Catalysis Communications 27 (2012) 88–91

Contents lists available at SciVerse ScienceDirect

Catalysis Communications

journal homepage: www.elsevier.com/locate/catcom

Short Communication

Dehydration of carbohydrates to 2-furaldehydes in ionic liquids by catalysis with ion exchange resins

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ARTICLE INFO

Article history:
Received 12 April 2012
Received in revised form 27 June 2012
Accepted 3 July 2012
Available online 10 July 2012

Keywords:
Ion-exchange resins
Ionic liquids
Dehydration
2-Furaldehydes
Carbohydrates

ABSTRACT

The dehydration of several sugars, including pentoses, hexoses, di, tri, and polysaccharides, in ionic liquids with acidic ion-exchange resins as heterogeneous catalysts was investigated. Good 2-furaldehydes recovery yields, reaching 92% in some cases, were achieved when Dowex® 50W ion-exchange resins and 1-*n*-butyl-3-methylimidazolium chloride ([C_4mim]Cl) were used. Our results show that this aproach could represent a promising route towards the cost-efficient production of 2-furaldehydes from carbohydrate-based feedstocks.

1. Introduction

Interest in the chemistry of biomass-derived compounds has led to efforts aimed on the use of lignocellulosic materials as alternative sources of chemicals and energy. The dissolution of sugars and their dehydration into renewable feedstocks, such as 2-furaldehydes, are an example. These compounds represent valuable building blocks that could be obtained from biomass and used to synthesize a broad range of value added compounds currently derived from non-renewable sources [1,2].

5-(Hydroxymethyl)furfural (HMF) can be prepared by acid catalyzed dehydration of hexoses (Fig. 1) [3]. Similarly, furfural can be obtained by dehydration of pentoses. Both are produced industrially from agricultural byproducts such as sugarcane bagasse and corn cobs using methods that date back to the early 1900s. These processes have relatively high costs, operate at less than 50% yield, use vast ammounts of steam, and generate of large quantities of effluent waste [4,5]. These acid dehydrations have been studied using a broad range of catalytic systems and solvents. On the other hand, many catalysts, such as mineral and organic acids and salts, have been investigated using ionic liquids (ILs) as reaction media [6–8]. ILs possess a number of advantages over conventional solvents, including negligible vapor pressure, non-flammability, and thermal stability [9]. These characteristics have made them attractive to industries, as their use has the potential of alleviating regulatory constraints and manufacturing costs associated with disposing of volatile organic compounds (VOCs). Given their ability to dissolve cellulose and lignocellulosic materials, ILs have been proposed as media for the generation of biomass-based renewable energy [10–12]. Consequently, they could play an important role in the development of alternative and bio-renewable energy sources and feedstocks, as well as making the traditional routes cleaner and more efficient. The use of heterogeneous catalysts for these reactions has been limited to ion-exchange resins [13–16] and zeolites [17–19], and only a few report using ILs as media [20–25]. In this communication we present the dehydration of sugars and their conversion into HMF and related compounds using ILs as solvents and several heterogeneous catalysts. We initially surveyed a number of catalysts for the dehydration of fructose, glucose, arabinose, and xylose. The results obtained with ion-exchange resins were particularly encouraging, and the study was thus extended to a broader series of mono, di, tri, and polysaccharides as models to evaluate the reaction on carbohydrate-based biomass. Additionally, chloride and bromide salts were added in certain cases, as the anions in these salts could enhance the solvation of the carbohydrates in the IL [26], as well as to promote the aldose to ketose isomerization process [27].

2. Experimental

The following catalysts were assayed: 3 Å, 4 Å, 5 Å, and 13X molecular sieves, Montmorillonite, Montmorillonite K10, zeolites ZSM-5 and HZSM-5 (prepared according to Zhang et al. [28]), Amberlyst® 15, Amberlite® IR120, Dowex® 50Wx4-50, Dowex® 50Wx8-100, and Dowex® 50Wx8-200. Dehydrations were performed using sealed tubes in concentrations of 10% (w/w) for both the carbohydrate and the heterogeneous catalyst, using 3 mL of [C_4mim]Cl and keeping the

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doi:10.1016/j.catcom.2012.07.002

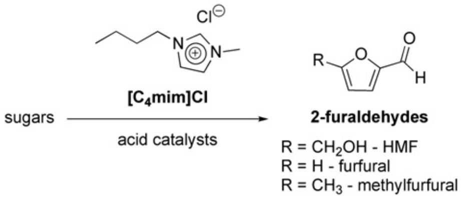

Fig. 1. Dissolution and dehydration of sugars to 2-furaldehydes.

temperature at 100 °C with continuous stirring for 6 hrs. In specific experiments, 1% of different salt co-catalysts reported in the literature, including $CrCl_3$ LiBr, and LiCl, were used. The reaction mixtures were then diluted with water (10 mL), and extracted with ethyl acetate (4×10 mL). The combined organic extracts were dried with Na_2SO_4, filtered, and the solvent evaporated under reduced pressure to obtain the corresponding 2-furaldehyde as the only product for the cases where the reaction took place.

The identity of the products was confirmed by ^1H NMR analyses. These were performed on a Bruker AVANCE 400 spectrometer operating at ^1H frequency of 400.13 MHz using CDCl3 as solvent. Chemical shifts (δ) are in ppm relative to the residual solvent signal (7.28 ppm), and coupling constants (*J*) are reported in Hz. *Furfural*: δ 9.70 (s, 1H), 7.72 (dd, *J*=0.8, *J*=1.7, 1H), 7.26 (dd, *J*=1.7, *J*=3.6, 1H), 6.63 (dd, *J*=1.7, *J*=3.6, 1H). *Methylfurfural*: δ 9.52 (s, 1H), 7.20 (d, *J*=3.6, 1H), 6.26 (qd, *J*=0.6, *J*=3.6, 1H), 2.44 (d, *J*=0.6, 3H). 5-(*Hydroxymethyl)furfural*: δ 9.48 (s, 1H), 7.20 (d, J=3.5, 1H), 6.48 (d, *J*=3.5, 1H), 4.64 (s, 2H), 4.03 (bs, 1H).

3. Results and discussion

3.1. Production of HMF from fructose and glucose with different catalysts

The results obtained for the dehydrations of fructose and glucose into HMF with the different catalysts are summarized in Fig. 2. No dehydration products were observed with no added catalyst. Addition of $CrCl_3$ to the neat IL reaction mixture yielded HMF in 47% in the case of fructose and 26% in the case of glucose. The results using molecular sieves or zeolites were not encouraging. Except when a molecular sieve of 5 Å pore size was used with fructose, which yielded HMF in 4%, these slightly acidic catalysts resulted in no dehydration products. Using ZSM-5 and its acidic form gave higher yields with fructose (14 and 20% yields respectively), but poor yields with glucose (3% in both cases). Montmorillonite clay in its natural and acidic form (K10) showed low yields of HMF (3% or less). Acidic ion-exchange resins showed better results. Although using Amberlite® IR120 resulted in no production of HMF with either monosaccharide, Amberlyst® 15 catalysis afforded HMF in 61 and 34% yields from glucose and fructose, respectively. Dowex® resins in several forms showed better HMF yields from fructose, ranging from 44 to 60%. Glucose dehydration reactions showed large differences. Dowex® 50W-1x4 resin resulted in a 3% HMF yield, while under the same conditions the yield from fructose was 54%. Dowex® 50Wx8-100 and 200 showed moderate HMF yields from glucose (34 and 44 % HMF yields, respectively), while yields from fructose were higher when these resins were used (44 and 60%, respectively).

Given the results using $CrCl_3$ with no catalyst, the addition of salts to the resin trials was evaluated. However, the results were erratic. Addition of $CrCl_3$ to Amberlyst® 15 resin lowered the HMF yield in the case of glucose (21%), but slightly increased it when fructose was used as substrate (39%). In the case Dowex® 50Wx8-200, HMF recovery yields were lower for fructose (44%) and glucose (33%). Addition of lithium salts to the mixtures gave yields of HMF similar to the original reaction. HMF yields from fructose decreased to 46% when LiCl was added, and was 60% when LiBr was added. A similar profile was observed for glucose, which showed HMF yields of 39 and 50% with LiCl and LiBr, respectively.

3.2. Effects of temperature, reaction time, and catalyst recycling on HMF yields

Having established that Dowex® 50Wx8-200 gave the best results, the yield profiles with varying temperature and time were studied to establish the optimal operating conditions. These experiments were carried using glucose as a standard and in the same conditions as the initial trials (3 mL of [C_4mim]Cl, 10% sugar and catalyst, 6 h). The yields obtained with different temperatures are presented in Fig. 3.

At 50 °C, dissolution was incomplete and only trace amounts of HMF could be detected. At 70 and 80 °C clean solutions were obtained, indicating that polymerization was controlled. However, yields of only 8 and 35%, respectively, were obtained at these temperatures. At 90 °C the yield increased to 50%, comparable to the 44% yield obtained at 100 °C. Raising the temperature to 110 °C resulted in a HMF yield of 43%. An intense browning of the reaction mixtures was also observed at this temperature, suggesting that polymerization had taken place.

Time profiles were established at a temperature of 100 °C on the basis of the above mentioned results (Fig. 4). For glucose, a HMF yield of 11% was reached in the first hour, increasing to 21% in 2 hours, 53% at 3 hours and to 70% at 4 hours. A slight decrease to 67% was observed after 5 hours and at 6 hours the yield was down to 44%. At the same time, the darkening of the reaction mixture was intense, suggesting once again that polymerization reactions were occurring. Therefore, reaction times longer than 4 hours should be avoided.

The recyclability of the resin was then evaluated. Based on the data obtained as a function of temperature and time, 3 hour reaction cycles at 100 °C were used for these studies. In the first trial, the

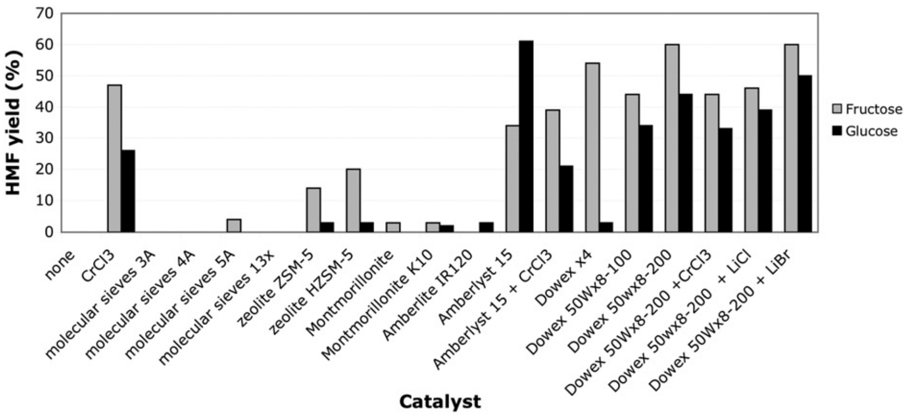

Fig. 2. Dehydration of fructose and glucose in IL solution with different heterogeneous catalysts.

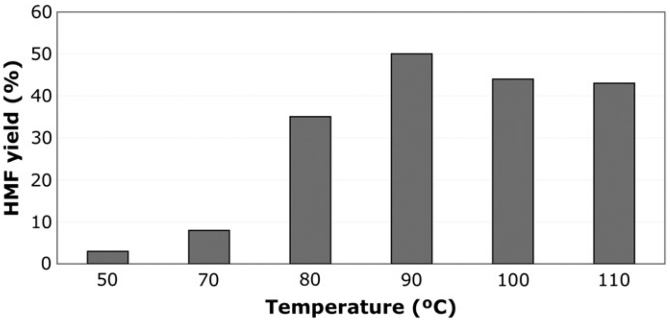

Fig. 3. HMF yields as a function of temperature using Dowex® 50Wx8-200 as catalyst and glucose as substrate.

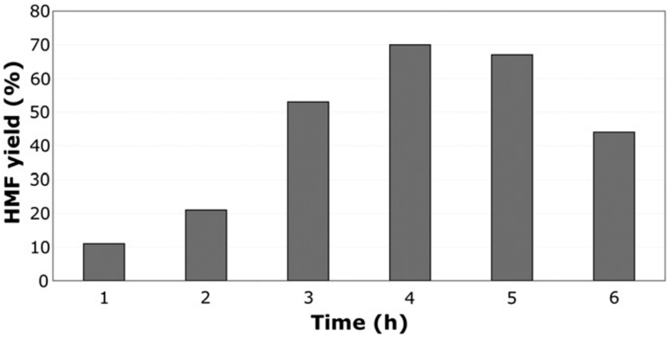

Fig. 4. HMF yields as a function of reaction time using Dowex® 50Wx8-200 as catalyst and glucose as substrate.

catalyst was recovered, washed with acetone, air dried, and employed in the second reaction cycle. A drop of 90% in the yield of HMF with respect to the first catalytic cycle was observed in this case. In a second trial, the resin was regenerated between cycles as indicated by the manufacturer (i.e., washed with 10% H_2SO_4 and brought to pH 6 with distilled water), washed with acetone, and air dried. Despite the resin acquired a dark brown color, the drop in the yield of HMF in the second cycle was only 16% in this case. However, regenerating the resing for a second time and using it in a third cycle leads to a drop in HMF yield of 92%. These results indicate that the acid sites of the resin require regeneration between catalytic cycles, and also suggest that gradual poisoning with decomposition products takes place.

3.3. Production of furfural from xylose and arabinose with different catalysts

Two pentoses, xylose and arabinose, were tested with the same set of heterogeneous catalysts and reaction conditions used for the hexoses. In this case, a positive reaction resulted in the production of furfural. Fig. 5 summarizes the results obtained.

As it was observed previously with the hexoses, there was no reaction in the neat IL. Addition of 1% $CrCl_3$ generated furfural in 33 and 30% yields for xylose and arabinose, respectively. Treatment with molecular sieves and zeolites ZSM-5 and HZSM-5 did not produce furfural. The same held for natural Montmorillonite and K10 clay. In the case of resins, Amberlite® IR120 showed no activity, while Amberlyst® 15 produced furfural in yields of 17% with xylose and 6% with arabinose. The addition of $CrCl_3$ to the Amberlyst® 15 reaction mixtures raised the yields to 19 and 29%, respectively. Dowex® resins showed good results. Using Dowex® 50Wx8-100, a 92% yield of furfural from arabinose was achieved. With Dowex® 50Wx8-200, the yield attained was 75%. Addition of $CrCl_3$ to the latter mixture lowered the yields (50%), as did the use of lithium salts (44% for LiCl and 23% for LiBr). Xylose showed lower yields than arabinose, producing furfural in 59% yield when Dowex® 50Wx8-100 was used, and only 28% for Dowex® 50Wx8-200. Again, addition of $CrCl_3$ to the mixture containing the 200-mesh resin lowered the yield to 8%, while LiCl and LiBr raised the yields to 56 and 68% respectively.

Despite the distinct behavior of the four tested carbohydrates, acidic ion-exchange resins such as Dowex® 50Wx8 and Amberlyst® 15 show the most promising results overall. In some cases the yields can be modulated by the addition of salts to the mixture.

3.4. Dehydration of other carbohydrates using Dowex® 50Wx8-200 ion-exchange resin

Trials with Dowex® 50Wx8-200 were extended to several types of carbohydrates and these results are presented in Fig. 6. These experiments were carried out with an adapted set of parameters, using 3 mL of [C_4mim]Cl, the appropriate carbohydrate and Dowex® 50Wx8-200 in 10% concentration, and heating for 3 hours at 100 °C.

In these conditions, ribose showed the highest yield of furfural among pentoses, reaching 90%. Arabinose lyxose, and xylose yielded furfural in 49%, 75%, and 28%, respectively. Hexoses displayed different profiles of reactivity, with galactose showing the lowest HMF yield (17%). Sorbose and mannose showed moderate yields (48 and 41%, respectively). As shown above, fructose and glucose generated HMF in 60 and 53% yields, respectively. Rhamnose, a 6-deoxyhexose, was dehydrated in these conditions to methylfurfural in 63% yield. Dehydration of the disaccharides lactose, trehalose, maltose, and sucrose produced HMF in

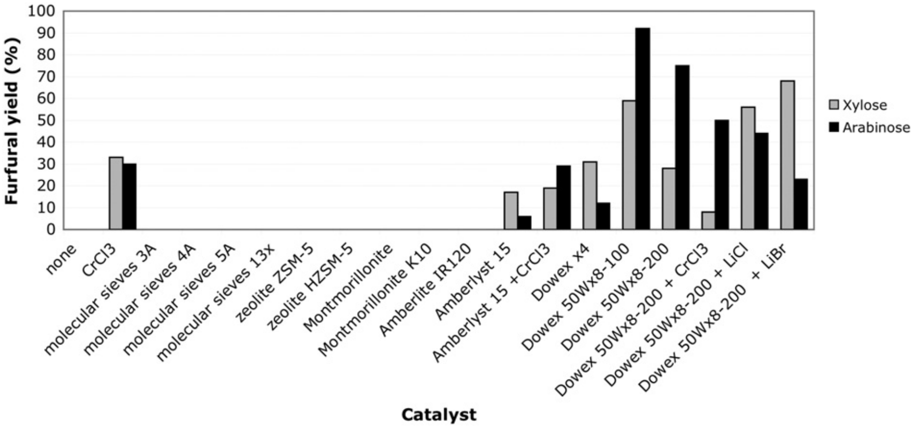

Fig. 5. Dehydration of xylose and arabinose in IL solution with different heterogeneous catalysts.

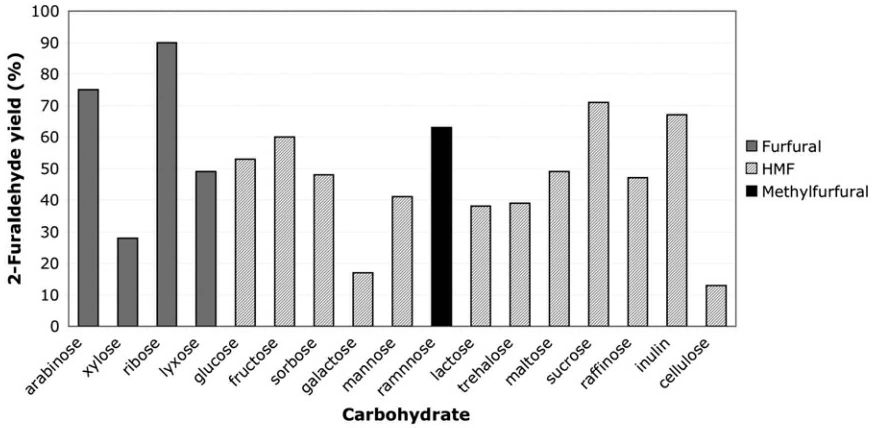

Fig. 6. Dehydration of carbohydrates with Dowex® 50Wx8-200 ion exchange resin.

38, 51, 49, and 71% yields, respectively. It can be pointed out that sucrose, the only disaccharide tested containing a fructose unit, showed a yield similar to that of the monomer. The trisaccharide raffinose produced HMF in 47% yield. In the case of polysaccharides, inulin (a fructan) reached a 67% yield, while microcrystalline cellulose resulted in low yields (13%).

4. Conclusions

The acid degradation of sugars to 2-furaldehydes in ILs with several heterogeneous catalysts was surveyed. Zeolites displayed poor or negligible dehydration yields, probably due to their relatively low acid strength. On the other hand, ion-exchange resins such as Dowex® 50W showed the best yields. The highest furfural yield was found to be 90% in the case of ribose, and for pentoses the order of reactivity was ribose > arabinose > lyxose > xylose. These results could be explained by the presumed open chain mechanism postulated for the dehydration of pentoses [29], in which ribose and arabinose share the same ketose form (ribulose), both having the highest furfural yields. In addition, xylose and lyxose dehydrations may proceed via their ketose form (xylulose), and therefore presenting lower dehydration yields. If the dehydrations proceed from structures with a furanose ring, the slight yield differences of ribose and arabinose on the one hand, and xylose and lyxose on the other could be better explained [30]. These results are not yet conclusive, and NMR experiments are currently underway to decipher the dehydration mechanism. In the case of hexoses, no correlation between steric factors and observed reactivities could be found for the furanose forms, being these data consistent with an open-chain form mechanism. The addition of salts can have an influence on the yields, and these results also imply a further evaluation of the alternative mechanisms suggested so far [29,30]. In the case of lithium salts, the hexoses evaluated showed little differences, but there were sharp decreases for arabinose and sharp increases for xylose. $CrCl_3$ seems to somehow disrupt the action of the resin catalyst as the yields are lower in all cases.

Although furfural and HMF are produced industrially by using high temperatures and strong acid catalysts, this work shows that ion-exchange resins in ILs allows for their production from sugars at moderate temperatures. This process offers an interesting route to 2-furaldehydes, and could thus be considered as a cost-efficient method for the conversion of carbohydrate-based biomass into materials of industrial interest.

Acknowledgements

The authors wish to acknowledge the financial support of the Fondo Sectorial de Energía (FSE-ANII) through project ANII-PR-FSE-2009-1-06, and the assistance of the Programa de Desarrollo de las Ciencias Basicas (PEDECIBA) and Facultad de Química for contributions to the research project.

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