## Correlation between coordination chemistry and aldose isomerization characteristics of metal chlorides in a chloride-based ionic liquid

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### Introduction

A growing economy based on the renewable hydrocarbons will not only support the ultimate sustainable societal need for chemical products and liquid fuels, but also benefit the environment with carbon-neutral greenhouse gas emissions. Glucose is the most abundant bio-molecules the fundamental building block of cellulose and starch. One of the most notable advances toward biorefineries in recent years is the discovery of new catalytic systems that enabled the conversion of glucose to potential platform chemicals – 5-HMF. Since the discovery of chromium (II, III) chlorides as the most effective catalysts in 1-alkyl-3-methylimidazolium ([EMIM][Cl]) for the isomerization of glucose to fructose, which is readily dehydrated to form 5-HMF in high yield,[2] a considerably large number of publications have appeared that reported results from a combination of a wide variety of ionic liquids,[3,4] other solvents,[5] other catalysts, and process conditions. A key question remains unanswered regarding the fundamental characteristics of chromium chloride catalysts responsible for their superior catalytic performance over many other metal chlorides for the isomerization of glucose to fructose. In this work, we employed FIR as an *in-situ* tool to follow the progress of the coordination chemistry changes of four classes of metal chlorides, CrCl₃, VCl₃, FeCl₃, and PtCl₂, during glucose conversion. To correlate the coordination structure of the metal chlorides to the catalytic performances, model compounds of different oxygen sources which include cyclohexanone, n-butyl alcohol, glycolaldehyde and deionized water, and a combination of both glucose and a model compound are studied in [BMIM][Cl].

### Materials and Methods

A sample of 1-butyl-3-methylimidazolium was vacuum dehydrated at 90 °C for at least 8h before use. Specified amounts of metal chlorides and [BMIM][Cl] were weighed and each metal chloride was dissolved in [BMIM][Cl] under agitation using a magnetic stirrer bar. For reaction studies, the content in liquid inside each vial was stirred at 500 rpm, at 100 °C for 1 h before HPLC analysis. Typically, the weight of metal chloride corresponds to 15 mol % with respect to glucose. The masses of [BMIM][Cl] and glucose were 500 mg and 50 mg, respectively. And the amount of model compounds was approximately equal mol with respect to 50 mg glucose.

A leveled attenuated total reflectance (ATR) accessory with a 3-mm-diameter diamond plate purchased in 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. The background and sample were scanned for 128 times. It was verified that the absorbance of a non-reaction system stay unchanged even though the thickness of the sample was changed.

HPLC analysis was performed on an Agilent 1260 series with a refractive index detector and a PL Hi-Plex H column (300 × 7.7 mm, 8 μm). Diluted H₂SO₄ solution (0.005 M) at a flow rate of 0.6 mL/min was used as the mobile phase. The column and detector temperatures were 65 °C and 50 °C, respectively.

### Results and Discussion

The relative bond strengths and the number of ligands that the metal ions are coordinated by oxygen atom of different sources and by chloride as revealed by using an *in-situ* far infrared (FIR) are shown in Table 1. The superior performance of CrCl₃ for this reaction is now distinguished from other metal chlorides, on the basis of its selective Cr (III) ene-diol coordination chemistry. The effect of competitive oxygen atoms coordination to the metal ions by the model compounds on glucose conversion was determined by reaction studies, which revealed that monoglycoaldehyde coordination to Cr(III) prevailed. Other O sources did not complete favorably again this glycoaldehyde coordination. *In-situ* FIR is established as a powerful tool in the study of the coordination chemistry of metal complexes in ionic liquids.

### Significance

The use of FIR as an *in-situ* tool in combination with model compound reaction study enabled us to distinguish the dominant pathways by different metal chloride catalysts in the conversion of glucose.

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### References