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# Conversion of glucose and cellobiose into 5-hydroxymethylfurfural (HMF) by rare earth metal salts in *N*,*N*′-dimethylacetamide (DMA)

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ABSTRACT

D-Glucose and cellobiose were converted into 5-hydroxymethylfurfural (HMF) by rare earth metal chlorides $LnCl_3$ (Ln = Sc, Y, La) in *N*,*N*′-dimethylacetamide (DMA). Both conversion and selectivity strongly depend on the ionic radii of the rare earth metal center. Conversion of fructose into HMF proceeds significantly faster and with higher selectivity than of glucose, suggesting a mechanism that involves the transformation of glucose into fructose as a crucial, rate determining step.



## 1. Introduction

For the production of chemical energy carriers for transportation from biomass, two basic routes can be considered: one is breaking up biomass to synthesis gas and building up fuel molecules using Fischer-Tropsch process; the other would be breaking down biomass molecules to directly give combustible molecules. The latter is confined to the utilization of biomass celluloses, hemicelluloses, and lignin to avoid conflict with the food chain that starch as feedstock would inevitably bring [1]. As one of the promising candidates as fuel components or platform chemicals, 5-hydroxymethylfurfural (HMF) plays a pivotal role as it is directly accessible from hexoses and can be transformed into a variety of furan-based compounds [2].

In the ongoing search for simple, cheap and environmentally benign processes for HMF production, chromium(II) and chromium(III) chlorides have drawn considerable attention as effective catalysts [2c,3]. They have been studied in ionic liquids as well as in DMA/LiCl (DMA = *N*,*N*′-dimethylacetamide) and afforded up to 53% HMF after 3 h (6 mol% chromium; 120 °C) in the latter system and up to 70% in IL. Available data suggest that the isomerization of glucose into fructose is a crucial step in the formation of HMF. On the other hand, Brønsted acids have shown their ability to catalyze the dehydration of saccharides at elevated temperatures [4]. Since initial studies showed little efficiency for rare earth metal salts in comparison to chromium catalysts [3a], not much attention has been paid to the use of rare earth metal catalysts. Lewis acidic rare earth metal salts were reported to generate HMF in water under hydrothermal conditions [5] and in ionic liquids [6].

Potential solvents for saccharides and glucose oligomers are ionic liquids (IL) and DMA/LiCl. Of these, ionic liquids have been studied for the formation of HMF from glucose in combination with rare earth metals. While the reaction occurs, the stability of the product depends strongly on the nature of the IL. In general HMF yields as well as selectivity, are low for all the rare earth metal based catalysts examined [3a,6], with a maximum yield of 25–30% HMF depending on reaction conditions. In DMSO on the other hand, rare earth metal salts were reported to yield HMF from fructose and fructose-containing oligomeric saccharides, but from glucose only moderate amounts (around 10% in case of $LaCl_3$) were obtained [7].

Since it is desirable to reduce the number of separation steps for the valorization of cellulosic materials, efficient routes for the direct conversion of cellulose or cellulose oligomers such as cellobiose are needed. Rare earth metal salts can be expected to act as multifunctional catalysts for several steps on the route from cellulose to HMF including hydrolysis, isomerization of glucose to fructose, and dehydration. They are strongly Lewis acidic and allow for high coordination numbers, but have not been investigated in the reaction with glucose oligomers in organic solvents under conditions reported for HMF formation by chromium catalysts.

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## 2. Experimental

### 2.1. General

DMA (98%), DMF p. A., D-glucose (96%) and cellobiose (98%) were purchased from Aldrich, fructose (99.5%) was purchased from Südzucker, $YCl_3 \cdot 6\ H_2O$ was purchased from Nanosolutions, $ScCl_3$ and $LaCl_3$ were purchased from Strem chemicals and LiCl extra pure from Riedel-de Haën; all chemicals were used without further purification.

Experiments at temperatures up to 145 °C were performed on a Chemspeed ASW 1000 synthesizer with up to 36 wells with a reaction volume of 13 mL connected to argon supply. The hood containing the reactor blocks with the wells was permanently flushed with nitrogen. Temperature was controlled by a Huber Tango Nuevo cryostat. Reactions were vortexed at 600 rpm.

4 mL of a stock solution of the substrate (and LiCl where appropriate; see below) in DMA containing DMF as internal standard were transferred to the reactor wells. Where necessary, 0.5 mL of DMA were added to adjust the overall volume to 5 mL and the atmosphere in the reactor wells was exchanged against argon by repeated cycles of decreasing pressure and flushing with argon. The reaction zone was heated to the desired temperature. A 0.1 mL sample of the mixture was injected into 0.5 mL of $D_2O$ as a reference for NMR spectroscopic analysis prior to the transfer of 0.5 mL of stock solution of the appropriate metal chloride in DMA (1 mL for $ScCl_3$ stock solution), giving reaction mixtures that contained 2.24 mmol of glucose or fructose (1.12 mmol of cellobiose) and 0.22 mmol of metal chloride. The sampling procedure was repeated at the respective times.

Experiments at temperatures above 150 °C were performed in a thick-walled Büchi glass reactor and stirred with a magnetic stirring bar. Stock solutions where transferred manually with a plastic syringe and the mixture was flushed with argon for 1 min before the reactor was closed.

The results with scandium were reproduced manually as scandium(III) chloride had to be applied as a suspension in DMA due to its low solubility.

Experiments with fructose were conducted manually as deviation of reaction times were to high due to the sampling speed of the Chemspeed ASW 1000.

The following stock solutions were used:

Yttrium(III) chloride: 673 mg (2.22 mmol) of $YCl_3 \cdot 6\ H_2O$ in 5 mL of DMA, giving a 0.444 M solution.
Lanthanum(III) chloride: 544 mg (2.22 mmol) of $LaCl_3$ in 5 mL of DMA, giving a 0.444 M solution.
Scandium(III)chloride: 168 mg (1.11 mmol) of $ScCl_3$ in 5 mL of DMA, giving a 0.222 M solution.
Glucose: 10 g (0.056 mol) D-Glucose (and 4.71 g LiCl where appropriate) were transferred to a 100 mL volumetric flask. 5 mL of *N*,*N*′-dimethylformamide (DMF) were added as internal standard for NMR measurement. Overall volume was adjusted to 100 mL with DMA.
Cellobiose: 9.5 g of cellobiose and LiCl (4.71 g) were transferred to a 100 mL volumetric flask. 5 mL of *N*,*N*′-dimethylformamide (DMF) were added as internal standard for NMR measurement. Overall volume was adjusted to 100 mL with DMA.

### 2.2. Analytical

NMR measurements were performed on a Bruker Avance 400 MHz spectrometer. For determination of glucose conversion the integrals of the hydrogen on the anomeric carbon at 4.52 and 5.11 ppm were used and correlated with the proton of the formic acid moiety of DMF at 7.83 ppm. As separation from the tailing of the water peak can cause problems, considerable deviations can occur for single points in the conversion curves. Determination of cellobiose conversion refers to the doublet of the proton on the glycosidic bond at 4.40 ppm. HMF content was determined based on the average of the doublets of the ring protons at 6.58 and 7.44 ppm. As there is no well separated signal for any single proton in fructose, the overall integral of all the protons was used to estimate fructose conversion.

In order to confirm the formation of HMF, several samples where further analyzed by GCMS. For GCMS analysis, 2 mL samples were diluted with water to 10 mL and extracted 3 times with $CH_2Cl_2$. The organic phase was separated and filtered over a glass fibre filter to remove any humins. The volume of the collected organic extracts was reduced to 5 mL and the analysis of the solution was performed on a Shimadzu GCMS-QP 2010 plus with helium as carrier gas. Oven temperature was raised from 60 °C to 250 °C at a heating rate of 10 K/min. A Supreme-5-MS column (30 m length, 0.25 mm diameter, 0.25 μm pores) at a column flow of 2 mL/min. No soluble products other than HMF could be detected.

## 3. Results and discussion

The conversion of fructose into HMF appears to be a fairly simple process as the five-membered ring is already formed and dehydration leads to the stable furan ring. The reaction with glucose or cellulose as starting materials becomes more complicated as additional equilibria and side reactions occur. Specifically, hydrolysis of glucose oligomers has to be addressed when HMF yield needs to be optimized (Scheme 1). Another crucial step in the transformation into HMF is the rearrangement of glucose to fructose [8]. If the equilibrium between these two hexoses is shifted towards fructose, or if equilibration proceeds quickly, the problem of HMF production from D-glucose is reduced to the optimization of fructose conversion.

Experiments in DMA revealed that substantial amounts of HMF are formed from D-glucose at elevated temperatures in the presence of rare earth metal chlorides but high yields are hampered by humin generation. At 145 °C and with 10 mol% of yttrium trichloride, glucose is fully converted after 3 h, while only 20% of HMF are formed (Fig. 1), with the HMF yield decreasing further at prolonged reaction times.

Analysis of the $^1H$ NMR spectra of samples suggests that there is no substantial build-up of intermediates such as open-chained saccharides, fructose, or coordination compounds. They should be visible in the double bond region of the spectra in the case of dehydration and in the region around $\delta$ 9–10 ppm for aldehydes that are present in many of the intermediates discussed in the literature [9]. Since there are no by-products that could be converted into HMF

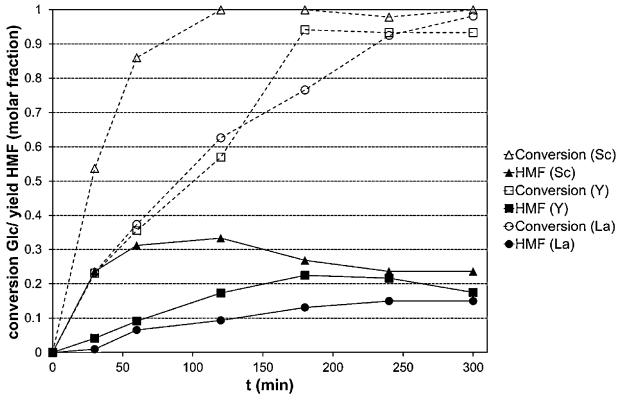
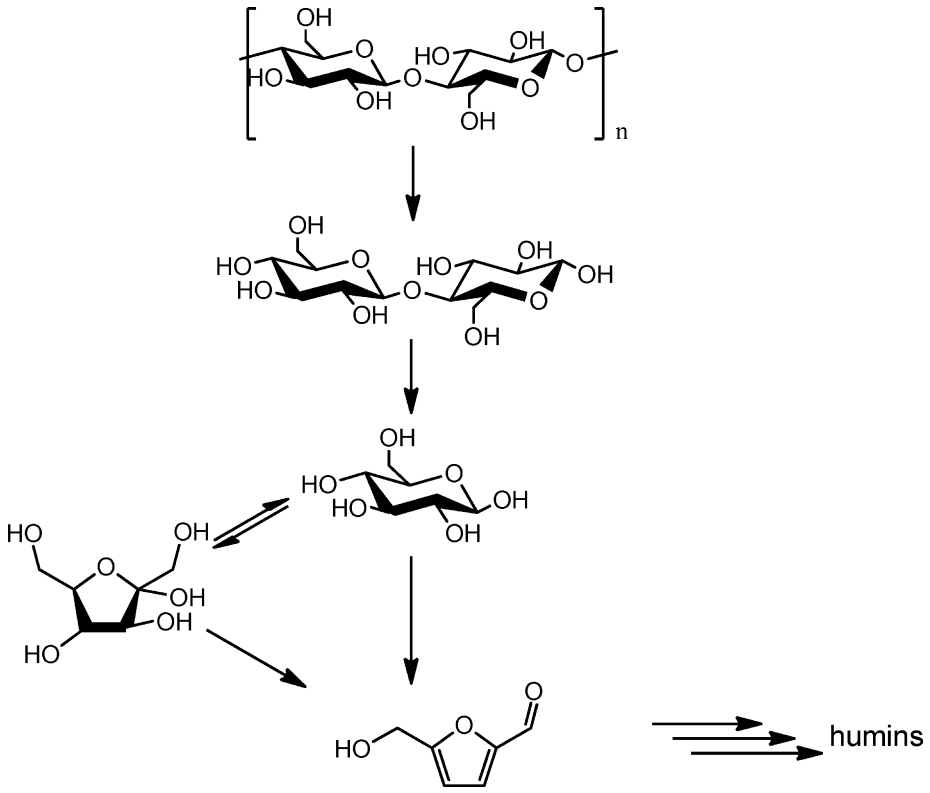



**Fig. 1.** Conversion of D-glucose into HMF in DMA at 145 °C with 10% $LnCl_3$.




**Scheme 1.** Reaction pathway from cellulose to HMF.

after full conversion of glucose, no significant further production of HMF can be expected for the reaction with $LaCl_3$ after 300 min as glucose is already fully converted.

The results for the yttrium(III) chloride mediated reaction raise the question whether group 3 metals with different radii can improve the selectivity for HMF. Indeed, the smaller scandium induces a faster overall conversion of glucose, while the reaction with lanthanum progresses at a comparable speed. The yield of HMF is actually even lower when $LaCl_3$ is used, while HMF forms considerably faster when $ScCl_3$ is used. Interestingly, scandium has an ionic radius of 0.75 Å for coordination number CN 6, which is strikingly close to 0.73 Å of chromium in oxidation state +II (CN 6) employed in HMF synthesis. It is considerably larger than the $Cr^{3+}$ (0.62 Å for CN 6) applied in DMA. Since both the six-coordinated $Y^{3+}$ (0.90 Å) and $La^{3+}$ (1.03 Å) [10] have considerably larger ionic radii, a marked difference in activity might be expected due to the different coordination behavior of the metals and glucose. In fact, the corresponding trichlorides give only moderate yields in the dehydration of glucose to HMF. These results also shed some light on the somewhat unexpected inefficiency of aluminium(III) cations during HMF production reported in the literature [3a,11]. This may be due to the small ionic radius of 0.54 Å (CN 6), favoring coordination modes that do not induce dehydration to HMF. The observation that scandium having the smallest ionic radius is the most efficient for the HMF formation from glucose is in agreement with the reported dependence of activity of lanthanides in ionic liquids on the ionic radii [6]. Analysis of $^1$H NMR spectra of samples from the reaction mixtures shows the formation of HMF as well as the loss of intensity for the glucose signals (Figs. 2 and 3). Comparison with an NMR spectrum of fructose recorded under identical conditions reveals the absence of significant amounts of fructose.

Fructose itself is converted at considerably higher rates, reaching maximum conversion after only 40 min. The formation of HMF reaches nearly 60% in the same time which, along with approximately doubling the yield is roughly nine times faster than with glucose in case of scandium chloride with an even larger difference for the other metals. This fast conversion is accompanied by higher selectivity for HMF. Also, this fast reaction leads to considerable deviation in product yield as the exact reaction parameters in the initial 20 min have a large influence on the ratio of the various reaction rates (see Supporting information).

By NMR spectroscopy, only minor amounts of by-products were detected, due to their insolubility in both water and organic solvents. Since the generation of HMF from fructose in DMSO has been reported to occur at 100 °C [12], we suspected that the formation of HMF in DMA at elevated temperatures could be dominated by a mechanism involving the solvent rather than the metal species. A blank run showed that at 145 °C no HMF was detected after 60 min. There are only minor amounts of by-products present in the NMR spectrum. Specifically, the absence of any signals in the area typical for furanic double bonds implies that dehydration of furanose rings does not occur in significant amounts (Figs. 4 and 5).

For the dehydration of fructose with the metal chlorides $LnCl_3$ (Ln = Sc, Y, La) conversions are practically identical up to 80% reached after 20 min in all cases. Afterwards, the reaction is slowed down due to the reduction of fructose concentration but reaches maximum conversions within 30–40 min. HMF formation is delayed with low amounts being present after 5 min and the reaction accelerating subsequently. Until the reaction is finished after approximately 30 min, 50–60% HMF are formed with $ScCl_3$ and $YCl_3$. In the case of $LaCl_3$, the reaction seems to be slightly more selective for dehydration giving HMF yield of 65–70% although the differences are difficult to understand completely as the reaction pathway includes several transformations and the rate constants for the formation of byproducts can be expected to be affected by the ionic radii of the cations as well. Similar behavior was reported recently in the dehydration of fructose by rare earth metal trifluoromethanesulfonates in organic solvents (DMSO or DMA) at 120 °C

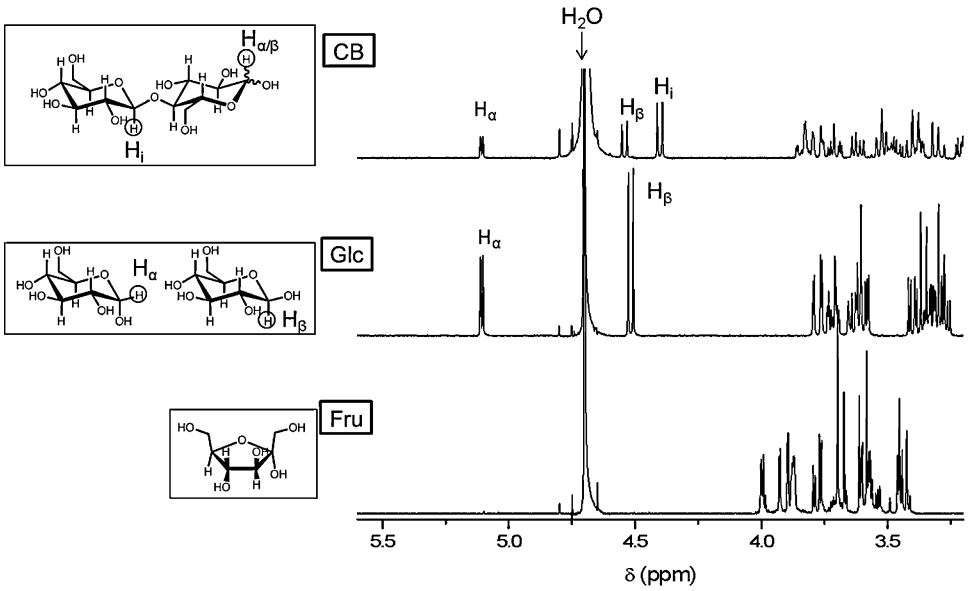



**Fig. 2.** $^1$H NMR spectra ($D_2O$, 25 °C) of D-fructose (Fru), D-glucose (Glc), and cellobiose (CB) in DMA showing the diagnostic signals of the carbohydrate species.

[13]. The striking similarity of the reaction profiles for all three metal species is in opposition to the marked differences in the reaction with glucose. This strongly suggests that the formation of HMF does not occur directly from glucose but by a mechanism involving the rearrangement of glucose to fructose which is consumed quickly. Given the strong dependence of the dehydration of glucose on the ionic radius of the metal species, this pathway can be expected to involve transient coordination compounds like open-chained saccharides coordinated to the cation or enediolato-complexes similar to those suggested for chromium (Scheme 2) [3a].

As there is an obvious competition between dehydration and condensation reactions, the latter leading to the formation of polymeric humins, the behavior of the reaction at various temperatures was investigated. At 120 °C the formation of HMF from glucose is slowed down considerably (Fig. 6).

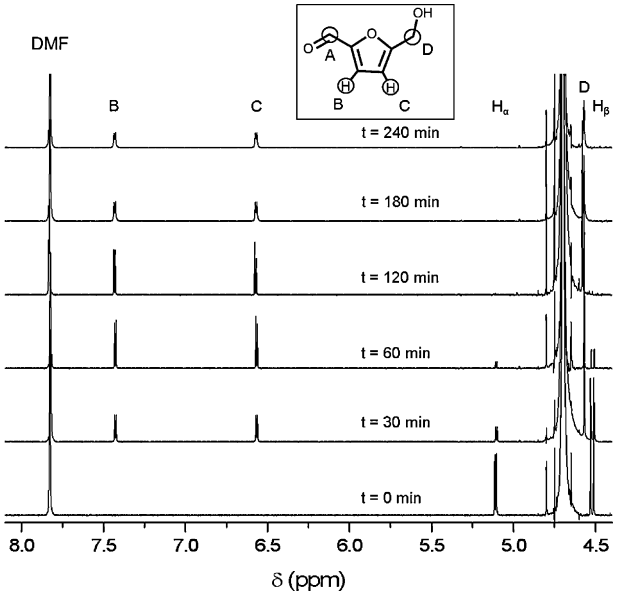



**Fig. 3.** $^1$H NMR spectra ($D_2O$, 25 °C) of the conversion of D-glucose into HMF in DMA at 145 °C in presence of 10% $ScCl_3$.

Raising the reaction temperature to 200 °C on the other hand strongly accelerates the reactions while the effect of scandium inducing a faster reaction is retained (Fig. 7). After only 15 min, a HMF yield of 22% is reached, corresponding to a twelve-fold increase of the reaction rate for yttrium (compared to the reaction at 145 °C) while in case of scandium a maximum of roughly 30% HMF yield is reached after just 7.5 min. These findings correspond to the behavior of glucose treated with lanthanide salts in ionic liquids [6]. By variation of the temperature one of the competing reactions (humin formation and HMF production) could become dominant in the overall reaction. This does not seem to be the case and the selectivity for HMF stays low at all temperatures.

Glucose itself is not a viable feedstock for the production of platform chemicals as it interferes with the human food chain if produced from starch. It is unnecessarily energy-intense when obtained by complete hydrolysis of cellulose. Therefore direct conversion of cellulose derived glucose oligomers such as cellobiose is attractive. These oligomers can be accessed by partial hydrolysis of cellulose, for which improved methods are being developed [14]. While glucose is soluble in DMA at high concentrations (0.555 M), cellobiose dissolves in significantly lower molar amounts, requiring the addition of lithium chloride to increase solubility. The

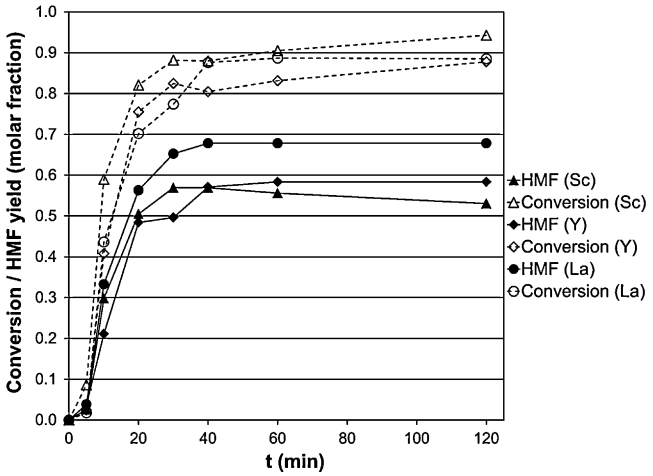



**Fig. 4.** Conversion of D-fructose into HMF in DMA at 145 °C with 10% $LnCl_3$.

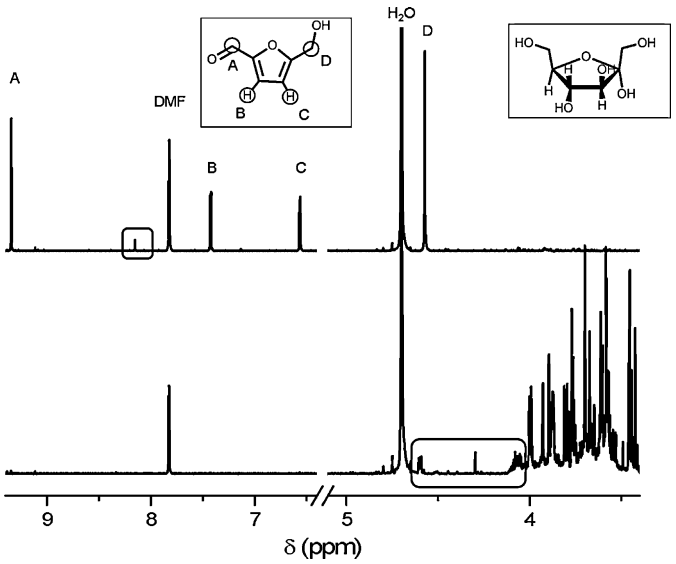



**Fig. 5.** $^1$H NMR spectra ($D_2O$, 25 °C) of D-fructose in DMA after 60 min at 145 °C in presence of $ScCl_3$ (above) and in a blank run (below). The frames mark minor by-products detected by $^1$H NMR.

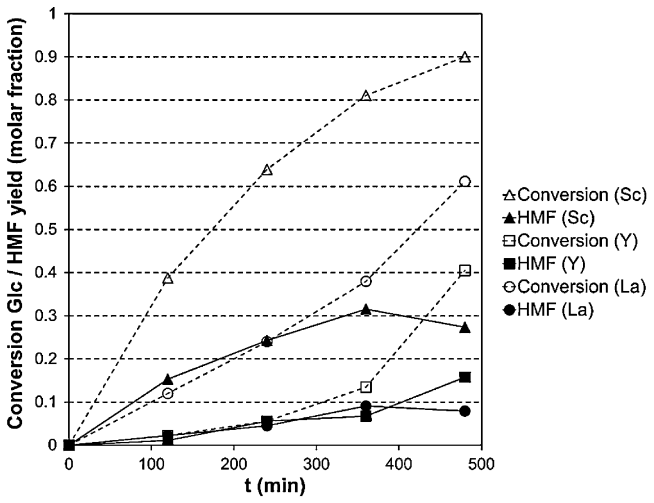
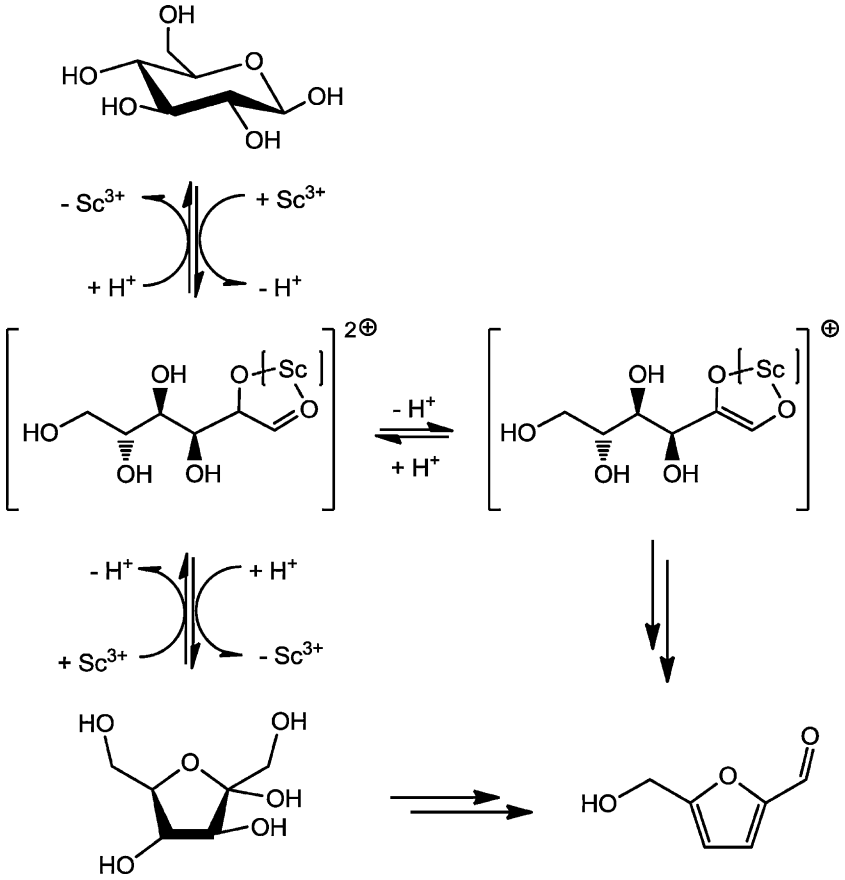



**Fig. 6.** Conversion of D-glucose into HMF in DMA at 120 °C with 10% $LnCl_3$.

presence of LiCl has practically no influence on the formation of HMF from glucose (Fig. 8) and can be added without altering the reaction outcome.

The reaction rates observed for cellobiose are lower than those for glucose. As with glucose, the formation of HMF from cellobiose proceeds considerably faster with $ScCl_3$ than with $YCl_3$. While the presence of glucose could be detected by NMR spectroscopy, exact quantification is difficult due to overlapping signals of the protons on the anomeric carbons of glucose and cellobiose and the necessity to manually adjust the baseline in many cases due to the large water signal. Estimation of the glucose content reveals that there is substantial accumulation of glucose in all cases. For yttrium and lanthanum this buildup reaches a maximum at around 180 min with approximately 12% conversion to glucose for yttrium and roughly 17% for lanthanum. At longer reaction times, glucose concentration drops again and cannot be detected after 300 min in the reaction with yttrium. At the same reaction time, there is a considerable amount of glucose (around 10%) still left when lanthanum




**Scheme 2.** Suggested pathway of the transformation of D-glucose to fructose and HMF via transient coordination compounds.

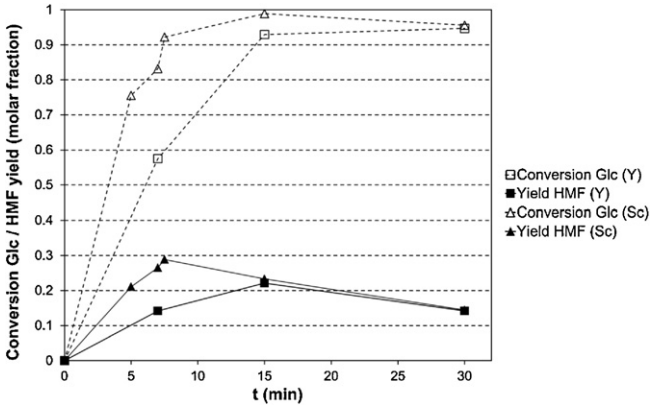



**Fig. 7.** Conversion of D-glucose into HMF in DMA at 200 °C in presence of 10% $YCl_3$ or $ScCl_3$.

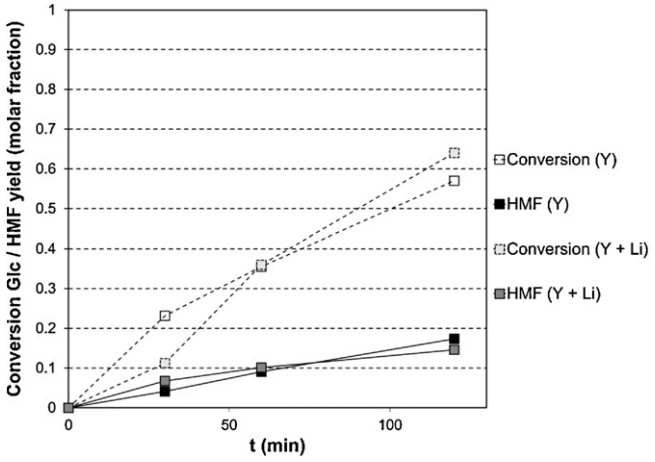



**Fig. 8.** Conversion of D-glucose into HMF in DMA at 145 °C with 10% $LnCl_3$ in presence and in absence of LiCl.

trichloride is used. Given the selectivity of the glucose conversion, it is not to be expected that this will contribute to any major gain in HMF at even longer reaction time. Scandium trichloride again shows distinctly different behavior, with glucose content peaking after 60 min at below 10%. Quick depletion is observed and after 240 min, glucose is virtually undetectable. While initial formation of glucose is similar for all three metal trichlorides, further reaction is dominated by the different behavior of scandium in the transformation of glucose into HMF (Fig. 9).

In all reactions, whether they start with fructose, glucose or cellobiose, the conversion of a large portion of the sugar species into humins is a major obstacle for an efficient process. These ill-defined compounds form from condensation processes in the sugar mixture with subsequent dehydration as well as from acetalization of HMF either with itself or with the sugar species present in the reaction mixture. The complex reaction pathways necessitate optimization of reaction conditions to avoid the exclusive formation of humin which is inevitable at excessive reaction times. Still even for fructose, typically more than 50% of the sugar are converted into humins at elevated temperature (at lower temperature selectivity is considerably higher [7]).

## 4. Conclusions

Glucose and cellobiose can be converted into HMF by the reaction of rare earth metal trichloride in DMA. The activity of scandium(III) chloride is higher than that of the trichlorides of the larger

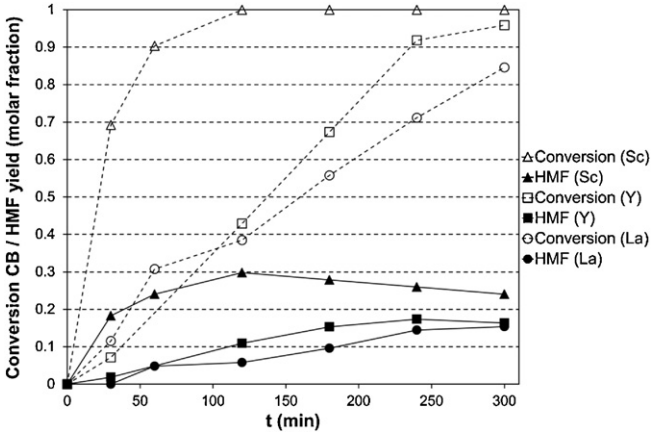



**Fig. 9.** Conversion of cellobiose into HMF in DMA at 145 °C with 10% $LnCl_3$ in presence of LiCl. Conversion is based on glucose equivalents with 1 CB equaling 2 Glc.

metals yttrium and lanthanum. At elevated temperatures, the reaction proceeds faster but there is no increase in selectivity. For the HMF formation from cellobiose following hydrolysis, it is necessary to break the glucosidic bond between the glucose units. This step requires water and is unfavorable for dehydration reactions. It is therefore crucial to properly adjust the rates of hydrolysis and dehydration. When the cellobiose can be converted rapidly into monomeric glucose units, HMF formation could be treated as separate reaction steps.

Absence of fructose in the NMR spectra during the transformation of glucose into HMF suggests that the reaction either proceeds via the transformation of glucose to fructose or via dehydration of open-chained carbohydrate species and subsequent ring closure. The lack of fructose build-up during the reaction either means that the conversion to fructose is the rate determining step on the route from glucose to HMF or that this conversion is actually a negligible side reaction. In light of the fast conversion of fructose, it seems plausible that any additive or catalyst that quickly converts glucose into fructose will enhance both conversion rates and selectivity. Transformation of glucose into fructose and fructose dehydration could then be addressed as separate reaction steps. The combination of enzymatic glucose conversion and HMF formation by acid catalysis has recently been reported [15]. The procedure reported here allows the use of a broad range of additives to optimize reaction rates and selectivity.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2012.01.008.

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