3.1.2 EXAFS of the glucose dehydration in [BMIm]Cl with chromium catalysts

The EXAFS meass surements where all made on a thin film setup. Fits for the first shell were made by Ph. D. Stud. J. Andersen. The results show that within the first 1.5 min. there was detectable amounts of something that resembles $[\text{CrCl}_6]^{3-}$ as seen in Figure 3.7 on the facing page. At t = 1.0 min the first shell fit corroborates with what was expected. Once a salt of the type $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ is dissolved in [BMIm]Cl the high concentration of Cl^- could be envisioned to generate the $[\text{CrCl}_6]^{3-}$ in situ. This is also the case at t = 0.0 min but as the reaction proceeds, the clear and sharp peak for $[\text{CrCl}_6]^{3-}$ is distorted and



Figure 3.7: R-Space function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 1.0 min. Fitted as $CrCl_6$



Figure 3.8: R-Space function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 1.0 min. Fitted as $CrCl_4O_2$
something resembling $\text{CrCl}_4\text{O}_2{}^{3-}$ appears. This tendency has been observed earlier by Mønsted.[151, 152] They observed that chromium with macrocyclic ligands coordinated sugars in a bidentate mode. This is to be expected to be the case in the homogeneous dehydration of glucose, as supported by all the different mechanisms in the literature. Therefore, the fits after 1.5 min were fitted with the compound $\text{CrCl}_4\text{O}_2{}^{3-}$ as this gave the best overall resemblance with the obtained spectra.

As can be seen from Table 3.1 on the next page, after the initial formation of $\text{CrCl}_4\text{O}_2^{3-}$ the reactions stays more or less constant, indicating that, at least in the resting state, the chromium is surrounded by only one glucose unit, if any. A major drawback from these measurements is that we only observe the first shell and therefore cannot say wether or not it is indeed glucose, water, HMF or a fourth entity that coordinates to the metal center. It has been postulated by a number of groups that dimeric species could be the source of the catalytic activity. [53, 66–69] These would probably not be directly visible in the EXAFS study here, a report showed that interaction between chromium centers in a [BMIm]Cl solution when starting with Cr(II) yields a trimeric structure upon crystallization. With a Cr–Cr bond of 2.94 Å this should be easily visible in the ionic liquid. [153] The structure was obtained by heavy dilution with methanol and the $[CrCl_3]_3[BMIm]_2[OMe]$ entity is not seen in our, spectra we only observe the $[CrCl_6]^{4-}$ in Figure 3.10 on page 52. The bond length variations over time can be visualized as shown in Figure 3.9 on the next page. It is evident that there is a change in the coordinational mode around the chromium center. As the reaction proceeds, the bond length between Cr–Cl and an unknown oxygen species stabilizes. This indicates that after 60 min. a steady state has been achieved, interestingly the bond lengths aren't similar to what is obtained in $[Cr(OH_2)_6]^{3+}.[154]$

Time [min]	Cr–Cl distance [Å]	Cr–O distance [Å]
0.0	2.26 ^a	
1.0	2.29	2.11
1.0	2.26^{a}	
1.5	2.30	2.04
1.5	2.26^{a}	
2.0	2.31	2.02
2.5	2.31	2.00
3.0	2.35	2.01
3.5	2.31	2.04
4.0	2.32	2.07
4.5	2.32	2.03
5.0	2.33	1.98
10.0	2.31	2.01
30.0	2.29	2.05
40.0	2.29	2.06
50.0	2.30	2.07
60.0	2.28	2.06

^{*a*}Fitted as $[CrCl_6]^3$

 Table 3.1: Chromium to ligand distances measured by EXAFS.



Figure 3.9: Bond length between Cr–Cl and Cr–O from Table 3.1 depicted as a function of Time.



Figure 3.10: *R*-Space function of Chromium(III)Chloride in BMImCl.

3.1.3 EPR of the glucose dehydration in [BMIm]Cl with chromium catalysts

Time resolved EPR was run in order to visualize the paramagnetic species in the reaction mixture. The EPR studies where conducted with only Cr(III) as the Cr(II) wouldn't be visible on X-band, due to the diamagnetic nature of these compound in their prefered crystal field arrangement(square planar or tetrahedral).[155] The time resolved spectra showed in Figure 3.11 on the facing page shows that there is an evolution of a paramagnetic species. The maxima is obtained after three min. A simplification of the time flow figure is seen in Figure 3.12 on page 54. The starting point at t = 0 min, shows great similarities to t = 60 min, however, the similarities in the spectra are not necessarily caused by structural characteristics as all we see is something that could resemble $s = \frac{3}{2}$ at t = 0 min. As the reaction proceeds intensity increases as a function of time until t = 3 min, this could be interpreted as the appereance of a $s = \frac{1}{2}$. Since there is no hyperfine or superhyperfine coupling to indicate anything about the ligand sphere during the catalysis, if we accept that there is a mononuclear pathway for the dehydration, then we could also envisage that during this pathway a system with a spin of $s = \frac{1}{2}$ would be present. As chromium



Figure 3.11: Time resolved EPR study of the dehydration of glucose in [BMIm]Cl with $Cr(III)Cl_3$

only appers in spin $s = \frac{3}{2}$, this leaves only one possible explanation if it is indeed a $s = \frac{1}{2}$, namely a radical.

As seen in Figure 3.13 on the following page, the paramagnetic species reaches its maximum after 2.5 min, and then there is a steady decline in concentration. This coincides with a local minima in the Cr–O distance, as seen in the EXAFS measurements. It is also seen that the paramagnetic nature of the system is stabilized.

3.1.4 UV-vis of the glucose dehydration in [BMIm]Cl with chromium catalysts

UV-vis was measured to clarify whether or not the environment around the catalyst changes during the course of the reaction. At t = 5 min, the change in the spectra compared to when one has a pure sample of $CrCl_3$ is limited. The two d \leftarrow d transitions typically seen in $Cr(III)Cl_3$ can be seen throughout the experiment, indicating that the metal center does not change oxidation state during the reaction, these correspond to the



Figure 3.12: Time resolved EPR study of the dehydration of glucose in [BMIm]Cl with $Cr(III)Cl_3$, showing the two minima and one maxima.



Figure 3.13: 2nd integration of the EPR signal, normalized with respect to the initial paramagnetic concentration.

 ${}^{2}t_{2g}^{1}T_{1g} \leftarrow {}^{3}t_{2g}^{2}$. Two transitions can happen, a spin allowed and a spin forbidden, both of which should have very low intensities as seen.[156] The ligand fields changes observed during the course of the reaction makes it plaussible that no substantial ligand exchange is happening during the reaction, as a difference in ligand field would greatly effect the optical absorption bands. It is also seen that during the reaction something that can only



Figure 3.14: Time resolved optical absorption spectroscopy study of the dehydration of glucose in [BMIm]Cl with $Cr(III)Cl_3$.

be described as a charge transfer band (anionic oxygen to the chromium center) evolves around 400 nm, indicating that there is a change in the ligandsphere as seen in EXAFS. However, as is the case with EXAFS, EPR and FTIR, optical absorption spectroscopy does not yield any information other than there is a change in the ligandsphere.

Summation

The ATR-FTIR results corroborated what was previously seen in the literature, namely that $CrCl_3$ initial rate was faster than $CrCl_2$, but also that upon letting the reaction run its course, the $CrCl_2$ ran to completion where as the $CrCl_3$ got hindered, by what can

be interpreted as being either water or HMF. It was further seen that the activation energy under the same conditions for the two reactions were similar. The catalytic yields etc. all corresponded to what was obtained in the literature before.[1, 77] It was showed that the temperature played a major part in the dehydration of glucose, and the higher temperature the faster reaction. Ranging from more than 2 hours to 16 min. to reach completion at 80 °C and 130 °C, respectively. It was also shown, that running the reaction under a steady flow off nitrogen provided a faster reaction, and therefore we concluded that the chromium catalyzed dehydration of glucose was hindered by the formation of water. Combining this with what we saw in EXAFS, namely the formation of compounds of the type $CrCl_4O_2$ we propose the following reaction scheme:



Figure 3.15: A simplified catalytic reaction scheme proposed for the $Cr(III)Cl_3$ catalyzed glucose conversion in [BMIm]Cl.

The EXAFS measurements shows that in the first shell of chromium there is indeed two oxygens, these can stem from just about anything, but in the thin film experiment, one must assume, that no water can coordinate and therefore the only observed species can be $[CrCl_4(Glucose)]^{3-}$ where the glucose is assumed to be a dianionic chelate ligand, and $[CrCl_4(HMF)]^{2,3-}$, it is unclear if the HMF will act as a mono aninoic or dianionic ligand in this case.

In an attempt to identify the first shell ligand we turned to EPR, hoping that we would see super hyper fine coupling to the axial oxygens. This was, however, not the case, instead we saw something that resembled a radical appearing and disappearing quickly during the reaction. The nature of this entity is still being pursued. The UV-vis spectroscopy results were in alignment with all the above mentioned techniques, as it was evident that there was a change in the coordination sphere, yielding something that could be interpreted as a charge transfer band.

3.2 Homogeneous Decarbonylation in Ionic Liquids

The homogeneous decarbonylation of aldehydes has been described in Chapter 1. The solvents described in Chapter 1 do not allow for recycling of the catalyst and the hope was that the novel class of solvents, ionic liquids, could aid in obtaining a recyclable system as well as increase the catalytic activity and ease of separation.

3.2.1 Study of IL's

A series of ionic liquids where chosen to test if the ionic liquids could introduce a solvent system that yielded catalyst reusability and avoided catalyst degradation:



Figure 3.16: The ionic liquids used in the study.

In order to study the influence of the ionic liquid, 5 ionic liquids composed of different cations (Figure 3.16) and anions were tested in the decarbonylation of p-toulaldehyde using 3 mol% of the prepared [Rh(dppp)₂]Cl complex as catalyst. The results are depicted in Figure 3.17 on the facing page. The five ionic liquids in Figure 3.16 were thermally stable at temperatures higher than 165 °C. The TGA graphs in the appendix show that the thermal stability of IL's is sufficient for the temperatures needed to run the catalysis. Furthermore, the focus of the IL's were to be commercially available. Introducing an

expensive solvent to an already expensive catalyst would make the system less desirable in both academia and industry.



Figure 3.17: Yield of homogeneous decarbonylation of p-tolualdehyde in various IL's. All reactions ran with 3 mol% catalyst([Rh(Dppp)₂]Cl). Reaction conditions: 1 g IL, 165 °C, 8 h.

As seen in Figure 3.17, the five chosen IL's all showed a certain degree of activity, the highest yield (48%) was achieved when [BMIm]Cl was used as reaction media and the lowest one (16%) when [BMIm]OAc was selected. First and foremost, the [BMIm]Cl was the best solvent for the homogeneous decarbonylation of *p*-tolualdehyde. Both shortening and lenghtening the alkyl chain showed a decrease in activity, to 30% and 36% respectively for [EMIm]Cl and [OMIm]Cl. In the case of the acetates the shorter alkyl chain ([EMIm]⁺) showed better performance than the longest one ([BMIm]⁺), 23% and 16% yield respectively. The change in alkyl substituent length points to the fact that a sterically hindered cation is preferred to a certain degree compared to the sterically unhindered ones. Seeing as the [OMIm]Cl has a higher activity than [EMIm]Cl, by changing

Entry	Catalyst(mol %)	Solvent	Substrate	Yield ^[%]
1	2	[BMIm]Cl	<i>p</i> -Tolualdehyde	20
2	3	[BMIm]Cl	<i>p</i> -Tolualdehyde	48
3	4	[BMIm]Cl	<i>p</i> -Tolualdehyde	97
4	5	[BMIm]Cl	<i>p</i> -Tolualdehyde	> 99
5^a	1	[BMIm]Cl	<i>p</i> -Tolualdehyde	71
6^b	1	[BMIm]Cl:Diglyme	<i>p</i> -Tolualdehyde	56
7^a	1	Diglyme	<i>p</i> -Tolualdehyde	80
8	3	[BMIm]Cl	o-Tolualdehyde	> 99
9	3	[BMIm]Cl	<i>m</i> -Tolualdehyde	> 99
10	3	[BMIm]Cl	<i>p</i> -Anisaldehyde	62
11	3	[BMIm]Cl	Nonanal	> 99

Table 3.2: Aldehyde decarbonylation in ionic liquids. ^a 24 h reaction, ^b 24 hreaction, 1:1 ratio. Reaction conditions: 1 g IL, 165 °C, 8 h.

the cation from $[BMIm]^+$ to $[EMIm]^+$ we observed the same tendency as the one with Cl^- as anion, namely an increase compared to the one with OAc^- as anion, 30% and 23% respectively. Taking these results into account, we found an strong influence on the reaction rate due to the ion, offering Cl^- a much better performance than OAc^- . The increased performance of the Cl^- based ionic liquids can be attributed to the stability of the solvents under our reaction conditions being that the Cl^- based ionic liquids are more thermodynamically stable than the OAc^- ones. All of these things indicate that while the solvent does generate a more ionically charged environment, this does not alter the catalytically activity. Since [BMIm]Cl showed to be the better solvent, this was chosen for further testing.

3.2.2 Catalytic Testing

Having established that system was indeed active, a series of experiments was conducted with the objective to clarify how reactive and how active the system was.

The organometallic compound $[Rh(dppp)_2]Cl$ is well known to easily decarbonylate aldehydes in a wide variety of solvents and temperatures. [96, 99, 106, 114, 116, 117,

129] Therefore, we selected this for further testing under our reaction conditions using [BMIm]Cl as reaction media, as the previous studies proved that this was the most effective solvent. Firstly, different amounts of $[Rh(dppp)_2]Cl$ catalyst were tested in the decarbonylation reaction of p-tolualdehyde, the obtained results are showed in Table 3.2 on the preceding page. As expected, the yield increased as the amount of catalyst increased, going from 20% to almost quantitative conversion in the range of 2% to 5%catalyst in an 8 hours reaction (Table 3.2, entries 1-4). In order to compare the catalytic activity of the ionic liquid system with the established systems obtained by the group of Madsen, [117] an attempt was made to run a direct comparison to their solvent under our reaction conditions. The results show a better performance for the ionic liquid giving, 10% more yield than in the case of pure diglyme, 80% and 71% respectively (Table 3.2, entries 5 and 7). For a mixture of [BMImCl] and diglyme (1:1) used as a reaction media in order to generate a biphasic mixture that could facilitate the separation process of the product, the performance was less desirable yielding a 56% conversion (Table 3.2 on the facing page, entry 6), this lower yield compared with diglyme can be attributed to the phase separation in which the reaction takes place slowing down the reaction rate. The three variations of solvents can be seen in Figure 3.18.



Figure 3.18: Left vial pure [BMIm]Cl after 8 hour reaction. Center vial: 1:1 mixture of Diglyme:[BMIm]Cl after 8 hour reaction. Right: Pure diglyme after 8 hour reaction.

Upon getting the results it was obvious why the catalyst has never been attempted

to be recycled. As seen in Figure 3.18 on the preceding page, the reaction that ran with [BMIm]Cl kept its orange color after the reaction had run for 8 hours, whereas the other solvent combinations showed clear signs of rhodium black.



Figure 3.19: Some substrates used in this study.

In order to study the steric and electronic influences of the substrates in the decarbonylation reaction, different aromatic aldehydes were tested (Figure 3.19, 1-4). In order to compare the activity with the different substrates, the catalyst loading was selected to be 3 mol% since a moderate yield of 48% was obtained in the case of p-tolualdehyde (Table 3.2, entry 2) making the comparison between the substrates easier than at higher yields. The best results were obtained with *o*-tolualdehyde and *m*-tolualdehyde, in both cases almost quantitative yield was achieved. The high conversion compared with the other two substrates with the methyl and methoxy group in para position (Table 3.2, entries 2 and 10) could only be attributed to steric effects. Taking into account the catalytic results, the steric hindrance due to the methyl groups in ortho- and meta- position has a beneficial effect in the migratory extrusion step - proposed to be the rate determining step in the catalytic cycle for decarbonylation of aldehydes proposed by Fristrup *et al.*[129] - as well as in the reductive elimination pathway. Concerning electronic effects, with the more electron donating -OMe group in para- position (4) yield up to 62% was achieved while with the less electron donating -Me in para- position (3) only 48% yield was obtained under the same reaction conditions. In order to extend the scope of our work, the Rh catalyst was also tested in a decarbonylation of an aliphatic aldehyde, namely nonanal, achieving an excellent yield of octane (Table 3.2, entry 11).



Figure 3.20: Yield of homogeneous decarbonylation of *p*-tolualdehyde in [BMIm]Cl, the reaction was run with 5% catalyst in 8 hours cycles.

A recyclability study was performed and, as seen in Figure 3.20, the yields after each cycle of use decreases slowly. The catalyst sustains at least three runs while still obtaining yields above 85%, this is of course not acceptable and should be further investigated as to how to further stabilize the catalytic system. The color of the solution stays as shown in Figure 3.18 on page 61 in the vial to the left, the orange color can be attributed to the $[Rh(dppp)_2]Cl$ in solution. Upon using longer reaction times and lower catalyst loading i.e. 1% for 24 hours, one can generate a biphasic system in which the product is separated

from the ionic liquid. This could provide a unique chance for the upscaling of the process. Having a reusable catalyst is one thing, but the limitations of this process so far are staggering. Having an ionic liquid may provide the platform for the recyclable catalyst. This does, however, not yield a perfect system. A series of experiments where run with naphthaldehyde as a substrate, but only with limited succes, as the aldehyde evaporates from the ionic liquid and goes into gas phase and then condenses on the cooling unit, effectively stopping the reaction as both substrate and product are trapped in the cooling unit.

Having shown that homogeneous decarbonylation could be achieved, we attempted heterogenization of our catalyst, these results will be described in the following section.

3.3 Heterogeneous Decarbonylation in Continuous Flow

Having obtained good results in the homogeneous decarbonylation of aldehydes in ionic liquids, we shifted our focus towards heterogenization of the catalytic system. The prepared supported catalysts with rhodium/iridium complexes immobilized on silica were tested for the very first time in continuous flow gas-phase decarbonylation of aromatic and aliphatic aldehydes. When the catalysts were tested at 250 °C in runs lasting up to 4 hours, the yield was found to depend on the metal, the ligand employed and/or the metal loading. The results are compiled in Table 3.3 on the following page. An array of substrates where chosen, all seen in Figure 3.21, these were chosen in order to obtain a fully characterized reaction, with both activated and deactivated carbonyls. Unless otherwise mentioned, the reaction ran with p-tolualdehyde as the substrate.



Figure 3.21: Structures of some substrates tested in the heterogeneous decarbonylation. Reaction conditions: 300 mg catalyst, 0.05 ml min⁻¹ liquid flow (50 vol.% of substrate in 2-propanol), 10 ml min⁻¹ He as carrier gas, p = 1 bar, T = 250 °C.

Firstly, we investigated the influence of metal loading from 0.3 to 3 wt.%, with p-

Entry	Catalyst	Metal	Substrate	Yield	Yield	TOF
11101	$/SiO_2$	(wt.%)	Sabstrate	$(\%)^{a,b}$	$(\%)^c$	$(h^{-1})^a$
1	$[Rh(dppp)_2]Cl$	0.3	<i>p</i> -Tolualdehyde	18	25	246
2^d	$[Rh(dppp)_2]Cl$	0.3	<i>p</i> -Tolualdehyde	3	5	42
3	$[Rh(dppp)_2]Cl$	3	<i>p</i> -Tolualdehyde	74	53	102
4	RhCl ₃ ·aq	0.3	<i>p</i> -Tolualdehyde	17	5	234
5	$[Rh(COD)Cl]_2$	0.3	<i>p</i> -Tolualdehyde	3	1	42
6	$[Ir(dppp)_2]Cl$	3	<i>p</i> -Tolualdehyde	23	2	30
7	$[Rh(dppp)_2]Cl$	3	o-Tolualdehyde	95	83	132
8	$[Rh(dppp)_2]Cl$	3	<i>m</i> -Tolualdehyde	31	9	42
9	$[Rh(dppp)_2]Cl$	3	p-Anisolaldehyde	56	44	80
10	$[Rh(dppp)_2]Cl$	3	1-Nonanal	94	85	126
11^e	$[Rh(dppp)_2]Cl$	3	<i>p</i> -Tolualdehyde	80	57	114
12	None	0	<i>p</i> -Tolualdehyde	0	0	0

Table 3.3: Decarbonylation of aldehydes with supported silica catalysts.Reaction conditions: 300 mg catalyst, 0.05 ml min⁻¹ liquid flow(50 vol.% of substrate in 2-propanol), 10 ml min⁻¹ He as carriergas, p = 1 bar, T = 250 °C. ^a After 1 h. ^b Selectivity towards thedecarbonylation product > 99% for all tested substrates. ^c After 4h. ^d 215 °C. ^e n-pentane was employed as solvent

tolualdehyde as a substrate. As expected, the toluene yield increased with metal loading from 18 to 74% after 1 h of reaction, confirming the rhodium metal to be catalytically active in continuous flow reaction conditions (Table 3.3 on the facing page, entries 1 and 3). Due to the high reaction temperature and in order to avoid possible issues related with the decomposition of the employed catalysts, the catalytic reaction was performed at a lower temperature (215 °C) (Table 3.3 on the preceding page, entry 2) showing little to no activity, therefore it was decided to perform the decarbonlyation reaction at 250 °C. Then, other Rh precursors were employed containing Cl⁻ and COD as ligands in order to study the influence of ligand field on the catalytic system (Table 3.3 on the facing page, entries 4 and 5). RhCl₃ xH₂O/SiO₂ gave toluene yield of 17 % (TOF = 234 h⁻¹) after 1 h reaction which was comparable to [Rh(dppp)₂]Cl/SiO₂ whereas [Rh(COD)Cl]₂/SiO₂ gave by far the lowest yield of only 3% (TOF = 42 h⁻¹). The comparability of RhCl₃xH₂O did vanish over time, after only 4 hours the catalyst was completly deactivated.

Since the best catalytic activity was obtained with the $[Rh(dppp)_2]Cl/SiO_2$ (TOF = 246 h⁻¹) catalyst, the corresponding iridium catalyst was also tested in the continuous flow set-up, as such catalysts also previously have proven active for decarbonylation (Table 3.3 on the preceding page, entry 6), the iridium catalyst was furthermore chosen due to the work done by Geilen *et al.* who showed that the complex could decarbonylate HMF in compressed CO₂.[127] Compared to the 3 wt.% Rh catalyst (Table 3.3 on the facing page, entry 3) [Ir(dppp)_2]Cl/SiO₂ showed much lower catalytic activity yielding only 23 % toluene (TOF = 30 h⁻¹) after 1 h reaction. This result can be rationalized by inspection of FTIR spectra of the two catalysts measured before and after reaction, respectively, where a characteristic peak at 700 cm⁻¹ belonging to the ligand (dppp) disappeared after the reaction, the spectra can be found in Figure A.2 on page 113. In addition, the spectra showed that the phosphine was removed to a larger extent from the iridium center than the rhodium center, as the signal from the Ir sample collided with the signal for the pure silica, depicting the complete thermal decomposition of the catalyst.

The results obtained with the $[Rh(dppp)_2]Cl/SiO_2$ catalyst with *p*-tolualdehyde (Figure 3.21 on page 65, (3)) encouraged us to test the versatility of the prepared catalyst with other aromatic and aliphatic aldehydes. Following this we chose the analogous *o*- and *m*-tolualdehydes (1) and (2), in Figure 3.21 on page 65 were also used to study the steric effects on the catalytic activity. In addition, related aromatic aldehydes with both electron donor (4) and electron withdrawing groups (6)-(9) in th para-position, and naph-thaldehyde (10) were attempted tested in the reaction conditions seen in Figure 3.21 on page 65. Unfortunately, the aromatic aldehydes with electron withdrawing groups (6)-(9) and naphthaldehyde (10) were to poorly soluble in the applied solvents (i.e. 2-propanol and n-pentane). To provide comparable data, they were soluble to some extend but only in the range of 5 - 10% of the amount required to compare the reactions. The obtained results are summarized in Table 3.3 on page 66 (entries 7 to 10).

When the more electronically activated substrates with ortho and para substituents were applied, larger conversion was obtained compared to the meta-substituted tolualdehydes. Previously, it has been shown thet for homogeneous decarbonylation reactions with Rh-complexes upon addition of electron withdrawing substituents to the aromatic ring reaction rates are increased.[129] This was further corroborated when the methyl substituent was exchanged with a methoxy group. However, in the current study with immobilized catalyst, the activity was apparently 25 % lower for p-anisaldehyde than for p-tolualdehyde resulting in TOFs of 80 and 102 h⁻¹, respectively. On the other hand, the higher activity towards o-tolualdehyde decarbonylation (Table 3.3 on page 66, entry 7; TOF = 132⁻¹) was possibly related to steric hindrance induced by the methyl group in the ortho-position, thus making the expected rate-determining reductive elimination step more facile, yielding the desired product. In order to extend the scope of the continuous flow decarbonylation process and the versatility of our catalysts, an aliphatic aldehyde n-nonanal, (Figure 3.21 on page 65 (5)) was tested under the selected reaction conditions. Excellent results were obtained with a TOF as high as 126 h⁻¹ (Table 3.3 on page 66, entry 10). A blank experiment was also carried out in the absence of the Rh complex and as expected no conversion was observed after the reaction time (Table 3.3 on page 66, entry 12).

To get additional information on catalyst stability, the continuous decarbonylation was performed with the aldehyde substrates for 4 h. Figure 2 shows the product yields obtained as a function of time-on-stream. The best results (and catalyst stability) were attained in the decarbonylation of o-tolualdehyde and n-nonanal, resulting in approx. 95 % yield during the first 2 h of reaction, before activity decreased to around 85 % after an additional hour of reaction in both cases. A similar trend in activity decrease was also noticed for the other tested substrates, this can be seen in Figure 3.22 on the following page.

After complete reaction, the catalyst had changed color from pale yellow to dark gray/black. We subjected the catalyst to TEM:

As is evident from the TEM pictures, Rh-ligand complex decomposition during catalysis resulted in generation of Rh nanoparticles with average size of 3.2 ± 0.7 nm (Figure 3.23 on page 71). The generated nanoparticles had high crystallinity with face-centered cubic (FCC) structure. The corresponding Fast Fourier Transformations (FFT) can be seen in Figure A.1 on page 113 and revealed inter planar distances of 1.96 and 2.80 Å, respectively, which are in good agreement with the values of the (200) and (110) atomic planes for metallic Rh.[157] To examine if Rh nanoparticle formation was facilitated by 2propanol prior to the decarbonylation reaction, and to rule out a possible contribution to the observed catalytic activity, an analogous decarbonylation experiment was performed using *n*-pentane as solvent where formation of Rh nanoparticles is unlikely before the decarbonylation reaction. The results employing *n*-pentane were similar to the ones obtained using 2-propanol as solvent (Table 3.3 on page 66, entries 3 and 11), suggesting that the formation of Rh nanoparticles occurred during the course of the decarbonylation reaction, leading to decay in the catalytic activity over time and not prior to the decar-



Figure 3.22: Yield of products as a function of time after decarbonylation reactions with $[Rh(dppp)_2]Cl@SiO_2$ (3 wt.% Rh). Reaction conditions: 300 mg catalyst, 0.05 ml min⁻¹ liquid flow (50 vol.% of substrate in 2-propanol), 10 ml min⁻¹ He as carrier gas, p = 1 bar, T = 250 °C.



Figure 3.23: TEM micrographs of the [Rh(dppp)2]Cl/SiO2 (3 wt.% Rh) catalyst a) before and b) after decarbonylation. A histogram of determined Rh nanoparticle sizes is inserted in b)

	Average $\frac{P}{Rh}$ ratio
Before Catalysis	3.4
After Catalysis	2.7

 Table 3.4: Ratio between phosphorus and rhodium on the nanoparticles meassured by EDX.

bonylation reaction. In Figure 3.24 on the following page, TEM images of the catalyst before and after reaction are shown. It is clear that metal nanoparticles are formed during the course of the reaction. Hence, the observed catalyst instability can be linked to catalyst decomposition leading to the generation of metal nanoparticles and dppp ligand loss during the course of the reaction.

The observed drop in catalytic activity can be explained by the formation of rhodium nanoparticles and this is corroborated by the drop seen in the ratio between P and Rh in the EDX measurments. The drop in the ratio corresponds to 20.8% and the drop in catalytic activity to 28.3% after 4 hours. All of these results introduce novel questions, such as: Is it possible to stabilize the rhodium metal center? And it is evident, that a



Figure 3.24: TEM micrographs of the [Rh(dppp)2]Cl/SiO2 (3 wt.% Rh) catalyst a) before and b) after decarbonylation reaction in n-pentane.

thermally stable catalyst would be of great interest for the heterogeneous decarbonylation of aldehydes.

Chapter 4

Perspective and Conclusion

4.1 From Glucose til 5-Hydroxymethylfurfural

New insight into the apparent rates of the catalytic conversion of glucose to HMF with Cr(II) chloride and Cr(III) chloride in ionic liquids have been obtained from EXAFS, EPR, optical absorption and *in situ* ATR-FTIR spectroscopic experiments. The EXAFS measurements confirmed that $[CrCl_6]^{3-}$ was a major component formed when dissolving $CrCl_3 \cdot GH_2O$ in [BMIm]Cl. When glucose was added Cr(II)/Cr(III) complexes with coordinated glucose(e.g. $[CrCl_4Glucose]^{3-}$) were formed as important intermediates in the reaction mixture. Fitting a linear combination of the EXAFS data with Cr reference samples further showed, that some degree of oxidation of Cr(II) to Cr(III) (about 12%) took place under the reaction conditions. The *in situ* ATR-FTIR experiments revealed that the initial rate for the Cr(III)-catalyzed reaction was significantly higher than the corresponding Cr(II)-catalyzed reaction (about eight times). However, the Cr(III)-catalyzed reaction from going to completion. This was not the case with the much more labile Cr(II) catalyst system, where near quantitative conversion of glucose to HMF was observed provided that the water was continuously removed from the system as shown in the thin-film

experiments. Combining the results clearly suggests that the Cr(III) present in the system provides the most catalytically active species, but at relative high water concentrations only the Cr(II) species provide catalytic activity. EPR studies granted information as to the environment around the chromium, it was observed that a compound with $S = \frac{1}{2}$ emerged and disappered again over time, indicating the presence of radicals. Optical absorption spectroscopy corroborated the EXAFS results, which clearly stated that a change in the coordination environment was present, as Cr went from a hexachloro species to a dioxotetrachloro entity.

Perspectives

In order to ensure complete certainty as to what the reactive species is, the use of *in situ* EPR and mass spectroscopy makes sense. These techniques would provide data as to the coordination sphere. Furthermore, EPR in other frequencies could show the Cr(II) present in the solution.

4.2 Decarbonylation

Homogeneous Decarbonylation

For the first time in the reported literature, ionic liquids have been shown to be viable solvent for the homogeneous decarbonylation of aldehydes, with the use of $[Rh(dppp)_2]Cl$ as a catalyst. The homogeneous decarbonylation of both aromatic and aliphatic aldehydes proved possible, by using the ionic liquids, to an excellent extent. A series of ionic liquids where tested, and the results reflected a difference in activity based on both anion and cation composition. The most optimal system was comprised of $[Rh(dppp)_2]Cl$ in [BMIm]Cl. This system showed that the decarbonylation of a variation of substrates could be obtained, however, it also showed some limitations. The substrate and product had to be specifically chosen in order for the reaction to occur. It was shown that if the

substrate was a liquid at room temperature, the reaction could proceed. Solid substrates were not a possibility as these condensed in the cooling unit. Therefore attempts to run the reaction with cosolvents where attempted, these results showed that with the best reported solvent in the literature as a cosolvent, the reaction proceeded but yielded rhodium black as a byproduct. It was shown that the ionic liquid stabilized the catalytic system to a degree where the reuse of the catalyst was possible. The reaction ran three cycles while maintaining good catalytic activity (99% - 85%). The catalysis yielded a biphasic system and therefore the separation of the product from the reaction mixture was done with ease, showing the benefits of this system compared with traditional organic solvents.

Perspectives

The future application of ionic liquids in decarbonylation requires further development. The development of a biphasic system would yield the possibility for the decarbonylation of solid substrates as well as ease with the separation of product and improve the reusability of the catalytic system. A major drawback of this system is the thermal stability or lack of, it is known that the catalyst decomposes at the reaction temperatures. The development of a thermally stable catalyst with the same bite angle as dppp would be of vital importance to obtain a better catalytic system.

Heterogeneous Decarbonylation

In this thesis is has been proven that a continuous flow decarbonylation of aldehydes is possible. The catalyst was comprised of $[Rh(dppp)_2]Cl$ impregnated on a silica support. The catalyst showed yields of up to 95% at temperatures elevated compared to the homogeneous decarbonylation. When the temperature was increased to 250 °C, the system yielded excellent results. The catalyst was subjected to a variety of substrates, and it was found to be able to decarbonylate both aromatic and aliphatic aldehydes. The activity of the catalyst was good for three to four hours after which it simply deactivated. A reason for the deactivation of the catalyst was the formation of nanoparticles of rhodium on the silica. These showed little to no activity. The influence of the ligand was investigated via the exchange of the dppp ligand with other varieties. It was observed that the ligand was indeed necessary to obtain an active catalyst, and that the oxidation state of the catalyst also played a pivotal role.

Perspectives

The gas-phase decarbonylation of aldehydes showed a promising trend. This setup could generate a new and fascinating way to run an industrial decarbonylation. But in order for this to be possible, the thermal stability of the ligand needs to be investigated further. If possible a system that is stable above 250 °C should be synthesized.

Appendix A

Graphs

A.1 From Glucose to 5-Hydroxymethylfurfural

A.1.1 XANES



EXAFS of Chromium(II)Chloride in BMImCl.



EXAFS of Chromium(II)Chloride hydrate in BMImCl.



EXAFS of Chromium(III)Chloride in BMImCl.



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=0.0~{\rm min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=1.0~{\rm min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=1.5~\mathrm{min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=2.0~{\rm min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=2.5~\mathrm{min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t= 3.0 min



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=3.5~\mathrm{min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=4.0~\mathrm{min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=4.5~\mathrm{min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=5.0~{\rm min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=10.0~{\rm min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t= 30.0 min



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=40.0~\mathrm{min}$



EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t $=50.0~{\rm min}$


EXAFS of the Chromium catalyzed dehydration of glucose in BMImCl. At t= 60.0 min

A.1.2 *R*-Space functions



R-Space function of Chromium(II)Chloride in BMImCl.



R-Space function of Chromium(II)Chloride hydrate in BMImCl.



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_6.$ At t = 0.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_6.$ At t = 1.5 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 1.5 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 2.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 2.5 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 3.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 3.5 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 4.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 4.5 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 5.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 10.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 30.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 40.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 50.0 min



 $R\text{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl, fitted as ${\rm CrCl}_4{\rm O}_2.$ At t = 60.0 min

A.1.3 k-Space functions



k-Space function of Chromium(II)Chloride in BMImCl.



k-Space function of Chromium(II)Chloride hydrate in BMImCl.



k-Space function of Chromium(III)Chloride in BMImCl.



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 0.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 1.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 1.5 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 2.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 2.5 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 3.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 3.5 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 4.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 4.5 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 5.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 10.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 30.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 40.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 50.0 min



 $k\mbox{-}{\rm Space}$ function of the Chromium catalyzed dehydration of glucose in BMImCl. At t = 60.0 min

A.1.4 EPR Spectroscopy



Time resolved EPR study of the dehydration of glucose in [BMIm]Cl with $\rm Cr(III)Cl_3.$ Integrated once.



Time resolved EPR study of the dehydration of glucose in [BMIm]Cl with $\rm Cr(III)Cl_3.$ Integrated twice.

A.2 Homogeneous Decarbonylation

A.2.1 TGA Meassurements



TGA of [EMIm]Cl with a heating rate of 10 $^{\circ}\mathrm{C/min}$ from room temperature to 600 $^{\circ}\mathrm{C}.$



TGA of [BMIm]Cl with a heating rate of 10 $^{\circ}\mathrm{C/min}$ from room temperature to 600 $^{\circ}\mathrm{C}.$



TGA of [OMIm]Cl with a heating rate of 10 $^{\circ}\mathrm{C/min}$ from room temperature to 600 $^{\circ}\mathrm{C}.$



TGA of [EMIm]OAc with a heating rate of 10 $^{\circ}\mathrm{C/min}$ from room temperature to 600 $^{\circ}\mathrm{C}.$



TGA of [BMIm]OAc with a heating rate of 10 $^{\circ}\mathrm{C/min}$ from room temperature to 600 $^{\circ}\mathrm{C}.$



TGA of $[\rm Rh(Dppp)_2]\rm Cl$ with a heating rate of 10 $^{\circ}\rm C/min$ from room temperature to 600 $^{\circ}\rm C.$

A.3 Heterogeneous Decarbonylation

A.3.1 TGA Meassurements



TGA of SiO₂ with a heating rate of 5 $^{\circ}{\rm C}$ min⁻¹ from room temperature to 260 $^{\circ}{\rm C}$ followed by constant temperature for 6 h.



TGA of $RhCl_3@SiO_2$ with a heating rate of 5 °C min⁻¹ from room temperature to 260 °C followed by constant temperature for 6 h.



TGA of $[Rh(COD)Cl]_2@SiO_2$ with a heating rate of 5 °C min⁻¹ from room temperature to 260 °C followed by constant temperature for 6 h.



TGA of $[Rh(dppp)_2]Cl@SiO_2$ with a heating rate of 5 °C min⁻¹ from room temperature to 260 °C followed by constant temperature for 6 h.



TGA of $[Ir(dppp)_2]Cl@SiO_2$ with a heating rate of 5 °C min⁻¹ from room temperature to 260 °C followed by constant temperature for 6 h.

A.3.2 TEM pictures

A.3.3 IR meassurements



TEM picture showing the lack of nanoparticle formation after heating to 250 $^{\circ}\mathrm{C}$ for 4 h.



Figure A.1: TEM micrographs and corresponding fast Fourier transforms (FFTs) showing atomic resolution of the nanoparticles formed during the decarbonylation reaction with $[Rh(dppp)_2]Cl/SiO_2$ under the described experimental conditions.



Figure A.2: FTIR spectra of a) Rh and b) Ir catalysts compared to the silica support material before and after reaction.

Appendix B

Publications

B.1 Peer-reviewed Publications - Project Related

$\mathbf{2014}$

In-situ Spectroscopic Studies on the Chromium Catalyzed Glucose Conversion to 5-(hydroxymethyl)furfural in Ionic Liquids.

P. Malcho, J. Andersen, A. J. Kunov-Kruse, K. Ståhl and A. Riisager Submitted to: Chemistry - a European Journal, 2014

Supported Rh-Phosphine Complex Catalysts for Continuous Gas-Phase Decarbonylation of Aldehydes.

P. Malcho, E. J. García-Suárez, U. V. Mentzel, C. Engelbrekt and A. Riisager. Submitted to: Dalton Transactions, 2014

Ionic Liquids as Recyclable Reaction Media for the Rh-Catalyzed Homogeneous Decarbonylation of Aromatic and Aliphatic Aldehydes.P. Malcho, E. J. García-Suárez and A. Riisager.

Submitted to: Green Chemistry, 2014

2013

A Method for Effective Conversion of Saccharides to Furfural Compounds.
A. J. Kunov-Kruse, P. Malcho, K. Ståhl, J. Andersen, R. Fehrmann, A. Riisager.
Patent Application No. EP13176259.3

B.2 Peer-reviewed Publications - Project Unrelated

Selective Synthesis of Clinoata
camite $\rm Cu_2(OH)_3Cl$ and Tenorite CuO Nanoparticles via pH Control

C. Engelbrekt, P. Malcho, J. Andersen, L. Zhang, K. Ståhl, B. Li, J. Hu and J. Zhang Accepted to: Journal of Nanoparticle Research, 2014

B.3 Oral Presentations

2013

Merging Heterogeneous and Homogeneous Decarbonylation.

P. Malcho, E. J. García-Suárez, C. Engelbrekt, U. V. Mentzel and A. Riisager. Europacat XI, 2013, Lyon France.

2012

Ionic liquids as Solvents for Catalytic DecarbonylationP. Malcho, C. F. Gomez and A. Riisager.243th ACS National Meeting and Expo, 2012, San Diego, USA.

B.4 Poster Presentations

2014

Supported Rh-Phosphine Catalysts for Continuous Gas-Phase Aldehydes Decarbonylation

E. J. García-Suárez, P. Malcho and A. Riisager.

16th Nordic Symposium on Catalysis, 2014, Oslo, Norway.

Homogenous Decarbonylation in Ionic Liquids - a New Tool for Biomass Deoxygenation.

P. Malcho, E. J. García-Suárez, and A. Riisager.

4th International Congress on Green Process Engineering, 2014, Sevilla, Spain.

2013

Merging Heterogeneous and Homogeneous Decarbonylation.

P. Malcho, E. J. García-Suárez, C. Engelbrekt, U. V. Mentzel and A. Riisager. Europacat XI, 2013, Lyon France.

2012

Ionic Liquids as Solvents for Catalytic Decarbonylation.

P. Malcho, C. Fernandez Gomez and A. Riisager.

International Congress on Catalysis, 2010, Münich, Germany.

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