Green Chemistry

PAPER

A catalytic aldol condensation system enables one pot conversion of biomass saccharides to biofuel intermediates†

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Producing bio-intermediates from lignocellulosic biomass with minimal process steps has a far-reaching impact on the biofuel industry. We studied the metal chloride catalyzed aldol condensation of furfural with acetone under conditions compatible with the upstream polysaccharide conversions to furfurals. *In situ* far infrared spectroscopy (FIR) was applied to guide the screening of aldol condensation catalysts based on the distinguishing characteristics of metal chlorides in their coordination chemistries with carbonyl-containing compounds. $NiCl_2$, $CoCl_2$, $CrCl_3$, VCl_3, $FeCl_3$, and $CuCl_2$ were selected as the potential catalysts in this study. The FIR results further helped to rationalize the excellent catalytic performance of VCl_3 in furfural condensation with acetone, with 94.7% yield of biofuel intermediates (C8, C13) in 1-butyl-3-methylimidazolium chloride ([BMIM]Cl) solvent. Remarkably, addition of ethanol facilitated the acetal pathway of the condensation reaction, which dramatically increased the desired product selectivity over the furfural pathway. Most significantly, we demonstrate for the first time that VCl_3 catalyzed aldol condensation in acidic medium is fully compatible with upstream polysaccharide hydrolysis to monosaccharide and the subsequent monosaccharide isomerization and dehydration to furfurals. Our preliminary results showed that a 44% yield of biofuel intermediates (C8, C13) can be obtained in one-pot conversion of xylose catalyzed by paired metal chlorides, $CrCl_2$ and VCl_3. A number of prior works have shown that the biofuel intermediates derived from the one-pot reaction of this work can be readily hydrogenated to biofuels.

Introduction

Fossil fuels based on petroleum, coal, and natural gas provide more than 75% of the world's energy today. However, these nonrenewable resources are being increasingly depleted, and the heavy utilization of fossil resources causes harmful impacts on the environment.[1–3] To meet the growing demand for bio-based fuels and chemicals, lignocellulosic biomass as a potential sustainable source of feedstock has been broadly explored through many different thermal and biological processes.[4] However, the structure of such a biomass is rather complex. Multiple process steps are typically involved to convert biomass feedstock to potential products.[5,6] The multiple unit operation will decrease the energy efficiency and the

product yield. In addition, the increased waste by-products in solvents or in gas phase cause environmental issues. Therefore, it is critical to reduce the number of processing steps for the development of economically viable biomass conversion technologies.

The US Environmental Protection Agency (EPA) has recently proposed that biofuel intermediates have far-reaching impacts on the biodiesel industry.[7] While direct pyrolysis of lignocellulosic biomass is a single step process in producing bio-intermediates, upgrading of the bio-intermediates remains faced with some serious challenges due to poor oil stability.[8,9] Dissolution of raw solid biomass in a solvent and the subsequent reactions in converting cellulosic biomass to biochemicals and biofuels is an important strategy for the establishment of bio-refineries.[10–13] The objective of this work was to enable the one-pot production of readily processable biofuel intermediates in high yield from cellulosic biomass by addressing the compatibility of aldol condensation with upstream polysaccharide conversions.

Scheme 1 depicts the general route of cellulosic biomass conversion to biofuel intermediates. Typically, cellulosic feedstock is hydrolyzed to yield monosaccharide, followed by

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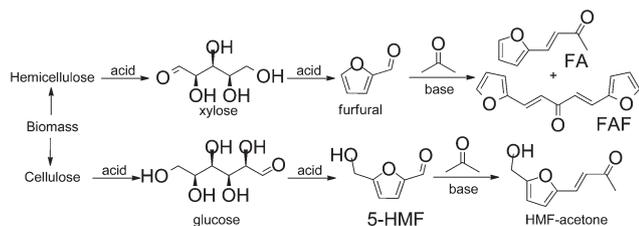
Scheme 1 A general route of biomass conversion to diesel fuel range multi-carbon precursors, FA, FAF, and HMF−acetone.

selective catalytic monosaccharide dehydration to produce platform compounds such as furfural and 5-hydroxymethyl-furfural (5-HMF) in acidic media.[14–22] Brønsted acids such as HCl, H_2SO_4, CH_3COOH, and maleic acid are widely used as catalysts in cellulosic biomass hydrolysis. Our previous works based on the ionic liquid system have established the hydrolysis of polysaccharides to monosaccharides catalyzed by metal chlorides.[23] In addition, chromium(II,III) chlorides showed excellent catalytic effects in selective conversion of mono-saccharide isomerization and dehydration to produce 5-HMF and furfural in an ionic liquid,[24] such as 1-butyl-3-methyl-imidazolium chloride ([BMIM]Cl). To exploit the full potential of furfural and 5-HMF as platform chemicals,[25,26] their transformation by aldol condensation with ketones such as acetone has been studied as a pathway to produce fuel range intermediate molecules – 4-(2-furyl)-3-buten-2-one (FA), and 1,5-bis-(2-furanyl)-1,4-pentadien-3-one (FAF).[27–29] Typically, aldol condensation is catalyzed by base catalysts,[30–33] such as sodium, magnesium and calcium hydroxides and an activated dolomite catalyst. However, base catalyzed condensation reactions are incompatible with the upstream hydrolysis and dehydration reactions in acid medium[34] (Scheme 1). Therefore, it is highly desirable to develop an efficient aldol condensation catalyst compatible with one-pot conversion of biomass polysaccharides to biofuel intermediates in a single medium.

Results and discussion

We explored cellulosic biomass conversion to biofuel intermediates in a one-pot process in [BMIM]Cl by first focusing on screening and characterization of metal chlorides as potential catalysts for aldol condensation (Scheme 2) under conditions compatible with upstream polysaccharide processing conditions. In our recent study, *in situ* far infrared (FIR) spectroscopy was employed to follow the coordination chemistry of
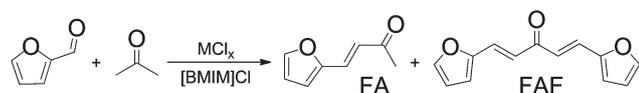
Scheme 2 Furfural condensation with acetone catalyzed with metal chlorides – MCl_x in [BMIM]Cl·cyclohexanone.

several classes of metal chlorides in the process of glucose conversion to 5-HMF.[35,36] FIR was demonstrated as a unique tool capable of differentiating the bond strength among some metal chlorides in forming complexes with compounds having a carbonyl group. In this work, for the first time, we extend *in situ* FIR as a tool to guide the screening of metal chlorides as a potential catalyst to catalyze the aldol condensation reaction. We use the coordination bond strength as the initial screening criteria for the identification of the aldol condensation catalyst. $NiCl_2$, $CoCl_2$, $CrCl_3$, VCl_3, $CuCl_2$, and $FeCl_3$ were selected to investigate the coordination bond strength of these metal ions with the carbonyl group of the cyclohexanone model compound using FIR spectroscopy (Fig. 1).

An intense absorption band near 300 cm^{-1} for the MCl_x/[BMIM]Cl system is ascribed to a stretch vibration of M–Cl bonds (M = Ni, Co, Fe, Cr, V, Cu, x = 2, 3).[36] When cyclohexanone was added to the MCl_x/[BMIM]Cl system, the M–Cl bond absorbance decreased as a result of carbonyl coordination to the added model compound, but the absorbances by Co–Cl, Ni–Cl, and Cr–Cl were restored to different extents when cyclohexanone was removed from the solvent by evaporation (as indicated by the upward arrows in Fig. 1a, b, and c, respectively). The Cr–Cl absorption peak was partially restored and the peaks of Co–Cl and Ni–Cl were fully restored under the same conditions. For Fe–Cl, Cu–Cl, and V–Cl, the FIR absorption peaks continued to decrease to different extents even when cyclohexanone was evaporated gradually (as indicated by the downward arrows in Fig. 1d, e, and f, respectively). Thus the coordination strength of metal chloride with carbonyl can be summarized in the sequence based on the variation of the
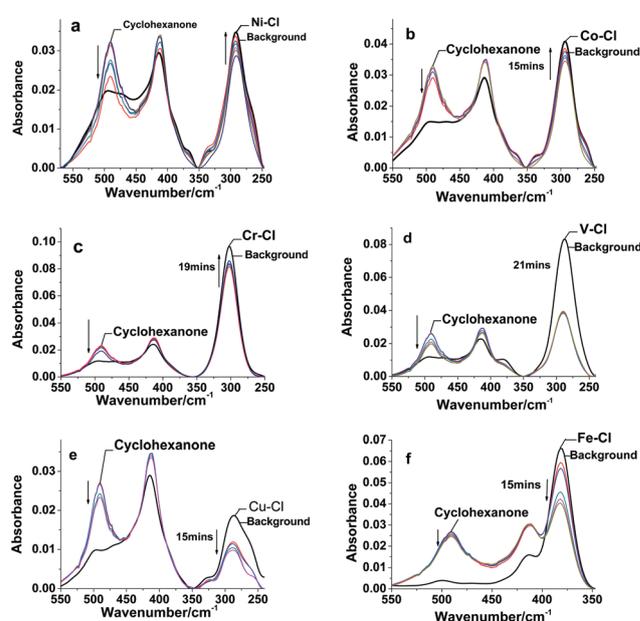
Fig. 1 Far infrared spectra of the MCl_x/[BMIM]Cl/cyclohexanone system. (a) $NiCl_2$; (b) $CoCl_2$; (c) $CrCl_3$; (d) VCl_3; (e) $CuCl_2$; (f) $FeCl_3$; 100 °C, the spectrum in black and bold is the background without cyclohexanone.

intensity of M–Cl FIR absorption peaks in the MCl_x/[BMIM]Cl/ cyclohexanone system: $NiCl_2$, $CoCl_2$ (very weak) < $CrCl_3$ (moderate) < VCl_3 (strong) < $FeCl_3$, $CuCl_2$ (very strong). To use the coordination strength of metal chloride with carbonyl as the initial screening criteria for the aldol condensation catalyst, it must be recognized that, for an ideal catalyst, the interaction between the catalyst and the reagent should be moderate; very weak and very strong represent both extremes of no activation for the aldol condensation and quantitative metal chloride consumption, respectively. Therefore, it seemed that $CrCl_3$ and VCl_3 could be suitable catalysts based on the FIR spectroscopy results.

We then investigated the catalytic performance of these metal chlorides for furfural condensation with acetone. The results are in excellent agreement with our hypothesis, as $CrCl_3$, and VCl_3 showed good catalytic results in furfural condensation with acetone (Fig. 2). The yield of furfural condensation products in the presence of $CuCl_2$, $FeCl_3$, $NiCl_2$, $CoCl_2$ was much lower than that in the presence of $CrCl_3$ and VCl_3. The desired function of the metal chloride is to activate acetone to an enol form which subsequently condensates with furfural.[37,38] Thus the good catalytic results of $CrCl_3$ and VCl_3 may be attributed to the moderate coordination strength with acetone by forming an activated enol intermediate. In addition, the higher furfural conversions catalyzed by $CrCl_3$, $NiCl_2$, and $CoCl_2$ than that by VCl_3, $CuCl_2$, and $FeCl_3$ is likely due to the reversible coordination of the carbonyl in furfural with $CrCl_3$, $NiCl_2$, and $CoCl_2$. However, the weakest coordination of $NiCl_2$ and $CoCl_2$ with the carbonyl group resulted in the least activated acetone for the desired FA and FAF condensation products, and was found to favor the formation of undetectable oligomers of furfural molecules. The strongest coordination of $CuCl_2$ and $FeCl_3$ with the carbonyl group resulted in their lowest furfural conversion as expected due to the fixation of these two metal chlorides by a fraction of the carbonyl compounds. The low selectivity to FA and FAF products with $CuCl_2$ and $FeCl_3$ also suggests the formation of undetectable oligomers from furfural or acetone molecules.

Although the selectivity for FA and FAF products by $CrCl_3$ and VCl_3 catalysts was the highest, a significant portion of furfural was converted to undetectable oligomeric products. We
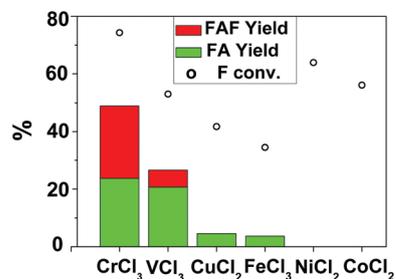
hypothesized that (1) the coordination of the furfural C=O group with $CrCl_3$ and VCl_3 was not productive for the desired condensation reaction, (2) such coordination reduced the effective concentration of $CrCl_3$ and VCl_3 for the activation of acetone, and (3) the free furfural molecules tended to form undetectable oligomers. Therefore, several additives, ethylene glycol dimethyl ether (GDE), ethanol, and methyl *tert*-butyl ether (MTBE) were evaluated to suppress the oligomerization of furfural and to promote the activity of furfural to condense with acetone (Fig. 3a). The addition of ethanol was found to improve the performance of VCl_3 for the aldol condensation reaction with the most significant improvement, both in furfural conversion and in FA and FAF selectivity. The overall selectivity of FA and FAF was elevated from 56% to 94.7% (FA in 40.1% and FAF in 54.6%) with the added ethanol (Fig. 3a). With $CrCl_3$, however, the addition of ethanol didn't show as dramatic an improvement in the catalytic performance as with VCl_3 (Fig. 3b).

We further investigated the basis of the most favorable ethanol promotion, and the optimum ethanol amount. The results are shown in Fig. 4. 2-Furaldehyde diethyl acetal (FDEA) as a new product was detected. The amount of FDEA increased with the ratio of ethanol but its concentration remained low. FDEA may have been an intermediate in the
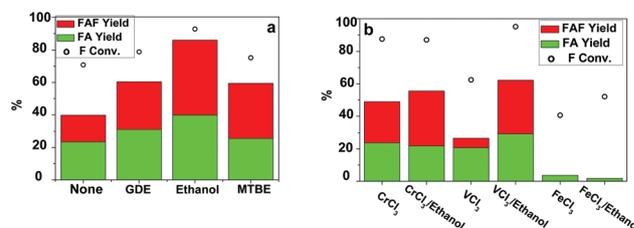
Fig. 3 (a) The effect of several additives on furfural condensation with acetone catalyzed by VCl_3 in [BMIM]Cl; additive 22.0 mmol, reacted for 3 h; (b) the effect of ethanol on $CrCl_3$, VCl_3, $FeCl_3$ in aldol condensation reaction; ethanol 12.5 mmol, reacted for 1.5 h. Reaction conditions: furfural 2.1 mmol, [BMIM]Cl (IL) 2.0 g, MCl_x 0.1 mmol, acetone 10.4 mmol; 140 °C.
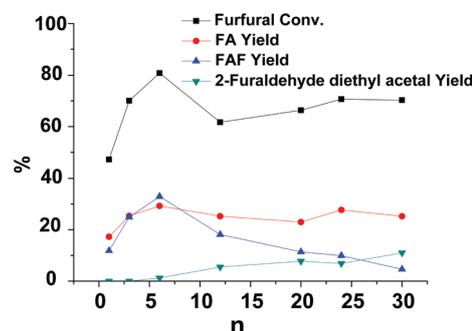
Fig. 2 The FA and FAF products were yielded by metal chloride catalyzed furfural condensation with acetone in [BMIM]Cl. Reaction conditions: furfural 2.1 mmol, [BMIM]Cl (IL) 2.0 g, MCl_x 0.1 mmol, acetone 10.4 mmol; 140 °C; 90 min.

Fig. 4 The effect of the amount of ethanol on furfural condensation with acetone catalyzed by VCl_3 in [BMIM]Cl; n is the molar ratio of ethanol to furfural. Reaction conditions: furfural 2.1 mmol, [BMIM]Cl 2.0 g, VCl_3, 0.1 mmol, acetone 10.4 mmol; 140 °C, 1.5 h.

reaction system. Accordingly, the reaction pathways of furfural condensation with acetone are proposed as shown in Scheme 3. Without ethanol, furfural was converted to undetectable compounds which are soluble in [BMIM]Cl based on the GC-MS analysis. In addition, furfural reacted with acetone and produced FA. FA further condensed with furfural and produced FAF (in the furfural path). With the addition of ethanol, firstly furfural reacted with the ethanol to form FDEA (acetal) as an intermediate, which then condensed with acetone to form FA. FA further condensed with the FDEA to form FAF (in the acetal path). Thus ethanol changed the reaction pathway from the furfural path to the acetal path. We further compared the relative reactivities of the furfural path and the acetal path (Fig. S1†). Only 15% FA and 6% FAF were obtained in the furfural path, as compared with 26% FA and 14% FAF in the acetal path. Obviously the reactivity of the acetal path to FA and FAF is higher than that of the furfural path.

Thus it is plausible that the ethanol protected the furfural from oligomerization and from coordinating with the metal center directly by forming the acetal FDEA. The activity of FDEA with the activated acetone is higher than that of the furfural in the condensation reaction. The dramatic improvement in the catalytic performance of VCl_3 as compared with that of $CrCl_3$ (Fig. 3b) may be attributed to the stronger coordination strength of VCl_3 with carbonyl in acetone than that of $CrCl_3$. We propose that activation through carbonyl coordination in acetone remains the rate controlling step for $CrCl_3$ catalyzed condensation, such that activating furfural to acetal FDEA does not help. Because VCl_3 coordinates with carbonyl more strongly than $CrCl_3$, making furfural activation the rate controlling step, furfural activation by ethanol to acetal FDEA promoted the condensation with the activated acetone. Although Fe(III) in $FeCl_3$ also coordinates with carbonyl strongly, it is non-selective as it also coordinates strongly with hydroxyl groups. In fact, ethanol may be considered a poison to $FeCl_3$. Therefore, the already low catalytic activity of $FeCl_3$ further declined (Fig. 3b) with the addition of ethanol. The electronegativity values of metal ions are in the order of Co^{2+} (2.706) < Ni^{2+} (2.891) < Cu^{2+} (2.952) < V^{3+} (3.813) < Fe^{3+} (3.835) < Cr^{3+} (4.026).[39] The corresponding Lewis acid strength of the metal ions is expected to follow the same order, in proportion to the generalized electronegativity of metal ions.[40] The catalytic performance of metal chlorides for aldol condensation as determined in this work increased in the order of $FeCl_3$ < $CrCl_3$ <
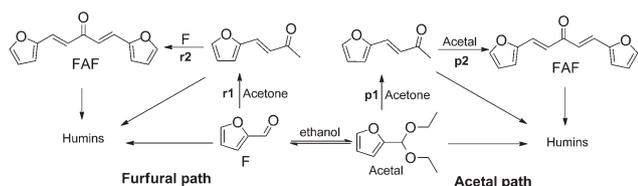
VCl_3 in the acetal path and $NiCl_2$, $CoCl_2$ < $CuCl_2$, $FeCl_3$ ≪ VCl_3 < $CrCl_3$ in the furfural path, at clear variance from the order of the Lewis acid strength. Thus the Lewis acidity does not account for the metal chloride catalyzed aldol condensation. The superior performance of VCl_3 is due to its moderately strong and selective coordination with carbonyl.

The mechanisms of the furfural pathway and acetal pathway may proceed as detailed in Scheme 4. In the furfural pathway, the coordination of the carbonyl group in acetone or FA with the V(III) ion center resulted in an enol form and then condensed with the furfural to form biofuel intermediates through dehydration. In the acetal pathway, the carbonyl group in acetone or FA formed an enolate first. Meanwhile, the acetal FDEA was converted to an oxonium ion intermediate catalyzed by VCl_3. The enol form of the acetone or FA was subsequently condensed with the oxonium ion intermediate to form FA and FAF through dealcoholization (Scheme 4). The oxonium ion intermediate is a strong electrophile,[41] thus accounting for the higher reactivity of the acetal pathway.

Our recent work showed that a suitable choice of extraction solvent helped greatly to improve the extraction efficiency. By conducting reactions in a two phase system having an extraction phase over the reaction phase, continuous removal of the formed products into the extraction led to the efficient recovery of the product and minimized humins formation, resulting in a significantly improved ionic liquid recycle.[42,43] In this work, we demonstrated that the VCl_3 catalyzed aldol condensation system was reused 4 times without worsening its performance by extracting the products with diethyl ether after each run (Fig. S2†). As a future work, recycled use of the ionic liquid and improved product yield could be expected by adopting a similar two phase system.

The results above indicate the conditions under which the metal chloride catalyzed aldol condensation is compatible with cellulosic biomass conversion to biofuel intermediates in a one-pot process.

To verify the one-pot process strategy, we then evaluated the direct conversion of xylose in [BMIM]Cl with acetone to the biofuel intermediates, FA and FAF, with paired metal chlorides as the catalyst by the combination of VCl_3, $CrCl_3$, $CrCl_2$, $FeCl_3$,

Scheme 3 The reaction pathways of furfural condensation with acetone catalyzed by VCl_3 in [BMIM]Cl with (acetal path) or without ethanol (furfural path). F: furfural; A: acetone.
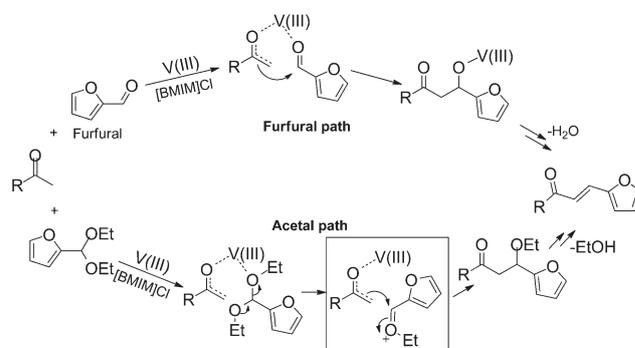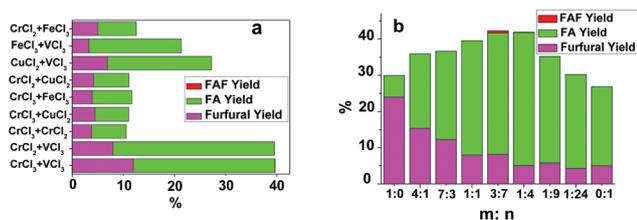

Scheme 4 The proposed reaction mechanism of furfural and FDEA condensation with acetone catalyzed by VCl_3 in [BMIM]Cl. R = H, 2-(furan-2-yl) vinyl (furfural path and acetal path).

Fig. 5 The catalytic characteristics of paired metal chlorides for one-pot xylose conversion to biofuel intermediates. (a) M_1Cl_x, M_2Cl_y, each 0.06 mmol; (b) the effect of molar ratio – $m:n$ of bimetallic chlorides $CrCl_2$ (m) and VCl_3 (n) on the catalytic reactivity. The total of the bimetallic chlorides is 0.10 mmol. Reaction condition: xylose 1.25 mmol, [BMIM]Cl (IL) 2.0 g, acetone 1.0 g, GDE 2.0 g, ethanol 0.6 g, 160 °C, 2 h.

and $CuCl_2$. The combination of $CrCl_2$ + VCl_3 showed the highest FA yield, 44% (Fig. 5a).

The results are consistent with the superior performance of $CrCl_2$ in isomerizing aldose to ketose, which is essential for the formation of furfural in the first step[24] and that of VCl_3 in catalyzing aldol condensation as discovered in this work. We further studied the effect of the molar ratio of the metal chlorides, $CrCl_2$ and VCl_3, on the catalytic performance (Fig. 5b). At the total metal chlorides in 10 mol% with respect to xylose, we achieved a FA yield of 44% when the molar ratio of $CrCl_2$ to VCl_3 was 1 to 4. It should be noted that either a $CrCl_2$ only or a VCl_3 only catalyst produced a less amount of FA and FAF (Fig. 5b).

Conclusions

We report a new catalytic system that enabled furfural condensation with acetone under conditions compatible with cellulosic biomass conversion to biofuel intermediates for a one-pot process in acidic media. Metal chlorides catalyze both the aldose isomerization and the aldol condensation reactions in [BMIM]Cl. Far infrared spectroscopy was successfully used in the study of the coordination strength of metal chloride ($NiCl_2$, $CoCl_2$, $CrCl_3$, VCl_3, $FeCl_3$, and $CuCl_2$ with carbonyl) and provided an insightful basis for the screening of suitable catalysts. VCl_3 catalyzed the condensation of furfural with acetone with high selectivity to FA and FAF, consistent with the FIR results. The insight gained from the FIR results led us to the use of ethanol for the dramatically improved performance of VCl_3 by generating FDEA as an active acetal. The total selectivity of biofuel intermediates reached 94.7% (FA in 40.1% and FAF in 54.6%). FDEA is a strong electrophile under acidic conditions by generating an oxonium ion intermediate with enhanced condensation with the activated acetone. For the first time, we demonstrate one pot conversion of xylose to biofuel intermediates, FA and FAF, catalyzed with paired metal chlorides. The biofuel intermediate yield of 44% was obtained in one-pot conversion of xylose catalyzed with the combination of $CrCl_2$ and VCl_3 (molar ratio of $CrCl_2$ to VCl_3 is 1 : 4). The FA and FAF are known stable biofuel intermediates that have been readily hydrogenated to high quality aviation biofuels.[44]

Experimental

Fourier transformation infrared spectroscopic analysis

A leveled attenuated total reflectance (ATR) accessory with a 3 mm-diameter diamond plate purchased from Pike Technologies was used for the infrared spectroscopy measurement, and the FIR instrument model is Nicolet iS 50 FT-IR. The accessory is equipped with a resistance wire for heating. In addition, a steady flow of nitrogen and a high-temperature vacuum-grease sealed glass lid were used above the sample to prevent air and moisture from leaking in. As soon as the dissolved metal halide was mixed with cyclohexanone, a drop of the sample was placed on the diamond plate and then *in situ* far-infrared spectroscopy was performed with a DTGS/Polyethylene detector, which has 16 cm^{-1} resolution. All samples were scanned 128 times at one go.

NMR analysis

NMR spectra were measured in $CDCl_3$ on a 400 MHz instrument and recorded at the following frequencies: proton (^{1}H, 400 MHz), and carbon (^{13}C, 100 MHz). ^{1}H NMR chemical shifts were reported in ppm using tetramethylsilane (TMS, δ (ppm) = 0.00 ppm) as the internal standard. ^{13}C NMR spectra were reported in ppm using $CDCl_3$ as the internal standard.

Acknowledgements

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