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Aerobic Oxidation of 5-(Hydroxymethyl)furfural in Ionic Liquids with Solid Ruthenium Hydroxide Catalysts

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Abstract The aerobic oxidation of 5-(hydroxymethyl)furfural was investigated over solid ruthenium hydroxide catalysts in ionic liquids at elevated temperatures and pressures. Several different catalyst supports were tested in combination with various ionic liquids. The best result was obtained in [EMIm][OAc] at 100 °C with 30 bar of oxygen over $Ru(OH)_x/La_2O_3$ which afforded 48 % of 2,5-furandicarboxylic acid and 12 % of 5-hydroxymethyl-2-furancarboxylic acid. During use the catalysts were found to leach some of the metal inventory. However, the leached Ru species did not contribute to the catalytic activity, thus verifying that the catalytic oxidation proceeded heterogeneously under the applied reaction conditions.

Keywords Oxidation · Supported ruthenium hydroxide · 5-(Hydroxymethyl)furfural · 2,5-Furandicarboxylic acid · Ionic liquids

1 Introduction

In all segments of the chemical industry oxidations of functional groups play a vital role in the derivatization of chemical compounds. These reactions have traditionally been carried out with stoichiometric reagents such as chromium(VI) compounds, permanganate, iodate compounds and peroxy acids which have toxicity issues and produce a large amount of waste compared to the amount of product [1, 2]. In order to relinquish the use of these reagents, the chemical industry, and the scientific community are pursuing oxidations with environmentally benign oxidants such as hydrogen peroxide and molecular oxygen together with efficient and selective catalysts [3, 4].

Recently, Yamaguchi and Mizuno [5] introduced supported ruthenium hydroxides as versatile and highly active catalysts for aerobic oxidations. These catalysts work exceedingly well in connection with common functional group transformations such as oxidations of alcohols [6] and the oxygenation of primary amines to amides [7].

Ionic liquids (ILs) are interesting alternatives to conventional molecular solvents due to their negligible vapor pressure, redox stability, non-flammability and unique dissolving abilities for polar compounds [8]. The redox stability has allowed oxidations to be widely studied in ILs for several applications such as the oxidative Glaser coupling [9], oxidations of alcohols to aldehydes or ketones [10–12] and the oxidation of alkanes [13, 14]. Several examples of epoxidations of alkenes [15–19] and other miscellaneous functional group transformations [20–24] in ILs are also found in the literature. In most cases the oxidant is H_2O_2, but also stoichiometric reagents such as NaOCl, Dess-Martin periodate, MnO_2 and *meta*-chloroperoxybenzoic acid (*m*CPBA) have been reported. The most commonly employed ILs are 1-butyl-3-methylimidazolium tetrafluoroborate ([BMIm][BF_4]) and 1-butyl-3-methylimidazolium hexafluorophosphate ([BMIm][PF_6]). The ideal oxidant for green chemical processes is molecular oxygen and aerobic oxidations with homogeneous catalysts in ILs have been reported by numerous groups [25–39].

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Deriving chemicals from biomass has received significant attention among chemists in later years. In particular 5-(hydroxymethyl)furfural (HMF), formed from the dehydration of hexose sugars, has been in the spotlight since it is believed to become an essential platform chemical in the future biopetrochemical industry [40, 41]. An important derivative of HMF is 2,5-furandicarboxylic acid (FDA), which is formed by oxidation and is intended to replace terephthalic acid as a monomer in polyesters [42]. As a matter of fact, Avantium has recently opened a pilot plant at the Chemelot site in Geleen (The Netherlands) using this technology to produce Polyethylene Furanoate (PEF) from HMF [43, 44]. The catalytic oxidation of HMF was initially studied by the group of van Bekkum using heterogeneous platinum and palladium catalysts [45, 46]. This study has been succeeded in later years with studies on $Co(acac)_3$ [47], gold nanoparticles [48–50] and a more detailed study of platinum catalysts on different supports [51]. The oxidation of HMF proceeds via diformylfuran (DFF) or 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) to 5-formyl-2-furancarboxylic acid (FFCA) which is rapidly converted to FDA [45]. HMF can also be oxidized to DFF and maleic anhydride selectively using vanadium catalysts, resulting in the formation of formic acid (FA) as a by-product [52–54]. The different oxidation products of HMF are depicted in Scheme 1.

The synthesis of HMF from sugars benefits particularly from using certain ILs as solvents, and thus an overall process from HMF to FDA in ILs would be advantageous [55]. In addition, the exceedingly low solubility of FDA in water and other conventional solvents makes an oxidation process of HMF in ILs by the use of heterogeneous catalysts an interesting option [56]. In such a process the catalyst would be filtered off after complete reaction, followed by the addition of water to the resulting IL/FDA mixture making FDA precipitate. The aqueous IL would then be stripped of water and recycled.

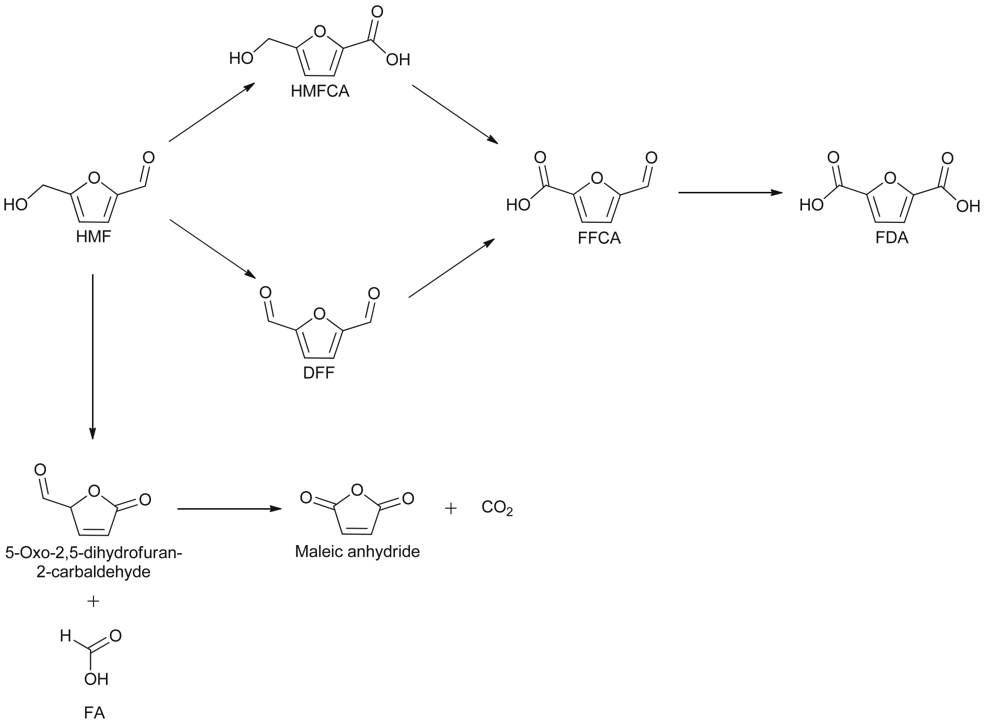
To the best of our knowledge no investigation of heterogeneous catalysts for the aerobic oxidation of HMF in ILs has been reported. Our objective in this study was to investigate the viability of the utilization of ILs as solvent for this reaction. In this particular case, heterogeneous $Ru(OH)_x$ catalysts on different supports in ILs were used in the aerobic oxidation of HMF to FDA. The reaction was studied at different reaction conditions and leaching tests of ruthenium were made to investigate the stability of the catalyst in ILs. However, further experiments are required to optimize the yield to FDA.

2 Experimental

2.1 Materials

5-(Hydroxymethyl)furfural (HMF) (>99 %), 2-furoic acid (98 %), levulinic acid (LA) (98 %), formic acid (FA) (98 %), ruthenium(III) chloride (purum), $Mg_6Al_2CO_3(OH)_{16}\cdot 4H_2O$ (HT), magnetite (>98 %), $Ca_5(PO_4)_3(OH)$ (HAp) (>97 %), aluminium oxide (>99.9 %), zirconium oxide (99 %), lanthanum(III) nitrate hexahydrate (99.99 %) and

Scheme 1 Different oxidation products of HMF



sodium hydroxide (>98 %) were acquired from Sigma-Aldrich. Ruthenium(III) nitrate hexahydrate (99.9 %) and magnesium nitrate hexahydrate (p.a.) were obtained from Merck. Cerium oxide (99.5 %) and lanthanum(III) oxide (99.9 %) were purchased from Alfa Aesar. Magnesium oxide (p.a.) was purchased from Riedel-de Haën AG. 2,5-Diformylfuran (DFF) (98 %) was obtained from ABCR GmbH & Co. 2,5-Furandicarboxylic acid (FDA) (>99 %) and 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) (>99 %) were purchased from Toronto Research Chemicals Inc. and dioxygen (99.5 %) from Air Liquide Denmark. The ionic liquids 1-ethyl-3-methylimidazolium dicyanamide ([EMIm][N(CN)$_2$]) (98 %) and 1,3-dimethylimidazolium dimethyl phosphate ([MMIm][dmp]) (98 %) were purchased from Solvent Innovation, while all other ionic liquids (>95 %) were obtained from BASF. All chemicals were used as received. All Ru(OH)$_x$/support catalysts were synthesized according to literature procedures [57].

2.2 Apparatus and Analysis

Catalytic oxidation experiments at ambient pressure were performed using a Radley Carousel 12 Plus Basic System, while high pressure oxidation reactions were carried out in stirred Parr autoclaves equipped with internal thermocontrol (T316 steel, Teflon^{TM} beaker insert, 100 mL). All reaction samples were analyzed by HPLC (Agilent 1200 series, Bio-Rad Aminex HPX-87H, 300 mm × 7.8 mm pre-packed column, 0.005 M H_2SO_4 mobile phase, 60 °C, 0.6 mL/min). The yields and selectivities were based on conversion of HMF and confirmed by calibration of standard solutions of the products and reactants.

Surface areas were determined by nitrogen sorption measurements at liquid nitrogen temperature on a Micromeritics ASAP 2020. The samples were outgassed in vacuum at 150 °C for 4 h prior to the measurements. The total surface areas were calculated according to the BET method. X-ray fluorescence (XRF) analyses were recorded on a Minipal 4 X-ray spectrometer (PANalytical).

2.3 Oxidation Procedures

In the catalytic screening experiments performed at ambient air pressure, catalyst (100 mg, 0.025 mmol Ru) and IL (1.0 g) were mixed in a 40 mL tube and stirred at 100–140 °C for 10 min. HMF (70 mg, 0.56 mmol) was added and the mixture was stirred in an open flask for 24 h. The reaction was subsequently cooled down to room temperature and diluted to 10 mL with 0.1 M NaOH. Finally, the catalyst was filtered off and the resultant solution analyzed by HPLC.

In the high pressure oxidation reactions, catalyst (0.5 g, 0.125 mmol Ru), HMF (350 mg, 2.78 mmol) and IL (12.0 g) were mixed in a Parr autoclave, pressurized with dioxygen (10–30 bar) and stirred at 100–140 °C for 5 h. The reaction mixture was cooled down to room temperature and diluted to 100 mL with 0.1 M NaOH. Finally, the catalyst was filtered off and the resultant solution analyzed by HPLC.

2.4 Procedure for Leaching Test

Catalyst (100 mg, 0.025 mmol Ru) and [EMIm][OAc] (1.0 g) were mixed in a 40 mL tube and stirred at 100 °C for 1 h. The reaction solution was diluted in 5 mL of water and the catalyst was filtered off. The water was evaporated by heating the ionic liquid at 120 °C overnight. HMF (70 mg, 0.56 mmol) was added to the liquid and the mixture was stirred in an open flask at 100 °C for 6 h. The mixture was cooled down to room temperature, diluted to 10 mL with 0.1 M NaOH, filtered and analyzed by HPLC.

3 Results and Discussion

3.1 HMF Oxidation at Ambient Pressure

The ILs best suited for the synthesis of HMF from fructose or glucose have proven to be 1-ethyl-3-methylimidazolium chloride ([EMIm]Cl) and 1-butyl-3-methylimidazolium chloride ([BMIm]Cl) [55]. Consequently, [EMIm]Cl was applied for the initial screening of catalysts with Ru(OH)$_x$ supported on different carriers for the HMF oxidation at ambient pressure. A relatively high temperature was chosen in order to reduce the impact of viscosity of the mixture formed between the catalyst and IL. Since the screening was performed to allow comparison of the influence induced by the different types of catalyst supports, the reduced solubility of oxygen at elevated temperature was at this stage disregarded. The experiments were performed in open tubes and the results are shown in Table 1.

All catalysts were found to exhibit activity in [EMIm]Cl. Even though the yields of FDA in all cases were low, an indication of which catalysts were the most promising candidates for further study could be derived from the yields of HMFCA. The best catalysts (Table 1, entries 3 and 7–9) were Ru(OH)$_x$/Fe$_2$O$_3$, Ru(OH)$_x$/HT, Ru(OH)$_x$/MgO and Ru(OH)$_x$/La$_2$O$_3$, which gave yields of HMFCA in the range of 14–25 %. No DFF was observed in any of these experiments.

After oxidation activity had been proven, albeit with low yields, the study was expanded to include other ILs. Notably, the study did not include [BMIm][BF$_4$] and [BMIm][PF$_6$] which have been commonly employed in earlier oxidation studies in ILs. These tend to form HF upon contact with moisture at elevated temperature which

Table 1 HMF oxidation in [EMIm]Cl with various $Ru(OH)_x$/support catalysts

Entry	Catalyst	BET surface area (m^2/g)	Conversion (%)	Yield (%)		
				DFF	HMFCA	FDA
1	$Ru(OH)_x/TiO_2$	128	92	0	1	3
2	$Ru(OH)_x$/spinel	54	89	0	7	3
3	$Ru(OH)_x/Fe_2O_3$	45	99	0	14	5
4	$Ru(OH)_x/ZrO_2$	97	84	0	3	5
5	$Ru(OH)_x/CeO_2$	8	86	0	7	4
6	$Ru(OH)_x$/HAp	25	81	0	4	4
7	$Ru(OH)_x$/HT	6	>99	0	20	5
8	$Ru(OH)_x$/MgO	27	>99	0	20	2
9	$Ru(OH)_x/La_2O_3$	5	>99	0	25	1

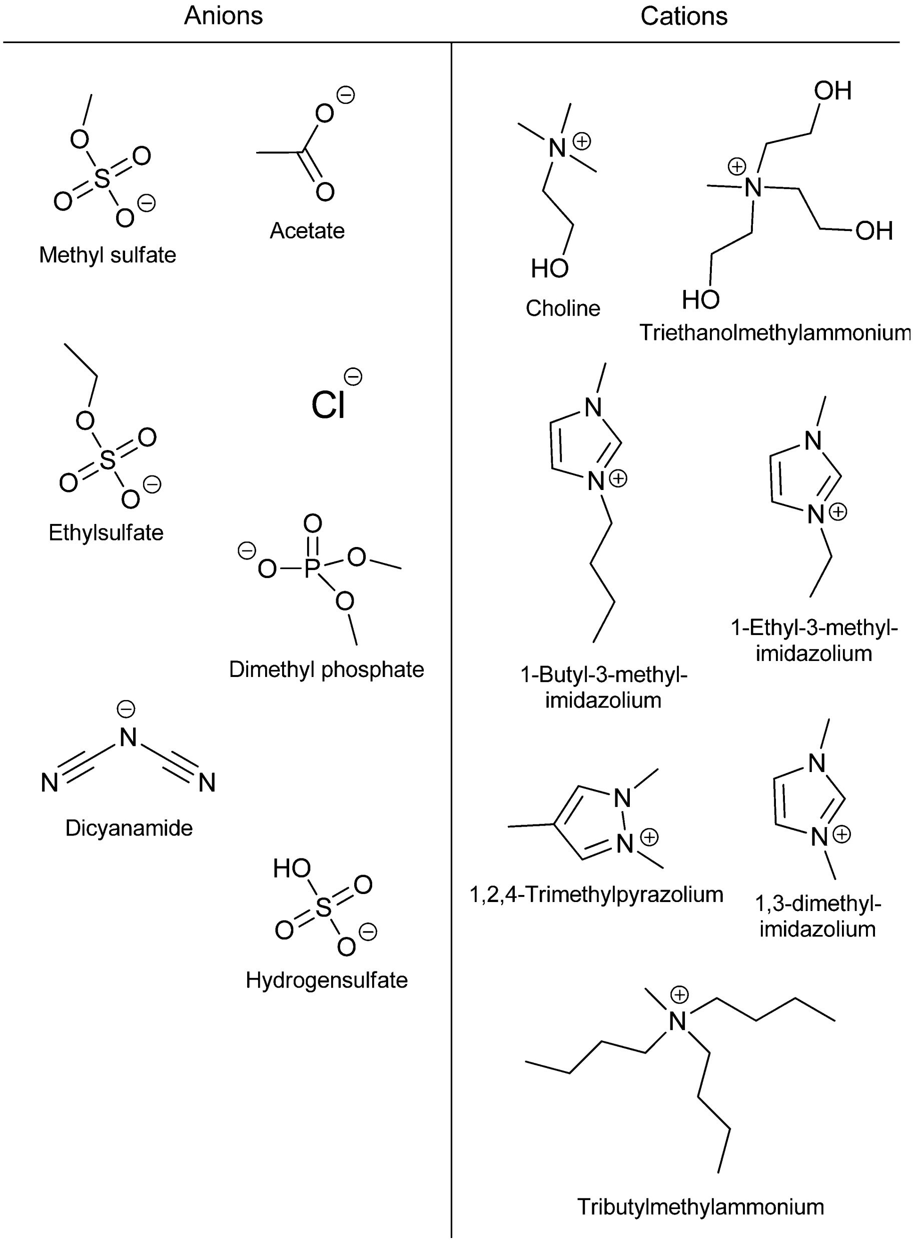
Reaction conditions 1.0 g [EMIm]Cl, 68 mg (0.54 mmol) HMF, 100 mg catalyst (2.5 wt% Ru, 0.025 mmol), 140 °C, 24 h, ambient air pressure

could be detrimental to reaction intermediates as well as catalyst [8, 58]. The ions of the ILs chosen are depicted in Scheme 2.

The most promising catalysts from the first screening were tested together with $Ru(OH)_x/CeO_2$ which had shown superior activity in water [57]. Additionally, the catalyst precursor $RuCl_3$ was included for comparison. Most of the reactions afforded very low yields for the different oxidation products and only a few gave interesting results for further studies. The results for the most interesting ILs are summarized in Table 2 while the complete screening results of all ILs can be found in supporting information (Table S1).

For 1-ethyl-3-methylimidazolium acetate ([EMIm][OAc]) formation of FDA was observed with $Ru(OH)_x/La_2O_3$ and $Ru(OH)_x$/spinel (Table 2, entries 7 and 10). Surprisingly, 6 % of FDA was also formed when using the homogeneous catalyst $RuCl_3$ (entry 9). Formation of HMFCA was also observed for all other catalysts in [EMIm][OAc] indicating that the oxygen solubility was higher compared to other ILs. No solubility data for dioxygen in [EMIm][OAc] was available in literature, but the solubility of O_2 is generally low in comparison to other gases in ILs [59–63]. Another IL that showed promising results was 1-ethyl-3-methylimidazolium hydrogen sulfate ([EMIm][HSO_4]) which afforded 19 % FDA using $Ru(OH)_x$/HT (entry 1). When employing $Ru(OH)_x/CeO_2$ in the same IL 9 % of DFF was formed. No other oxidation products were observed along with a slightly lower conversion of HMF compared to $Ru(OH)_x$/HT (entry 3). The catalyst precursor $RuCl_3$ had no activity in [EMIm][HSO_4] (entry 4). Tributylmethylammonium methyl sulfate ([Bu_3MeN][$MeOSO_3$]) and 1,2,4-trimethylpyrazolium methyl sulfate ([MMMPz][$MeOSO_3$]) gave DFF formation in combination with $Ru(OH)_x$/spinel. The HMF conversion was much higher in [MMMPz][$MeOSO_3$] with $Ru(OH)_x$/spinel compared to $Ru(OH)_x/La_2O_3$ suggesting that the interaction between the IL and spinel resulted in species that had a negative effect on HMF stability (entries 11–13).

In our previous work at high temperature [64] we have demonstrated that [EMIm][OAc] has a detrimental effect on HMF stability, lowering the carbon balance. Accordingly, we investigated the effect of lowering the reaction temperature. Both [EMIm][HSO_4] and [Bu_3MeN][$MeOSO_3$] proved to be very viscous in combination with the catalyst at 100 °C, which was why experiments with these liquids were only performed at lower temperature in autoclave with mechanical stirring in the later high-pressure experiments (vide infra). In Fig. 1 the product distribution for the oxidation of HMF in [EMIm][OAc] with $Ru(OH)_x$/spinel at 100 °C is shown as a function of time. The final yield of FDA was lower than in the high-temperature experiments and no DFF was detected, whereas the yield of HMFCA was higher and almost amounted to 50 %. The conversion of HMF remained high, accentuating the need of faster oxidation kinetics to avoid degradation. We did not detect any by-products on our HPLC system and assumed therefore that the degradation of HMF in [EMIm][OAc] resulted in polymeric condensation products, as has been previously reported [65]. Neither levulinic acid nor formic acid, common degradation products of HMF [66], were formed at ambient pressure. According to these results, we can propose a scheme of the formation of by-products during the aerobic oxidation of HMF, represented in Scheme 3. In this case, under high temperature conditions, the HMF, as well as the intermediates or the final FDA product can form higher molecular weight compounds via different mechanisms, like ketonization, condensation or even Diels-alder condensation [67–69]. As shown later, higher pressures and conversion values are required to form degradation products such as formic acid. Other oxidation products such as maleic anhydride are also possible, as presented in Scheme 1. These three types of side reactions lead to a



Scheme 2 The cations and anions of the ILs used in the HMF oxidation study

clear decrease in the carbon balance closures in the oxidation experiments.

The best result at 100 °C was obtained with La_2O_3 as catalyst support (Fig. 2). Here the HMF conversion reached a maximum already after 6 h which coincided with an HMFCA yield of 58 %. The amount of HMFCA then declined slowly to form FDA which reached a yield of around 10 % after 30 h.

3.2 HMF Oxidation at High Pressure

The open-flask experiments performed at ambient air pressure showed potential for oxidations at higher pressure. The generally low solubility of molecular oxygen in ILs leads to the assumption that pressures significantly higher than ambient were required to reach full conversion of HMFCA to FDA. In addition to the oxidation products obtained in the reactions at atmospheric pressure, formic acid (FA) was formed to various extent at higher oxygen pressure, as also depicted in Scheme 3. A summary of the results from the high pressure experiments is shown in Table 3.

The first series of autoclave experiments were conducted with 10 bar of dioxygen at 140 °C with a reaction time of 5 h. Using $Ru(OH)_x$/spinel in [EMIm][HSO_4] (Table 3, entry 1) a very similar result to the open flask experiment at ambient pressure was obtained (Table 2, entry 2). Evidently, the increased pressure was in this case insufficient

Table 2 HMF oxidation in different ILs with various $Ru(OH)_x$/support catalysts

Entry	Ionic liquid	Catalyst	Conversion (%)	Yield (%)		
				DFF	HMFCA	FDA
1	[EMIm][HSO_4]	$Ru(OH)_x$/HT	99	1	0	19
2	[EMIm][HSO_4]	$Ru(OH)_x$/spinel	55	3	0	0
3	[EMIm][HSO_4]	$Ru(OH)_x/CeO_2$	77	9	1	0
4	[EMIm][HSO_4]	$RuCl_3$	84	0	0	0
5	[EMIm][HSO_4]	$Ru(OH)_x/La_2O_3$	71	3	0	0
6	[EMIm][OAc]	$Ru(OH)_x$/HT	93	0	13	0
7	[EMIm][OAc]	$Ru(OH)_x$/spinel	99	0	27	13
8	[EMIm][OAc]	$Ru(OH)_x/CeO_2$	55	1	2	0
9	[EMIm][OAc]	$RuCl_3$	>99	0	27	6
10	[EMIm][OAc]	$Ru(OH)_x/La_2O_3$	>99	0	30	10
11	[Bu_3MeN][$MeOSO_3$]	$Ru(OH)_x$/spinel	64	12	0	0
12	[MMMPz][$MeOSO_3$]	$Ru(OH)_x$/spinel	95	6	0	0
13	[MMMPz][$MeOSO_3$]	$Ru(OH)_x/La_2O_3$	46	10	0	0

Reaction conditions 1.0 g IL, 68 mg (0.54 mmol) HMF, 100 mg catalyst (2.5 wt% Ru, 0.025 mmol), 140 °C, 24 h, ambient air pressure

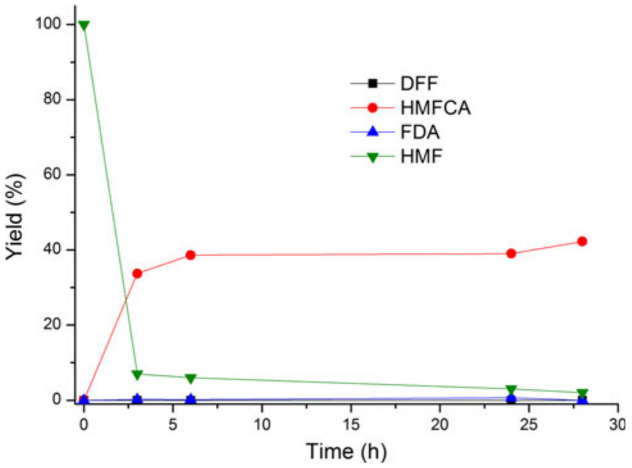


Fig. 1 Oxidation of HMF with $Ru(OH)_x$/spinel in [EMIm][OAc] at 100 °C. *Reaction conditions* 1.0 g IL, 68 mg (0.54 mmol) HMF, 100 mg catalyst (2.5 wt% Ru, 0.025 mmol), 100 °C, ambient air pressure

to impose an effect on the slow gas mass transfer. The use of $Ru(OH)_x$/spinel in [EMIm][OAc] resulted in a decrease in HMFCA yield from 27 to 4 %, while the yield of FDA only increased from 13 to 14 % (entry 2). The high temperature in combination with an increased pressure almost certainly accelerated degradation in [EMIm][OAc], leading to lower yields than at ambient pressure.

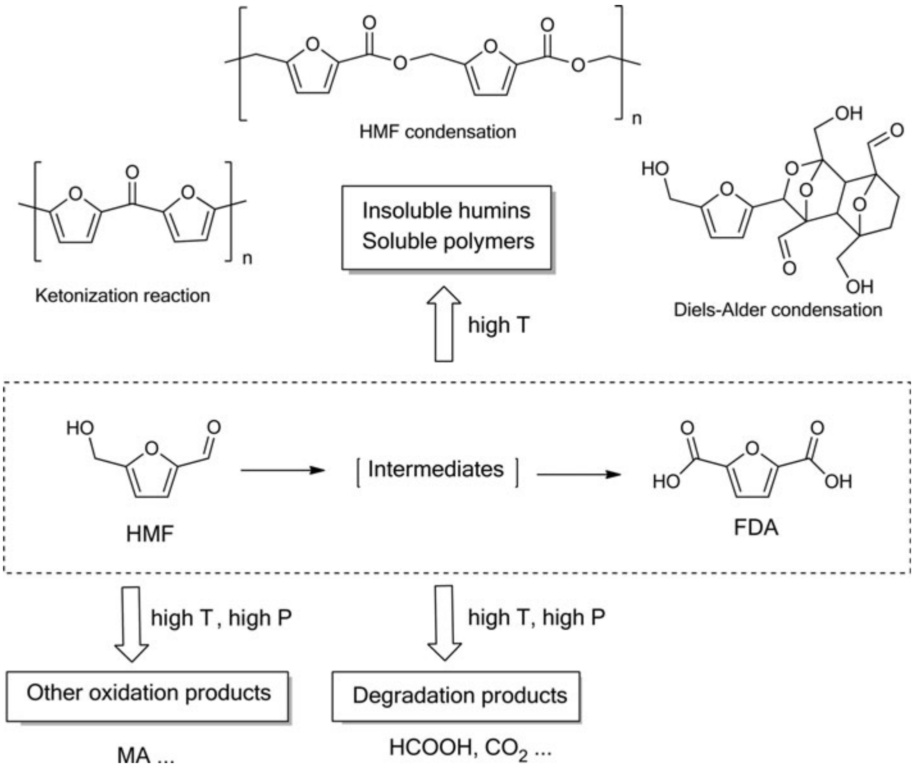
In light of the improved results obtained when lowering the reaction temperature for the open flask experiments, high pressure reactions were also conducted at 100 °C. For $Ru(OH)_x$/HT in [EMIm][HSO_4] this resulted in a significant reduction of HMF conversion from 99 to 32 % and no formation of FDA, whereas HMFCA and DFF were obtained in 3 and 18 % yield, respectively (entry 3). This was most likely a consequence of higher viscosity which made mixing more difficult, resulting in slower gas diffusion and accompanying mass transfer limitations. The same phenomenon appeared in the case of $Ru(OH)_x$/spinel in [Bu_3MeN][$MeOSO_3$] where the FDA yield was lowered drastically from 10 to 1 %. Improvement was observed at 100 °C for $Ru(OH)_x/La_2O_3$ in [EMIm][OAc] where 23 % of FDA was formed along with 34 % of HMFCA (entry 4). Clearly, the detrimental effect of [EMIm][OAc] on HMF stability was reduced and conversion to the desired product was favored when decreasing the temperature.

The final adjustment made was to increase the dioxygen pressure even further to 30 bars. This gave a slight increase in HMF conversion from 32 to 52 % for $Ru(OH)_x$/HT in [EMIm][HSO_4], but still with no FDA being formed (entry 7). The best result was obtained with $Ru(OH)_x/La_2O_3$ in [EMIm][OAc] which afforded an FDA yield of 48 % and an HMFCA yield of 12 % (entry 8). In addition to the desired products, 30 % of FA was formed, suggesting that some oxidative degradation was favored at elevated pressure in [EMIm][OAc], as suggested in Scheme 3.

3.3 Leaching Study at Ambient Pressure

Heterogeneous catalysts can be sensitive to leaching of the active catalytic specie from the support which can be deceptive when interpreting experimental results. The reaction conditions for the performed oxidation experiments were such that leaching was not unlikely, and the experiments using the catalyst precursor $RuCl_3$ at ambient pressure had already confirmed that HMF oxidation could also proceed homogeneously. Accordingly, the two most promising catalysts ($Ru(OH)_x/La_2O_3$ and $Ru(OH)_x$/spinel)

Scheme 3 Possible degradation products obtained during HMF oxidation at high temperature and/or pressures in the presence of IL and supported catalyst



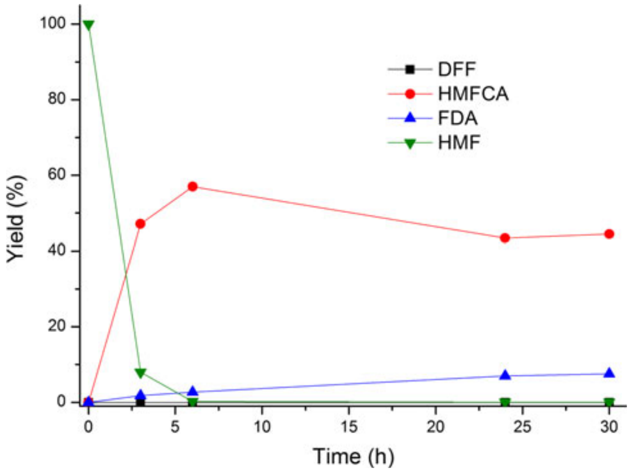


Fig. 2 Oxidation of HMF with $Ru(OH)_x/La_2O_3$ in [EMIm][OAc] at 100 °C. *Reaction conditions* 1.0 g IL, 68 mg (0.54 mmol) HMF, 100 mg catalyst (2.5 wt% Ru, 0.025 mmol), 100 °C, ambient air pressure

were tested towards leaching. This was made by stirring the catalysts in [EMIm][OAc] at 100 °C for 1 h, after which they were removed by filtration. A dilution with water was required to fully recover the catalyst, which was evaporated afterwards. In both cases the resultant liquid was used as solvent for the oxidation of HMF without addition of further catalyst. The recovered liquid after reaction was also analyzed by XRF to measure the amount of Ru leached into the solution by lixiviation of the catalysts. For comparison purposes, 6 h reactions were also carried out with both catalysts, and the Ru content in the liquid phase (expressed as wt.% of the initial Ru loading in the fresh catalyst) calculated.

As summarized in Table 4, 3–5 wt% of the total initial Ru was leached within the first hour of reaction (entries 1b and 2b) and 5–10 wt% of the Ru was detected after 6 h of reaction (entries 1a and 2a). Nevertheless, these leached Ru species did apparently not present any significant catalytic activity, since identical product yields of 36–38 % HMFCA and 4 % FDA were obtained in a comparative blank experiment without added catalyst (entry 3). These experiments thus verified that the catalytic oxidation proceeded heterogeneously under these conditions, with the active sites on the surface of the catalyst being responsible for the catalytic activity. However, during the contact of the catalyst with the reaction medium part of the supported Ru species are leached into the solution, causing a metal loss and making the long term reutilization of these catalysts difficult.

4 Conclusions

The aerobic oxidation of HMF was investigated in various ILs using solid ruthenium hydroxide catalysts supported on different carrier materials. The IL best suited for the oxidation was [EMIm][OAc] which afforded an FDA yield of

Table 3 HMF oxidation in different ILs with $Ru(OH)_x$/support catalysts

Entry	Ionic liquid	Catalyst	PO_2 (bar)	*T* (°C)	Conversion (%)	Yield (%)			
						FA[a]	DFF	HMFCA	FDA
1	[EMIm][HSO_4]	$Ru(OH)_x$/spinel	10	140	58	0	3	1	0
2	[EMIm][OAc]	$Ru(OH)_x$/spinel	10	140	>99	0	0	4	14
3	[EMIm][HSO_4]	$Ru(OH)_x$/HT	10	100	32	0	18	3	0
4	[EMIm][OAc]	$Ru(OH)_x/La_2O_3$	10	100	97	31	0	34	23
5	[Bu_3MeN][$MeOSO_3$]	$Ru(OH)_x$/HT	30	100	60	0	26	16	1
6	[Bu_3MeN][$MeOSO_3$]	$Ru(OH)_x$/spinel	30	100	62	0	18	26	3
7	[EMIm][HSO_4]	$Ru(OH)_x$/HT	30	100	52	0	25	8	0
8	[EMIm][OAc]	$Ru(OH)_x/La_2O_3$	30	100	98	30	0	12	48

Reaction conditions 12 g IL, 350 mg (2.78 mmol) HMF, 0.5 g catalyst (2.5 wt% Ru, 0.125 mmol), 5 h

[a] Calculated as 1 mol of FA produced per mol of initial HMF

Table 4 Leaching study for HMF oxidation in [EMIm][OAc] with $Ru(OH)_x$/support catalysts

Entry	Catalyst	Ru in fresh catalyst[a] (wt%)	Ru in solution[a] (wt% of the initial Ru loading)	Conversion (%)	Yield (%)	
					HMFCA	FDA
1a	$Ru(OH)_x$/spinel	2.5	4.7	99	43	6
1b	Lixiviated	–	2.7[b]	99	36	3
2a	$Ru(OH)_x/La_2O_3$	5.0	9.9	99	56	6
2b	Lixiviated	–	4.7[b]	97	37	4
3	No catalyst	–	–	99	38	4

Reaction conditions 1.0 g [EMIm][OAc], 68 mg (0.54 mmol) HMF, 100 mg catalyst (2.5 wt% Ru, 0.025 mmol), 100 °C, 6 h, ambient air pressure

[a] Measured by XRF analysis

[b] Amount leached after 1 h in contact with the IL

48 % using 30 bar of O_2 at 100 °C with $Ru(OH)_x$ on La_2O_3 support.

An apparent improvement of the yield was found when lowering the temperature and increasing the pressure. Even though [EMIm][OAc] is notorious in degrading HMF [64] and naturally not ideal as solvent for HMF oxidation, it appears to have a higher solubility for oxygen compared to other ILs, which made it the best solvent under the applied reaction conditions. In several ILs the stirring was hampered because of high viscosity which most likely also had an impact on gas mass transfer and consequently on conversion and yield.

We believe that this work provides valuable insights about the scope and limitations of aerobic oxidations in ILs using solid ruthenium hydroxide catalysts. The study also shows that the IL [EMIm][OAc] worked well as solvent for aerobic oxidations making it attractive as reaction media considering its unique dissolving properties. Future work will focus on synthesizing catalysts with higher chemical resistance by alternative preparation methods and investigating other oxidation reactions in [EMIm][OAc] or structurally similar ILs to increase the yield of FDA and reduce the amount of by-products.

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