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Dehydration of fructose and sucrose into 5-hydroxymethylfurfural in the presence of 1-H-3-methyl imidazolium chloride acting both as solvent and catalyst

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Abstract

The acid-catalyzed dehydration of fructose was performed in a microbatch reactor at 90 °C using 1-H-3-methyl imidazolium chloride, $HMIM^+Cl^-$, acting both as solvent and catalyst. A yield in 5-hydroxymethylfurfural (HMF) as high as 92% is achieved within 15–45 min. A productivity of 0.02 mmol of HMF, per min and per mmol of ionic liquid, can then be obtained. A remarkable feature, as compared with other catalytic systems, is the absence of decomposition of 5-hydroxymethylfurfural which can then be separately or continuously extracted in a simple manner with diethyl ether, thus allowing easier recycling of the ionic liquid after water removal. The absence of decomposition of 5-hydroxymethylfurfural is due to the lower free energy of activation calculated in the presence of the ionic liquid compared to other homogeneous or heterogeneous catalysts, which then makes, in a consecutive reaction network, the formation of the 5-hydroxymethylfurfural intermediate nearly quantitative.

Under similar operating conditions, sucrose is nearly quantitatively transformed into HMF and unreacted glucose.

Keywords: Fructose; Glucose; Sucrose; 5-Hydroxymethylfurfural; 1-H-3-methyl imidazolium chloride; Ionic liquids

1. Introduction

In a previous paper, we have shown that the acid-catalyzed dehydration of fructose into 5-hydroxymethylfurfural (HMF) could be easily achieved in the presence of 1-butyl-3-methyl imidazolium tetrafluoroborate ($BMIM^+BF_4^-$) as solvent and Amberlyst-15 sulfonic ion-exchanged resin as catalyst [1]. A maximum yield of 40–50% was obtained at 80 °C after 3 h of reaction. In order to avoid the further acid-catalyzed decomposition of 5-hydroxymethylfurfural, a liquid/liquid extraction device was used with toluene as the organic extraction solvent, followed by demixion of the organic phase with water [2]. The corresponding yield in HMF was then close to 85%.

However, as recently shown in the literature [3,4] and in our laboratory, the bulk of the catalysis was due to the formation of an acid via the ion exchange of the cation with the protons of H-form zeolites or sulfonic ion-exchanged resins. Then, we decided to search for ionic liquids capable of acting both as solvent and catalyst. It was recently reported that the protonation of 1-alkyl imidazoles by strong acids provided salts which act as ionic liquids and proton reservoir in proton-assisted catalytic processes [5]. In the series of such protic ionic liquids, 1-H-3-methyl imidazolium chloride denoted as $HMIM^+Cl^-$ (Scheme 1) was then used in the dehydration of fructose and sucrose into 5-hydroxymethylfurfural because of its facility of preparation as well as its commercial availability for comparison.

2. Experimental

2.1. Materials

Anhydrous 1-H-3-methyl imidazolium chloride was synthesized by neutralization of 1-methylimidazole with HCl according to a procedure reported in the literature [6]. A commercial sample of 1-H-3-methyl imidazolium chloride was obtained from Solvionic S.A., and used without further purification. Fructose, glucose, sucrose and 5-hydroxymethylfurfural were from Aldrich (99% purity).

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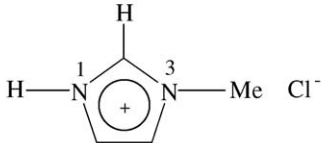

Scheme 1. Structure of $HMIM^+Cl^-$.

2.2. Work-up procedure

Experiments were carried out at 90 °C in 2 ml magnetically stirred (700 rpm) microbatch reactors. Zero time was taken to be when the temperature reached 90 °C.

2.3. Analyses

Samples were withdrawn periodically from the reactor, filtered and analyzed by HPLC. Analyses were performed using a Shimadzu LC-6A pump and a refractive index RID-6A detector. The column used was a BIORAD HPX-87H (300 mm × 7.8 mm). Deionized water was the eluent (0.6 ml min^{-1}), and isopropanol was the external standard. 5-Hydroxymethylfurfural yield was calculated as reported elsewhere [7].

2.4. Kinetics

The initial reaction rates were deduced from the experimental plots of mmol HMF versus time by determination of the slope at the origin.

3. Results and discussion

3.1. Fructose solubility

As in common organic solvents, carbohydrates are found to be sparingly soluble in ionic liquids [8,9]. In the present work, the solubilities of fructose and sucrose were calculated as around 2.5 g for 10 g of $HMIM^+Cl^-$ at saturation of the solution at 90 °C.

3.2. As-synthesized $HMIM^+ Cl^-$ properties

Anhydrous 1-H-3-methyl imidazolium chloride was synthesized by neutralization of 1-methylimidazole with HCl according to a procedure reported in the literature [6]. Its structure was confirmed by comparison, melting point and ^1H NMR spectroscopy, with the commercial sample. However, this ionic liquid must be handled with care because of its high hydrophobic properties. Fig. 1 illustrates the water uptake when 250 mg of ionic liquid are placed in a water-saturated atmosphere at 25 °C. As shown in this figure, the water uptake is particularly rapid in the two first hours. Moreover, by thermal gravimetric analysis, 1.35% of residual water were still found at 140 °C, temperature at which the ionic liquid starts to decompose.

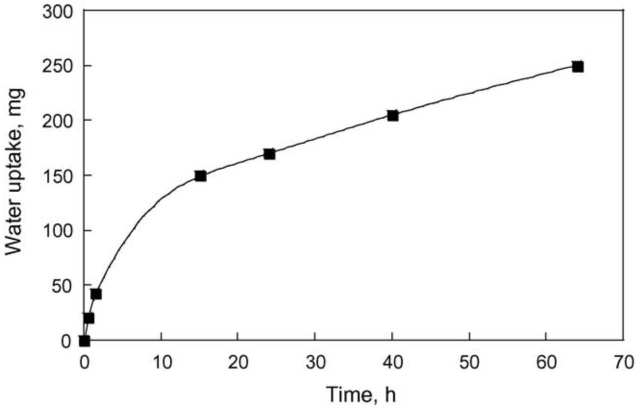

Fig. 1. $HMIM^+Cl^-$ water uptake vs. time.

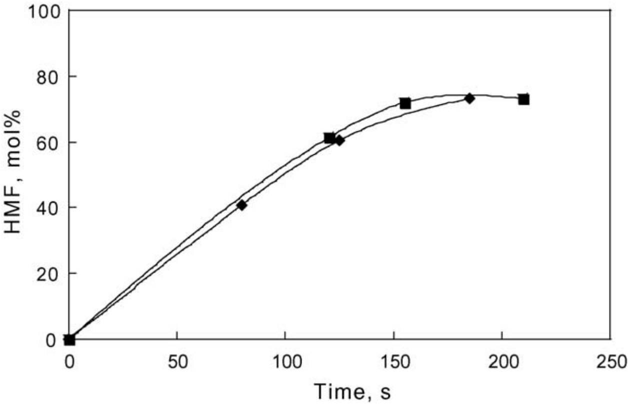

Fig. 2. Comparison between as-synthesized (◆) and commercial (■) $HMIM^+Cl^-$ samples.

3.3. Preliminary results

The first experiment was to compare as-synthesized and commercial $HMIM^+Cl^-$ ionic liquids samples. Starting from 350 mg of ionic liquid and 125 mg of fructose, the experimental results obtained at 90 °C in the presence of a sulfonic ion-exchanged resin (Amberlyst A15d) as catalyst are shown in Fig. 2 which does not reveal significant difference between both samples.

3.4. Dehydration of fructose

Experimental results obtained for different quantities of reactants are reported in Table 1, together with the corresponding calculated initial reaction rates.

Table 1
Experimental results for dehydration of fructose at 90 °C

HMIMCl (mmol)	Fructose (mmol)	Initial reaction rate (mmol/min)
3.37	2.44	0.044
3.37	1.16	0.056
602.87	119.44	11.8
3.37	0.56	0.066
3.79	0.39	0.057
3.37	0.067	0.014

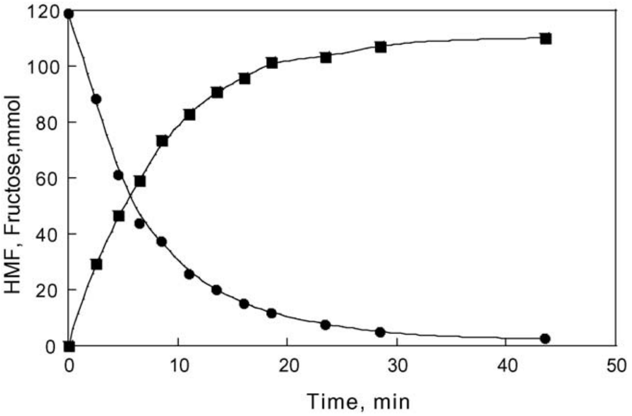

Fig. 3. “Large scale” dehydration of fructose at 90 °C; fructose (●), HMF (■).

The reaction profile for the dehydration of fructose at a larger scale, i.e., starting from 0.6 mol of ionic liquid and 0.12 mol of fructose is given in Fig. 3. The corresponding yield in HMF is 92% after a reaction time of 45 min.

The experimental results are first given as plots of initial reaction rates against the initial concentration in fructose at nearly constant concentration in ionic liquid (Fig. 4) and then rationalized as plots of initial reaction rates per mmol of ionic liquid against the molar fraction of fructose in order to account for the different amounts used of both ionic liquid and fructose (Fig. 5). A productivity of 0.02 mmol of HMF, per min and per mmol of ionic liquid, can then be calculated.

That kind of profile well agrees with the formation of an intermediate complex entity. A maximum reaction rate is observed, of the same kind as observed for reactions involving the formation of intermediate complexes, enzyme/substrate complex in enzymatic catalysis or solid/substrate adsorption complex in heterogeneous catalysis [10]. As a recent example, the kinetics of hydrogenation of sorbic acid with ruthenium complexes in an ionic liquid as catalyst medium was described with a Michaelis–Menten equation [11].

In the present work, the maximum reaction rate is obtained for a fructose molar fraction close to 0.14–0.15, i.e., for a ionic liquid to fructose molar ratio of 5–6. Such a complex could result from the presence of a solvation shell of the imidazolium salt as it was proposed in a recent work on the phase stability of mixtures of organic solvents with ionic liquids like imidazolium salts, which shows that gamma-butyrolactone is surrounded by four and five molecules of ionic liquid, $BMIM^+BF_4^-$ and $BMIM^+PF_6^-$, respectively [12].

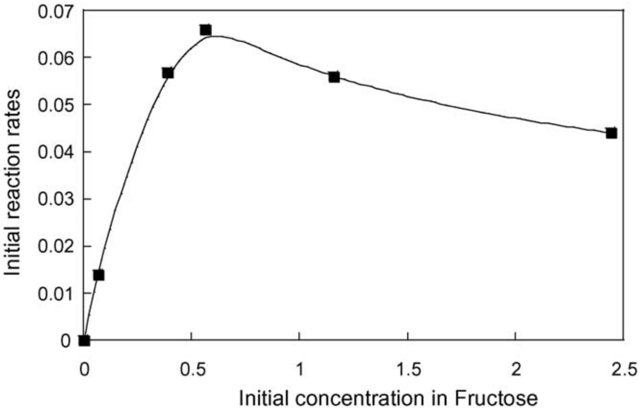

Fig. 4. Initial reaction rates (mmol HMF min^{-1}) vs. initial fructose concentration.

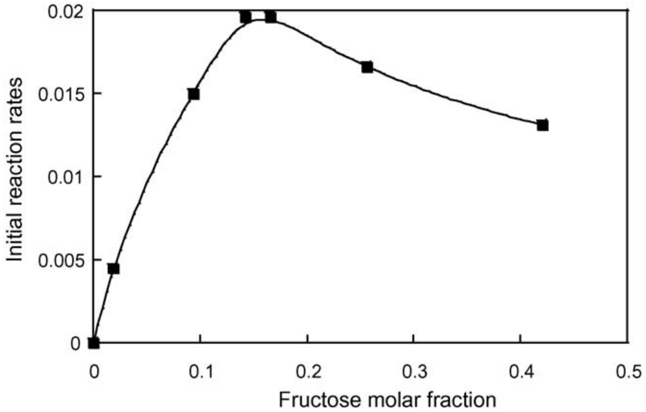

Fig. 5. Initial reaction rates (mmol HMF min^{-1} HMIMCl^{-1}) vs. fructose molar fraction.

In order to account for the high yield in 5-hydroxymethylfurfural in the presence of $HMIM^+Cl^-$, i.e., high selectivity in HMF at total conversion of fructose, the activation parameters were calculated from the Arrhenius plots for formation and decomposition of 5-hydroxymethylfurfural (Fig. 6). Energies of activation are obtained from the slope, and the preexponential factor $\ln A$, or frequency factor for first-order reactions, from the intercept. As not really expected, the energies of activation for formation and decomposition of 5-hydroxymethylfurfural were found to be similar to those reported for the reaction catalyzed by solid catalysts (Table 2). The increased selectivity observed for the formation of 5-hydroxymethylfurfural in ionic liquid as solvent and catalyst must then result from differences in the preexponential factors. Indeed, assuming similar energies of activation in the Arrhenius equations $\ln k = \ln A - E_a/RT$, the difference in the preexponential factors is 8 ln units between ionic liquid and zeolite, and reflects directly the difference in reaction rates between both catalytic systems. For the decomposition

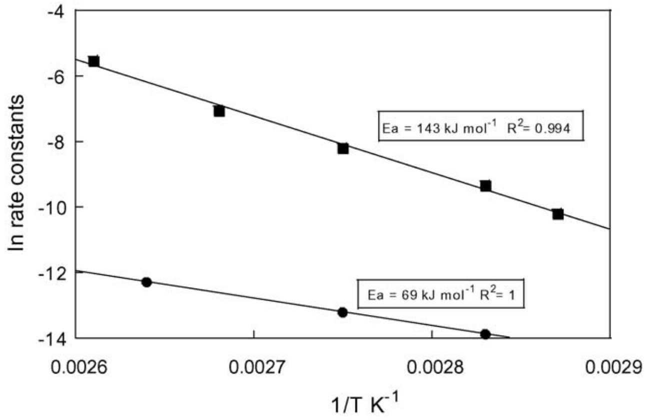

Fig. 6. Determination of activation parameters from Arrhenius equation for the formation of 5-hydroxymethylfurfural (■) and its disappearance (●).

Table 2
Activation parameters for formation and decomposition of HMF over zeolites [7] and ionic liquid $HMIM^+Cl^-$

Catalysts	Fructose → HMF	HMF → by-products
Zeolites	$E_a = 141\ \mathrm{kJ\,mol^{-1}}$ $\ln A = 31$	$Ea = 64\ \mathrm{kJ\,mol^{-1}}$ $\ln A = 8$
Ionic liquid $HMIM^+Cl^-$	$E_a = 143\ \mathrm{kJ\,mol^{-1}}$ $\ln A = 39$	$E_a = 69\ \mathrm{kJ\,mol^{-1}}$ $\ln A = 10$

of 5-hydroxymethylfurfural, a similar calculation leads to a difference of only 2 ln units in the preexponential factors. The influence of the ionic liquid as both solvent and catalyst is thus more important on the formation of 5-hydroxymethylfurfural than on its decomposition with direct consequence on the free energies of both reaction steps. Indeed, as observed from reaction kinetics, dehydration of fructose involves the formation of a complex between the ionic liquid and fructose. By comparison with enzyme catalyzed reactions, that could then contributes to a decrease of the activation barrier and to a subsequent increase in the rate of formation of HMF with no significant consequence on further HMF disappearance.

3.5. Dehydration of sucrose

When reacting sucrose, 106 mg (0.31 mmol) and 1-H-3-methyl imidazolium chloride, 431 mg (3.63 mmol) at 90 °C, a rapid cleavage of sucrose into fructose and glucose is observed before the working temperature was reached (Fig. 7). Crystallization water present in sucrose and/or residual water present in the “anhydrous” ionic liquid could be responsible for this rapid reaction.

Then, as shown in Fig. 7, fructose is nicely transformed into 5-hydroxymethylfurfural with a high yield and without further decomposition. The yellow color of the final solution is a significant test for the absence of polymeric substances commonly denoted as humins often observed in homogeneous as well as heterogeneous catalysis. At the same time, glucose does not significantly react with the ionic liquid, only 3% of glucose are transformed after 30 min.

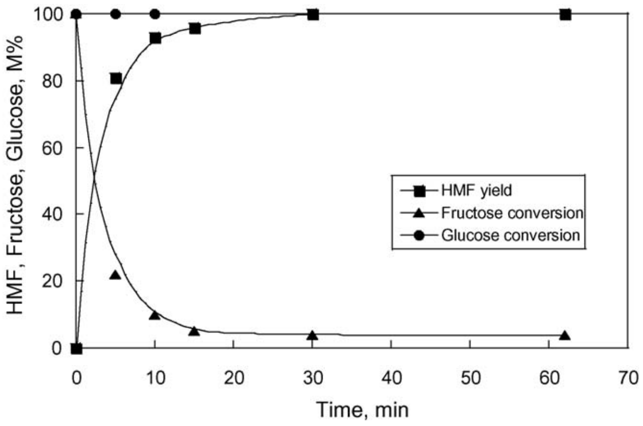

Fig. 7. Dehydration of sucrose in the presence of $HMIM^+Cl^-$.

Table 3
HMF yields after ionic liquid recycling, as such and after water removal

Ionic liquid	Run 1 (%)	Run 2 (%)	Run 3 (%)	Run 4 (%)	Run 5 (%)
As such	86	81	70	75	62
After water removal	86	88	85	84	82

3.6. Extraction and recycling

Taking into account the specific properties of carbohydrates, only hydrophilic ionic liquids can be used [13]. That also means that only apolar solvents or supercritical CO_2 may be used to extract reaction products. Unfortunately, 5-hydroxymethylfurfural was found to have a larger affinity for the ionic liquid than for an organic solvent such as diethyl ether or supercritical CO_2.

Nevertheless, for dehydration of fructose, we have shown, on one hand, that HMF could be completely extracted in a continuous manner with diethyl ether (50 ml for 8 h for 0.5 g of HMF in 2 g of ionic liquid) or in a stepwise manner (6× 150 ml for 1.2 g of HMF in 2 g of ionic liquid). On the other hand, preliminary results using supercritical CO_2 as extraction solvent do not seem to have better expected extraction properties.

After the extraction of 5-hydroxymethylfurfural with diethyl ether, the ionic liquid is recycled as such or after removal of the water formed during the course of the reaction (Table 3). Such operation is rather important since three water molecules are produced during the course of the reaction. Under the operating conditions used, 5.55 mmol of fructose and 25.3 mmol of ionic liquid at 90 °C for 1 h, and although the amount of water formed after three cycles was twofold higher than that of the ionic liquid, the yield in HMF is not affected in a spectacular manner, but is more affected than after water removal where no significant loss in activity is observed within the experimental error.

The situation is less simple for dehydration of sucrose since unreacted glucose is now present in the final reaction mixture and is not capable of being extracted with apolar solvents. However, we are presently investigating the possibility to transform glucose into a better extractable product in the same ionic liquid.

4. Conclusions

The acid-catalyzed dehydration of fructose and sucrose into 5-hydroxymethylfurfural (HMF) is easily achieved in the presence of 1-H-3-methyl imidazolium chloride, $HMIM^+Cl^-$, acting both as solvent and catalyst. High yields in HMF are obtained at relatively low temperature and short reaction times, whatever the starting material, fructose or sucrose. As compared with other catalytic systems, no decomposition of HMF occurs and then allows its facile extraction from the ionic liquid with diethyl ether. However, this extraction method is, of course, appropriate on a bench scale but is difficult, at the present time, to be transposed on a pilot scale.

References

[1] C. Lansalot-Matras, C. Moreau, Catal. Commun. 4 (2003) 517.

[2] A. Finiels, C. Moreau, P. Rivalier, L. Vanoye, unpublished results.

[3] C. Hardacre, S.P. Katdare, D. Milroy, P. Nancarrow, D.W. Rooney, J.M. Thompson, J. Catal. 227 (2004) 44.

[4] J.S. Yadav, B.V.S. Reddy, M. Sridhar Reddy, N. Niranjan, J. Mol. Catal. A: Chem. 210 (2004) 99.

[5] M. Picquet, I. Tkatchenko, I. Tommasi, P. Wasserscheid, J. Zimmermann, Adv. Synth. Catal. 345 (2003) 959.

[6] H. Ohno, M. Yoshizawa, Solid State Ionics 154/155 (2002) 303.

[7] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, Appl. Catal. A: Gen. 145 (1996) 211.

[8] S.A. Forsyth, D.R. Mac Farlane, R.J. Thomson, M. von Itzstein, Chem. Commun. (2002) 714.

[9] Q. Liu, M.H.A. Janssen, F. Van Rantwijk, R.A. Sheldon, Green Chem. 7 (2005) 39.

[10] R.L. Augustine, Heterogeneous Catalysis for the Synthetic Chemist, Marcel-Dekker, New York, 1996.

[11] S. Steines, P. Wasserscheid, B. Driessen-Hölscher, J. Prakt. Chem., Chem. Zeitung 342 (2000) 348.

[12] A. Chagnes, H. Allouchi, B. Carré, D. Lemordant, Solid State Ionics 176 (2005) 1419.

[13] S. Murugesan, R.J. Linhardt, Curr. Org. Synth. 2 (2005) 437.