Novel SnCl$_2$-H$_2$SO$_4$ Mixed Catalyst System for Fructose Conversion to 5-hydroxymethylfurfural

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Abstract

The effect of some metal salts in sulphuric acid mixed catalyst systems on the conversion of D-fructose to 5-hydroxymethylfurfural (HMF) have been studied using UV/VIS spectrophotometry. Differential increases in HMF yield were observed when the metal salts were synergized with 1 M sulphuric acid solution relative to what was obtained when the acid was used alone. This differential HMF yield increased in the order: ZnCl$_2$<Pb(NO$_3$)$_2$<NiS$_2$O$_4$<MnCl$_2$<CoCl$_2$<CuSO$_4$<HgCl$_2$<SnCl$_2$. The highest 101.8% contribution to HMF yield obtained when SnCl$_2$ salt was synergized with sulphuric acid solution was attributed to the strong reducing ability of this salt in protonic acid solutions. Kinetic studies of the effect of temperature and SnCl$_2$ concentration on rate of HMF production from fructose, predicts good thermal stability of the SnCl$_2$-H$_2$SO$_4$ mixed catalyst system.

Keywords: Fructose; 5-hydroxymethylfurfural; Tin (II) chloride; Mixed catalysts; Fructose dehydration

Introduction

Glucose and fructose are six-carbon sugar molecules which are potential feedstocks for the production of biofuels that can replace petroleum fuels [1]. Recent research efforts have focused on their conversion to 5-hydroxymethylfurfural (HMF) [2,3], the precursor of the most recent second generation biofuel 2,5 dimethylfuran (DMF). Current processes in HMF production involve the use of acid catalysts, and are mainly limited to fructose as the biomass feed [4-7].

The major problem associated with the use of protonic acid catalysts in aqueous solutions for the conversion of fructose to HMF is that the HMF decomposes in this medium to give levulinic and formic acids [8-11], with the levulinic acid being particularly difficult to separate from HMF.

Some researchers have used other non-aqueous solvent media for fructose conversion to HMF and yields have been shown to increase significantly in these systems because of their ability to partition HMF from water. Dumesic and coworkers demonstrated high yields from fructose by using the solvent dimethylsulphoxide [12]. Zhao et al. [13] have been able to catalyze the dehydration of fructose at 80°C to HMF, by the addition of catalytic amounts of different metal halides in 1-alkyl-3-methylimidazolium chloride as a solvent class. Best yield of HMF of up to 70% was obtained with chromium trichloride as catalyst. Sulphuric acid was also used as catalyst in this solvent, giving high conversion rate for fructose but with low HMF yield. HMF can also be formed in high yields from fructose in 1- H-3-methylimidazolium chloride solvent, which also serves as both acidic catalyst and solvent [14], and also in sub- and supercritical acetone [15].

The fact still remains that for the production of HMF to be made commercial for the purpose of biofuel production, the cheap and readily available solvent, water, should continue to be the solvent of choice. The use of cheap mineral acids as catalyst, which give quick conversions of fructose to HMF, with the only problem being side reactions that lead to HMF degradation remains the best bet for the production of commercially affordable biofuel. This paper therefore investigates the use of mixed catalysts in water, comprising sulphuric acid as a baseline catalyst with high fructose – HMF conversion abilities, and soluble metal salts as possible stabilizers to either inhibit the conversion of HMF to levulinic and formic acids, or further increase the HMF production rate to an extent that the earlier side reaction becomes negligible.

Experimental

Reagents and sample preparation

D-fructose, H$_2$SO$_4$ and metal salts used for this work were of analytical grade, purchased from FINLAB Nigeria PLC Lagos, and were used without further purification. The sample and reagents were further prepared with distilled water.

Instrumentation

Quantification of HMF in the acid solutions of metal salts was carried out using JENWAY 6405 UV/VIS Spectrophotometer [16,17]. The instrument was set at a wavelength range of 200-900 nm, and HMF was detected at a wavelength (λmax) of 285 nm [18].

Procedure

Preliminary studies of the effect of metal salts on HMF yield were carried out using nine salts: NiSO$_4$, CoCl$_2$, CuSO$_4$, ZnCl$_2$, MnCl$_2$, HgCl$_2$, Pb(NO$_3$)$_2$, SnCl$_2$ and FeSO$_4$. 100 cm$^3$ of 0.1 M D-fructose were prepared in 1 M solutions of H$_2$SO$_4$ and transferred into a 250 cm$^3$ beakers. 0.01 M weight of each metal salt was weighed and dissolved separately in each of the fructose solutions. 50 cm$^3$ of each of these solutions was transferred in triplicates into a series of ampoules. The ampoules were sealed and arranged on a rack, and were placed in a thermostated water-bath shaker set at 303 K and left for 24 hours. Thereafter, the ampoules were taken from the water-bath and directly quenched in an ice-bath at 278 K to stop the reaction. The ampoules were opened, and about 3 cm$^3$
of each reaction mixture was extracted and scanned in triplicates for HMF using a UV/VIS Spectrophotometer.

Rate Studies

The kinetics of the contributions of SnCl₂ and FeSO₄ to HMF yield was carried out using 0.1 M fructose in 1 M solution of H₂SO₄ as blank. 500 cm³ of this solution was prepared, and 50 cm³ samples were extracted and transferred in a series of eighteen ampoules. The ampoules and their contents were placed on a rack and immersed in a thermostated water-bath shaker set at 313 K and left for 10 minutes to attain thermal equilibrium with the bath. The ampoules were extracted in threes at 5 minutes intervals, and directly quenched in an ice-bath at 278 K to stop the reaction. The absorbance of HMF in each of the solutions was taken. Concentration of 10⁻⁴ M and 10⁻⁴ M each of SnCl₂ and FeSO₄ were dissolved in the blank and the procedure was repeated. The experiments were performed again at 333 K.

Results and Discussions

The absorbances of HMF in the different acid solutions were used to relate its concentration according to the Beer-Lambert’s Law [19]. Figure 1 gives the UV absorbances of HMF in the different acid – metal salt solutions at the same concentrations, at 303 K.

The results in figure 1 show that HMF can be produced from sulphuric acid in aqueous solution. This amount however is boosted by synergizing the HMF production ability of sulphuric acid with metal salts. The mixtures of metal salts in this system showed different degrees of increases in HMF yield. Best results were obtained with FeSO₄ and SnCl₂, as shown by the absorbance values of HMF at 1.106 and 1.263 respectively. The percentage contributions to HMF yield by the different metal salts used for this study in sulphuric acid is shown in figure 2. Highest percentages were obtained at 76.6% and 101.8% for FeSO₄ and SnCl₂, respectively. These values suggest that either the HMF formed in the solutions of these salts are very stable, or the metal salts create alternative pathways for faster fructose conversion to this product.

Tin (II) chloride forms a three-coordinate dihydrate, with one water molecule coordinated on to the tin, and a second water molecule coordinated onto the first (Figure 3). It is widely used as a strong reducing agent in acid solutions and forms complexes with ligands [20,21]. It is also used in the Stephen reduction [22], whereby a nitrile is reduced to an aldehyde.

These properties suggest that the high yield of HMF from this salt in sulphuric acid could be due to the ability of tin (II) chloride molecule to remove a proton from a hydroxyl group in a fructose molecule, which can then be hydrolyzed to an aldehyde. The HMF is finally formed by the removal of two more water molecules from the fructose moiety by the tin (II) chloride dehydrate. This hypothetical theory therefore attribute the high HMF yield in the SnCl₂–H₂SO₄ catalyst system to be as a result of faster rate of HMF production relative to its removal as levulinic and formic acids. FeSO₄ which is also a reducing agent as well as some of the metal salts used for this study, are very likely to follow a similar reaction mechanism as that postulated.

D-fructose dehydration kinetics in SnCl₂-H₂SO₄ and FeSO₄-H₂SO₄ catalyst systems

The rates of HMF production at 313 K and 333 K in the SnCl₂ – H₂SO₄ and FeSO₄-H₂SO₄ catalyst systems are shown in figures 4-7. Catalytic amounts of SnCl₂ and FeSO₄ in sulphuric acid were used to study the effect of temperature and catalyst concentration on rate of conversion of fructose to HMF. In the presence of 10⁻³ M and 10⁻⁴ M concentrations of SnCl₂ and FeSO₄ at 313 K, rate of HMF production increased steadily over time in the SnCl₂ system (Figure 6) with best yield obtained at 10⁻⁴ M concentration of the salt. In the FeSO₄ system at this temperature, rate of HMF production at both concentrations of the salt increased steadily, with the blank solution (acid and fructose without metal salt), showing the best yield of HMF (Figure 5). This feature was even more distinct at 333 K. The reduction in the catalytic ability of FeSO₄ to convert fructose to HMF is likely to be due to the oxidation of Fe²⁺ to Fe³⁺ at higher temperatures, which can rapidly reduce the concentration of the Fe²⁺ ions which are the catalyst...
imparting ions of the salt. This reduces the concentration of the salt in solution, and as such catalytic property.

At 333 K, the catalytic property of the SnCl$_2$ system towards HMF production was further enhanced, but with the higher concentration of 10$^{-3}$ M giving the best rate of HMF formation (Figure 7). This increase in yield by a higher SnCl$_2$ concentration at an elevated temperature, which was not the case at 313 K (Figure 6) could hypothetically be stated to be the result of an apparent reduction in SnCl$_2$ concentration around the fructose molecule arising from temperature induced molecular motion, which makes the reduction action of the salt on the fructose molecule difficult. This phenomenon would especially be imminent when the salt concentration is low in the solution. At high SnCl$_2$ concentrations, the prevalence of its molecules around the fructose molecule could reduce this effect, leading to higher rates of HMF production. Figure 7 is a clear indication of the thermal stability of the SnCl$_2$–H$_2$SO$_4$ mixed catalyst system in the conversion of fructose to HMF.

**Conclusion**

The results from this study show that HMF production in protonic acids like sulphuric acid can be enhanced by synergizing its catalytic ability with those of soluble metal salts. The loss of HMF normally experienced by the use of protonic acid catalysts can be reduced appreciably by this synergy especially in the SnCl$_2$–H$_2$SO$_4$ mixed catalyst system.

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**References**


