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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 far-reaching impact for the biofuel industry. We studied metal chloride catalyzed aldol condensation of furfural with acetone in 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. NiCl₂, CoCl₂, CrCl₃, VCl₃, FeCl₃, and CuCl₂ were selected as the potential catalysts in this study. The FIR results further helped to rationalize the excellent catalytic performance of VCl₃ in furfural condensation with acetone with 94.7% yield to 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 VCl₃ catalyzed aldol condensation in the acidic medium is fully compatible with the upstream polysaccharide hydrolysis to monosaccharide and the subsequent monosaccharide isomerization and dehydration to furfurals. Our preliminary results showed that 44% yield of biofuel intermediates (C8, C13) can be obtained in one-pot conversion of xylose catalyzed by paired metal chlorides, CrCl₂ and VCl₃. 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 provides more than 75% of the world's energy today. However, these nonrenewable resources are increasingly depleted, and the heavy utilizing of fossil resources causes harmful impacts to the environment ¹⁻³. To meet the growing demand for bio-based fuels and chemicals, lignocellulosic biomass as potential sustainable source of feedstock has been broadly explored through many different thermal and biological processes ⁴. However, the structure of such biomass is rather recalcitrant and complex. Multiple process steps are typically involved to convert biomass feedstock to potential products ^{5, 6}. The multiple units 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 impact for biodiesel industry⁷. 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 are an important strategy for the establishment of bio-refineries¹⁰⁻¹³. The objective of this work was to enable one-pot production of readily processible biofuel intermediates in high yield from cellulosic biomass by addressing the compatibility of aldol condensation with the upstream polysaccharide conversions.



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

Scheme 1 depicts the general route of cellulosic biomass conversion to biofuel intermediates. Typically, cellulosic feedstock is hydrolyzed to yield monosaccharide, followed by selective catalytic monosaccharide dehydration to produce platform compounds such as furfural and 5-hydroxymethylfurfrual (5-HMF) in acidic media¹⁴⁻²². Br\u00e9nsted acids such as HCl, H₂SO₄, CH₃COOH, maleic acid are

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widely used as catalysts in cellulosic biomass hydrolysis. Our previous works based on the ionic liquid system have established the hydrolysis of polysaccharides to monosaccharide catalyzed by metal chlorides.²³ In addition, Chromium (II, III) chlorides showed excellent catalytic effect in selective conversion of monosaccharide isomerization and dehydration to produce 5-HMF and furfural in ionic liquid ²⁴, such as 1-butyl-3-methylimidazolium 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-2one (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 activated dolomite catalyst. However, the 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

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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) in conditions compatible with the upstream polysaccharide processing conditions. In our recent study, in-situ far infrared (FIR) spectroscopy was employed to follow the coordination chemistry of 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 potential catalyst to catalyze aldol condensation reaction. We use the coordination bond strength as the initial screening criteria for the identification of aldol condensation catalyst. NiCl₂, CoCl₂, CrCl₃, VCl₃, CuCl₂, and FeCl₃ were selected to investigate the coordination bond strength of these metal ions with the carbonyl group of 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



Fig. 1 Far infrared spectra of the MCl_x/[BMIM]Cl/cyclohexanone system. a) NiCl₂; b) CoCl₂; c) CrCl₃; d) VCl₃; e) CuCl₂; f) FeCl₃; 100 °C, The spectrum in black and bold is the background without cyclohexanone

model compound, but the absorbance by Co-Cl, Ni-Cl, and Cr-Cl were restored to different extent when cyclohexanone was removed from the solvent by evaporation (as indicated by the upward arrows in Fig 1. a, 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 extent even when cyclohexanone was evaporated gradually (as indicated by the downward arrows in Figs. 1. d, 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 intensity of M-Cl FIR absorption peaks in the MCl_x/ [BMIM]Cl/ cyclohexanone system: NiCl₂, CoCl₂ (Very weak) < CrCl₃ (moderate) < VCl₃ (Strong) < FeCl₃, CuCl₂ (Very strong). To use the coordination strength of metal chloride with carbonyl as the initial screening criteria for 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 CrCl₃ and VCl₃ could be suitable catalysts based on the FIR spectroscopy results.



Fig. 2 The FA and FAF products were yield 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.

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 CrCl₃, and VCl₃ showed good catalytic results in furfural condensation with acetone (Fig. 2). The yield of furfural condensation products in the presence of CuCl₂, FeCl₃, NiCl₂, CoCl₂ were much lower than that in the presence of CrCl₃ and VCl₃. The desired function of the metal chloride is to activate acetone to enol form which subsequently condensates with furfural ^{37, 38}. Thus the good catalytic results of CrCl₃ and VCl₃ may be attributed to the moderate coordination strength with acetone by forming activated enol intermediate. In addition, the higher furfural conversions catalyzed by CrCl₃, NiCl₂, and CoCl₂ than that by VCl₃, CuCl₂, and FeCl₃ is likely due to the reversible coordination of carbonyl in furfural with CrCl₃, NiCl₂, and CoCl₂. However, the weakest coordination of NiCl₂ and CoCl₂ with 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 CuCl₂ and FeCl₃ with 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 CuCl₂ and FeCl₃ also suggests the formation of undetectable oligomers from furfural or acetone molecules.



Fig. 3 (a). The effect of several additives on furfural condensation with acetone catalyzed by VCl₃ in [BMIM]Cl; Additive 22.0 mmol, Reacted for 3 h; (b) The effect of ethanol on CrCl₃, VCl₃, FeCl₃ 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 $^{\circ}$ C.

Although the selectivity to FA and FAF products by CrCl₃ and VCl₃ catalysts were the highest, there was a significant portion of furfural converted to undetectable oligomeric products. We hypothesized that (1) the coordination of the furfural C=O group with CrCl₃ and VCl₃ 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, 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 VCl₃ for the aldol condensation reaction with the most drastic 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 CrCl₃, however, the addition of ethanol didn't show as dramatic improvement in the catalytic performance as with VCl₃ (Fig. 3b).

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Fig. 4 The effect of ethanol amount on furfural condensation with acetone catalyzed by VCl₃ in [BMIM]Cl; n is the mole ratio of ethanol to furfural. Reaction conditions: Furfural 2.1 mmol, [BMIM]Cl 2.0 g, VCl₃ 0.1 mmol, Acetone 10.4 mmol; 140 °C, 1.5 h.

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 stayed in low concentration. FDEA may have been an intermediate in the 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 GC-MS analysis. In addition, furfural reacted with acetone and produced FA. FA further condensed with furfural and produced FAF (in Furfural path). With the addition of ethanol, firstly furfural reacted with ethanol to form FDEA (acetal) as an intermediate, which then condensed with acetone to form FA. FA further condensed with FDEA to form FAF (in Acetal path). Thus ethanol changed the reaction pathway from Furfural path to Acetal path. We further compared the relative reactivities of Furfural path and Acetal path (Fig. S1). Only 15% FA and 6% FAF were obtained in Furfural path, as compared to 26% FA and 14% FAF in the Acetal path. Obviously the reactivity of Acetal path to FA and FAF is higher than that of Furfural path.

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Scheme 3 The reaction pathways of furfural condensation with acetone catalyzed by VCl₃ in [BMIM]Cl with (Acetal Path) or without ethanol (Furfural Path). F: furfural; A: acetone.

Thus it is plausible that ethanol protected furfural from oligomerization and from coordinating with metal center directly by forming the acetal FDEA. The activity of FDEA with activated acetone is higher than that of furfual in the condensation reaction. The dramatic improvement in the catalytic performance of VCl₃ as compared to that of CrCl₃ (Fig. 3b) may be attributed to the stronger coordination strength of VCl₃ with carbonyl in acetone than that of CrCl₃. We propose that activation through carbonyl coordination in acetone remains the rate controlling step for CrCl₃ catalyzed condensation, such that activating furfural to acetal FDEA does not help. Because VCl₃ coordinates with carbonyl stronger than CrCl₃, making furfural activation the rate controlling step, furfural activation by ethanol to acetal FDEA promoted the condensation with activated acetone. Although Fe(III) in FeCl₃ 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 FeCl₃. Therefore, the already low catalytic activity of FeCl₃ further declined (Fig. 3b) with the addition of ethanol. The electronegativity values of metal ions are in the order of $Co^{2+}(2.706) < Ni^{2+}(2.891) < Cu^{2+}(2.952) < V^{3+}(3.813) < Fe^{3+}(3.835)$ < Cr³⁺ (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 FeCl₃< CrCl₃< VCl₃ in acetal path and NiCl₂, CoCl₂< CuCl₂, FeCl₃<< VCl₃< CrCl₃ in furfural path, at clear variance from the order of Lewis acid strength. Thus the Lewis acidity does not account for the metal chloride catalyzed aldol condensation. The superior performance of VCl₃ is due to its moderately strong and selective coordination with carbonyl.

The mechanisms of Furfural pathway and Acetal pathway may proceed as that 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 enol form and then condensed with furfural to form the biofuel intermediates through dehydration. In Acetal pathway, carbonyl group in acetone or FA formed enolate first. Meanwhile, the acetal FDEA was converted to an oxonium ion intermediate catalyzed by VCl₃. The enol form of 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 Acetal pathway.



Scheme 4 The proposed reaction mechanism of furfural and FDEA condensation with acetone catalyzed by VCI_3 in [BMIM]Cl. R=H, 2-(furan-2-yl) vinyl. (Furfural path and Acetal path).

Our recent work showed that proper choice of extraction solvent helped largely improve the extraction efficiency. By conducting reaction in a two phase system having an extraction phase over the reaction phase, continuous removal of formed products into the extraction led to the efficient recovery of the product and minimized humins formation, resulting in significantly improved ionic liquid recycle.^{42, 43.} In this work, we demonstrated that the VCl₃ catalyzed aldol condensation system was reused 4 times without decreasing in its performance, by extracting the products with diethyl ether after each run (Fig. S2). As a future work, recycled used of the ionic liquid and improved product yield could be expected by adopting a similar two phase system.



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.

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

To verify the strategy of one-pot process, 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 VCl₃, CrCl₃, CrCl₂, FeCl₃, and CuCl₂.

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

The results are consistent with the superior performance of CrCl₂ in isomerizing aldose to ketose which is essential for the formation of furfural in the first step ²⁴ and that of VCl₃ in catalyzing aldol condensation as discovered in this work. We further studied the effect of the molar ratio of the metal chlorides, CrCl₂ and VCl₃, on the catalytic performance (Fig. 5b). At the total metal chlorides in 10 mol% with respect to xylose, we achieved FA yield of 44% when the molar ratio of CrCl₂ to VCl₃ was 1 to 4. It should be noted that either CrCl₂ only or VCl₃ only catalyst produced less amount of FA and FAF (Fig. 5b).

Conclusions

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We report a new catalytic system that enabled furfural condensation with acetone in 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 (NiCl₂, CoCl₂, CrCl₃, VCl₃, FeCl₃, and CuCl₂ with carbonyl) and provided insightful basis for the screening of suitable catalysts. VCl₃ 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 dramatically improved performance of VCl₃ 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 promoted condensation with 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 CrCl₂ and VCl₃ (mole ratio of CrCl₂ to VCl₃ 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-mmdiameter diamond plate purchased from Pike Technologies was used for the infrared spectroscopy measurement and the FIR instrument model is NICOLETIS 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 is mixed with cyclohexanone, a drop of the sample was placed on the diamond plate and then *in situ* far-infrared spectroscopy was recorded with a DTGS/Polyethylene detector, which has 16 cm⁻¹ resolution. The background and sample were scanned for 128 times at one time.

NMR analysis

NMR spectra were measured in $CDCI_3$ on a 400 MHz instrument and recorded at the following frequencies: proton (1H, 400 MHz), carbon (¹³C, 100 MHz). 1H 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 CDCl₃ as the internal standard.

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A Catalytic Aldol Condensation System Enables One Pot Conversion of

Biomass Polysaccharides to Biofuel Intermediates

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Producing bio-intermediates from lignocellulosic biomass with minimal process steps has far-reaching impact for the biofuel industry. We discovered an efficient catalytic aldol condensation system that enables one pot conversion of biomass polysaccharides to biofuel intermediates. *In-situ* far infrared spectroscopy successfully assisted the screening of metal chlorides as potential catalysts by studying the coordination chemistry of metal chlorides with carbonyl compounds. By converting furfural to 2-furaldehyde diethyl acetal with ethanol, V(III) ion coordinated moderately with acetone showed excellent performance in the condensation of furfural with acetone, with 94.7% yield to FA and FAF.