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**PAPER**

# Fructose Conversion in the Presence of Sn(IV) Catalysts Exhibiting High Selectivity to Lactic Acid

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The catalytic performance of a series of Sn(IV)-based organometallic complexes in fructose conversion
10 was studied under several reaction conditions, and the conversion, yields, and selectivity measurements of
this transformation have been evaluated. The results were compared to those obtained from non-catalysed
reactions and those in the presence of a conventional catalyst (H2SO4). These organometallic Sn(IV)-
based catalysts demonstrated the ability to fully convert fructose into valuable chemicals. Under
particular reaction conditions, lactic acid is obtained in good yields and selectivity.

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## 1. Introduction

The difficulty involved in the exploitation of fossil fuel reserves, associated with its decreased availability and an increased focus on environmental concerns, has encouraged research to develop
20 technologies for renewable energy sources and chemical production. In this context, biomass is a promising alternative, and carbohydrates are a very important raw material, owing to their abundance, relatively low cost and versatility. They can be used to synthesize a range of valuable chemical platforms, such
25 as 5-hydroxymethyl-2-furfural (5-HMF) and lactic acid. [1-3] For example, lactic acid can be applied to several fields in the industry: food, pharmaceutical, textile, leather and the production of biodegradable polymers. This category of polymer is biodegradable, biocompatible and exhibits good thermoplastic
30 processability; one example of its use is in package manufacturing.[4]

Several studies describe the development of catalysts based on Lewis acid species to convert carbohydrates into lactic acid and other products at different reaction conditions. [2,5-10] Lately,
35 works involving catalysts based on tin have presented promising results applied to different substrates because these systems show high conversion yields and selectivity to formic acid or lactates and other products. [11-19]

Lewis acid $SnCl_4$ in 1-ethyl-3-methylimidazolium
40 tetrafluoroborate ([EMim]$BF_4$) was used to convert glucose as well as fructose, sucrose, inulin, cellobiose and starch into 5-HMF. For glucose, the 5-HMF yield reach 61% when the concentration of glucose in the [EMim]$BF_4$ was as high as 23 wt %. [11]

45  Using mesoporous MCM-41 materials and transition-metal-free oxides (Al, Ga and Sn), very good results were obtained. The system based on tin oxide with the ordered mesoporous material Sn-MCM-41 attained complete conversion of trioses after 6 h with high selectivity. The excellent catalytic performance of Sn-
50 MCM-41 is attributed to a combination of strong Lewis acid sites and mild Brønsted acid sites.[12]

A recyclable MCM-41 filled with a polyaromatic was employed to convert mono- and disaccharides to lactic acid and its alkyl esters. The system containing well-balanced
55 Lewis/Brønsted acidity was capable of converting hexoses, glucose, fructose, and sucrose into lactate, and, for example, yields of 45 % in methyl lactate in methanol at a slightly elevated reaction temperature were obtained.[13]

In methanol, Lewis acidic zeotypes (Ti-, Sn- and Zr-Beta)
60 catalyse the conversion of mono- and disaccharides into methyl lactate at 160 °C. Using Sn-Beta, sucrose was also converted into methyl lactate with a 68% yield. The heterogeneous system can be recovered by filtration and reused multiple times after calcination without any substantial change in the product
65 selectivity (HOLM et al., 2010). Sn-Beta zeolite was also applied to investigate the isomerization of glucose and fructose, and the studies attest a mechanistic demonstration of Sn-Beta acting as a Lewis acid in an aqueous medium.[14]

Sn-MFI and Sn-BEA zeolites were used to investigate
70 isomerization reactions of dihydroxyacetone (DHA), xylose, and glucose in water. With Sn-BEA, at 90 °C for 3.5 h, yields of

lactic acid, xylulose, and fructose were 54%, 24%, and 34%, respectively, at conversions of 93%, 81%, and 65%, respectively. Employing Sn-MFI, the yields were 65%, 19%, and 4%, respectively, at conversions of 98%, 40%, and 9%, respectively.

5 Textural properties are very important in the justification of the strong activity of Sn-BEA for all sugars tested.[15]

Different sulfated metal oxides ($SO_4^{2-}/Al_2O_3$, $SO_4^{2-}/SiO_2$, $SO_4^{2-}/TiO_2$, $SO_4^{2-}/Fe_2O_3$, $SO_4^{2-}/ZrO_2$, $SO_4^{2-}/Nb_2O_5$, $SO_4^{2-}/SnO_2$, $SO_4^{2-}/HfO_2$) were used as solid acid catalysts for the dehydration

10 of xylose to furfural under milder conditions. The $SO_4^{2-}/SnO_2$ show better catalytic performance, with a conversion and yield of 57% and 26%, respectively, with the possibility of reuse.[16]

Metal oxide nanoparticles ($SnO_2$ and $ZnO$) were employed in the hydrothermal conversion of cellulose, and ZnO was active at

15 300 °C and $SnO_2$ at 400 and 500 °C.[17]

$SnO_2$-$Co_3O_4$/C biochar catalyst was used in corncob hydrolysis to furfural, involving the saccharification of hemicellulose to monosaccharide, isomerization of xylose to xylulose and dehydration of xylulose to furfural. The maximum

20 yield of furfural was 30.0 % using 0.3 g of catalyst at 180 °C for 3.3 h.[18]

Our group evaluated the use of organometallic Sn(IV)-based catalysts on cellulose hydrolysis and compared their catalytic performance when the reaction occurred without the presence of

25 catalysts and when sulphuric acid was employed as catalyst at 150 and 190 °C for 1, 2, 4 and 8 h of reaction time. The Sn(IV)-based catalysts were more efficient at 190 °C, and a series of products was detected; however, the catalytic complex of Sn(IV) is selective to lactic acid, whereas the catalyst-free reactions and

30 those catalysed by sulphuric acid were more selective for glucose and 5-HMF.[19]

In terms of reaction mechanism based on species containing Lewis acid sites (such as Sn(IV) species), it is possible to envisage the coordination of cellulose oxygen species or

35 derivatives (glucose, fructose, etc.) to the metal centre, activating bonds for subsequent reactions.[19-21]

In the present work, a systematic study of fructose conversion was conducted in the presence of Sn(IV) complexes by comparing the conversion obtained from a non-catalysed reaction

40 to that obtained using $H_2SO_4$ as a catalyst to establish the pathway these catalytic systems follow for the production of chemicals from fructose; it was determined that systems while have no significant influence in the hydrolysis of cellulose, they do affect the degradation reactions from glucose.[19]

45

## 2. Methods

### 2.1. Materials

50 All chemicals were used as received without further purification. Butylstannoic acid, $(C_4H_9)SnO(OH)$ – BTA; di-n-butyl-oxo-stannane, $(C_4H_9)_2SnO$ – DBTO; and dibutyltin dilaurate, $(C_4H_9)_2Sn(C_{12}H_{23}O_2)_2$ – DBTDL; were obtained from Sigma-Aldrich. $H_2SO_4$ was obtained from Merck (analytical grade), and

55 fructose, glucose, 5-HMF, glyceraldehyde, pyruvaldehyde and organic acids (lactic, formic and acetic) were purchased from Sigma-Aldrich and Fluka.

### 2.2. Reaction and analytical procedures

60 All experiments were performed in a 100 mL batch stainless steel reactor coupled to a manometer, temperature probe a magnetic stirrer working at 1000 rpm. The reactor was filled with a fructose solution (0.48 g of fructose in 60 mL of deionized water), and, for some experiments, with catalyst ($2.69 \times 10^{-5}$

65 mol). The system was heated to the desired temperature, and the reaction was allowed to proceed for a specified time.

To detect and quantify the different products formed, the solution was passed through a 0.45 μm Millipore filter before injection onto a ProStar 210 HPLC system (Varian) equipped

70 with a MetaCarb 87H column (300 mm × 7.8 mm). HPLC was conducted at 50 °C with a flow rate of 0.70 mL.min$^{-1}$ using acidified water $5.10^{-3}$ mol.L$^{-1}$. The products detected (glucose, 5-HMF, glyceraldehyde, pyruvaldehyde and organic acids (lactic, formic and acetic)) were quantified using calibration curves

75 obtained from standards.

The fructose conversion was calculated using equation 1, where C (%) = fructose conversion; $C_o$ = fructose initial concentration (mol/L); and $C_f$ = fructose final concentration. The error in the fructose conversion was 5%.

80

$$C(\%) = \left( \frac{C_o - C_f}{C_o} \right) \times 100 \qquad (1)$$

The yields and selectivities were calculated according to equations 2 and 3, respectively, where $Y_i(\%)$ = product i yield

85 (for example, i = 5-HMF); $C_i$ = product i concentration (mol/L); $C_o$ = fructose initial concentration (mol/L); $S_i(\%)$ = product i selectivity; and $C_{i1}$, $C_{i2}$, $C_{i3}$, $C_{i4}$, $C_{i5}$ = concentration of various products formed (mol/L).

90

$$Y_i\ (\%)\ =\ \frac{ci}{co}\ \times 100 \qquad (2)$$

$$S_i(\%) = \left( \frac{C_i}{\left(C_i + C_{i1} + C_{i2} + C_{i3} + C_{i4} + C_{i5}\right)} \right) \times 100 \qquad (3)$$

95 The solutions were also analysed by a Shimadzu TOC – V CPH Total Organic Carbon (TOC) analyzer (650°C, $Pt/Al_2O_3$ catalyst, IR detector). The pH of solutions was measured using a pH Meter (Potentiometric Automatic Titrator AT-500N.

Solid materials were characterized using a TM3000 TableTop

100 SEM (DRX) with a magnification of 2000× and SwiftED 3000 X-Ray software (Oxford Instruments, USA).

To investigate the hypothesis of oxides or hybrid oxide formation as a hydrolysis product of Sn(IV) molecular species, spectra in the medium infrared region of Sn(IV) catalysts were

105 obtained, before and after a hydrolysis procedure (190 ºC and 4 h), in the presence or without fructose. For the BTA and DBTO, after filtration, the solid was dried at vacuum and 90 ºC during 24 h. For DBTDL (liquid material, but not miscible with water), after centrifugation, the catalyst was dried at vacuum and 90 ºC

110 during 24 h. The spectra of solid material (KBr pellets) were acquired employing a Varian 660 spectrometer with 40 scans at a nominal spectral resolution of 4 cm$^{-1}$.

115 ## 3. Results and Discussion

The purpose of this work was to investigate the conversion of fructose in the presence of Sn(IV) organometallic catalysts, with the aim of expanding the studies conducted using these complexes in the degradation of cellulose.[19] For this purpose, the results are presented in terms of conversion, yield and selectivity.

Figure 1 presents the fructose conversion results, obtained at 150 and 190 °C, using Sn(IV) catalysts and sulphuric acid (2.69 × $10^{-5}$ mol of catalyst in all cases), compared to reactions run without a catalyst.
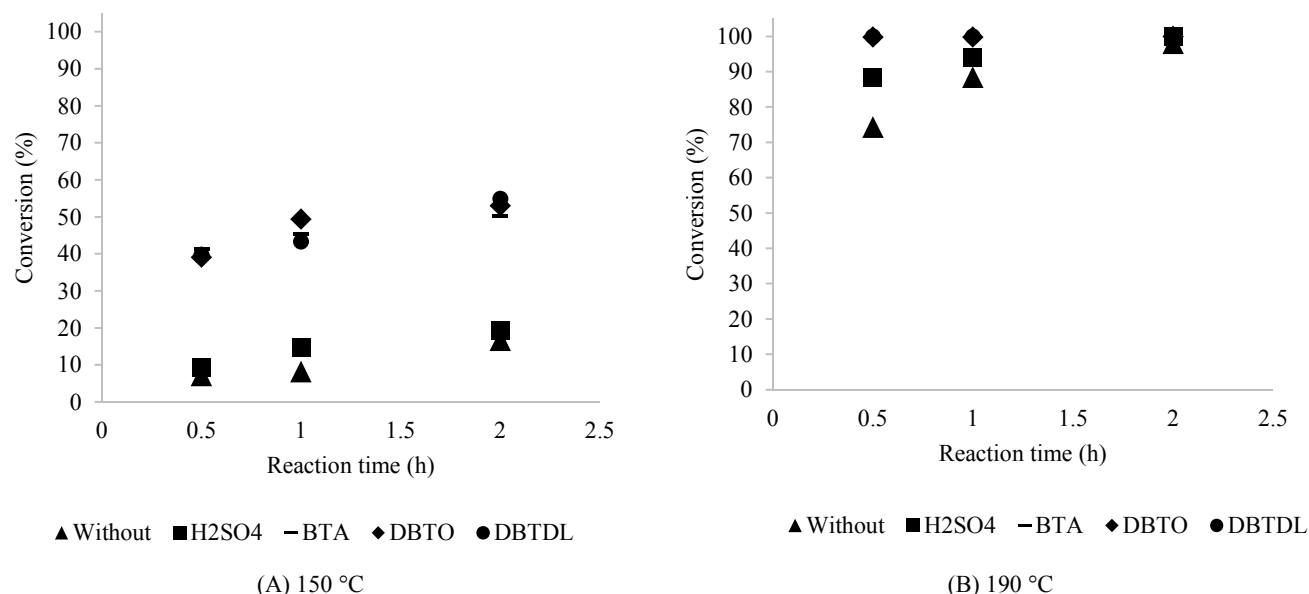


(A) 150 °C



(B) 190 °C

Figure 1. Fructose conversion, at 150 (A) and 190 °C (B), at several reaction times without catalyst using $H_2SO_4$ and Sn(IV) species

At 150 °C (Figure 1A) in the absence of catalyst or using sulphuric acid, fructose conversion is almost the same. With the augmentation of reaction time, a small conversion increase is detected, but it does not exceed 20 %. Nevertheless, in the presence of BTA, DBTO and DBTDL conversions of 40 % and 55 % were observed, respectively. However, at 190 °C, higher conversions than those observed at 150 °C were detected and, in the case of Sn(IV) catalysts, complete conversion was achieved at all reaction times, confirming the potential of these types of systems. This influence of temperature was also observed when these catalytic systems were employed in cellulose conversion. [19]

In the case of the DBTO, the conversion was investigated at 190 °C in a wider range of reaction times, and the results indicate that even at minor reaction times, 0.08 and 0.17 h, higher conversions are already attained (91 % and 99 %, respectively); from 0.25 h, total conversion was observed. Total conversion was also achieved when the reaction was investigated at 190 °C, duplicating the amount DBTO (5.38 × $10^{-5}$ mol), and at 210 °C, using 2.69 × $10^{-5}$ or 5.38 × $10^{-5}$ mol of DBTO.

Under the different conditions mentioned above and in the absence of catalyst, we detected the formation of glucose, 5-HMF, glyceraldehyde, pyruvaldehyde and organic acids (lactic, formic and acetic); Tables 1 and 2 show the product yields (%) at 150 and 190/210 °C, respectively.

As mentioned, at a temperature of 150 °C, low conversions were observed with or without catalyst (Figure 1A). In contrast, at 190 °C and 210 °C, superior conversions and yields were achieved. However, when the amount of catalyst and temperature (190 to 210 °C) are increased, the total yield is not significantly modified.

Figure 2 presents the selectivity results at 190 °C, in which the Sn(IV) catalysts exhibit total conversion (see Figure 1B).

In terms of chemicals formation, some considerations need to be taken into account: (i) first, fructose can isomerize to glucose or mannose (and vice versa), which explains the detection of glucose as a product of fructose conversion;[14,15,22] (ii) fructose undergoes dehydration to 5-HMF; by rehydrating HMF, it is possible to obtain levulinic and formic acids;[23] (iii) fructose can also be transformed into glyceraldehyde or dihydroxyacetone (isomers); both compounds (dihydroxyacetone and glyceraldehyde) can be dehydrated to yield pyruvaldehyde, which can be hydrated to lactic acid or reduced to hydroxyacetone;[23] and (iv) fructose can be cleaved via retro-aldol reaction, yielding glycolaldehyde and erythrose, which are cleaved to formic acid and acetic acid.[23] Parallel to these routes, insoluble products (polymeric materials as humins) can be formed.[23]

In this context, it is possible to observe (Figure 2) that without catalyst and in the presence of sulphuric acid, a high selectivity to 5-HMF is attained at 0.5 h. After this time, 5-HMF is transformed into other products, especially organic acids.

In the presence of Sn(IV) catalysts (BTA, DBTO and DBTDL), a high selectivity to lactic acid is observed (approximately 55 % for DBTO and DBTDL and 32 % for BTA),

followed, to a lesser extent, by the formation of formic and acetic acids.

Table 1. Soluble products identified from fructose conversion at 150°C (yield (%)), without catalyst and using $H_2SO_4$ and Sn(IV) species ($2.69 \times 10^{-5}$ mol)

| Catalyst | Time (h) | Glucos | 5-HMF | Formic aci | Glyceraldehyde | Dihydroxyacetone | Pyruvaldehyde | Lactic acid | Acetic acid | TOTAL Identified |
|---|---|---|---|---|---|---|---|---|---|---|
| Without | 0.5 | 0.5 | 1.5 | nd | 2.0 | nd | 3.0 | nd | nd | 7.0 |
| | 1 | 0.7 | 3.8 | nd | 1.7 | nd | 1.3 | nd | nd | 7.5 |
| | 2 | 1.5 | 7.4 | nd | 0.9 | nd | 0.9 | nd | nd | 10.7 |
| $H_2SO_4$ | 0.5 | 0.3 | 5.4 | nd | nd | nd | nd | nd | nd | 5.7 |
| | 1 | 0.4 | 7.2 | 1.1 | 2.2 | nd | nd | 0.2 | nd | 11.1 |
| | 2 | 0.4 | 11.7 | nd | 0.1 | nd | nd | 0.2 | nd | 12.4 |
| BTA | 0.5 | 1.0 | 2.2 | 3.6 | 8.2 | 9.1 | 12.5 | 2.6 | 4.4 | 43.6 |
| | 1 | 0.7 | 2.6 | 4.4 | 6.9 | 8.5 | 12.7 | 2.3 | 4.9 | 43.0 |
| | 2 | 1.1 | 5.4 | 6.8 | 2.2 | 10.2 | 5.2 | 4.9 | 7.4 | 43.2 |
| DBTDL | 0.5 | 0.6 | 1.1 | nd | 9.9 | 7.1 | 3.0 | 1.3 | 1.3 | 24.3 |
| | 1 | 1.0 | 2.6 | 3.6 | 5.9 | 10.3 | 4.1 | 4.1 | 2.9 | 34.5 |
| | 2 | 1.1 | 5.4 | 6.0 | 2.9 | 9.1 | 4.4 | 7.8 | 4.9 | 41.6 |
| DBTO | 0.5 | 1.0 | 2.0 | 2.8 | 7.3 | 10.1 | 9.2 | 2.8 | 1.8 | 37.0 |
| | 1 | 1.1 | 3.5 | 4.4 | 3.2 | 12.2 | 9.8 | 6.7 | 3.9 | 44.7 |
| | 2 | 1.0 | 5.2 | 4.4 | 2.1 | 6.7 | 3.5 | 4.9 | 3.9 | 31.7 |

nd = no detected

Table 2. Soluble products identified from fructose conversion at 190°C or 210 °C (yield (%)), without catalyst and using $H_2SO_4$ and Sn(IV) species ($2.69 \times 10^{-5}$ mol or $5.38 \times 10^{-5}$ mol)

| Catalyst | Temp. (°C) | [Catalyst] ($.10^{-5}$ mol)] | Time (h) | Glucose | 5-HMF | Levulinic acid | Formic acid | Glyceraldehyde | Dihydroxyacetone | Pyruvaldehyde | Lactic acid | Acetic acid | TOTAL Identified |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Without | 190 | 0 | 0.5 | 0.8 | 38.9 | 0.6 | nd | 0.4 | nd | 1.0 | 1.5 | 2.3 | 45.6 |
| | 210 | 0 | 0.5 | 0.7 | 30.2 | 1.9 | 6.4 | nd | nd | 0.5 | 6.6 | 3.4 | 49.9 |
| | 190 | 0 | 1 | 1.1 | 41.7 | 2.7 | 6.8 | nd | nd | 1.2 | 3.9 | 2.9 | 60.3 |
| | 190 | 0 | 2 | 0.8 | 43.0 | 3.9 | 8.5 | nd | nd | nd | 3.3 | 2.3 | 61.8 |
| $H_2SO_4$ | 190 | 2.69 | 0.5 | 0.7 | 58.9 | 3.9 | 7.6 | 0.4 | 0.5 | 0.7 | 1.5 | 1.8 | 76.1 |
| | | | 1 | 0.9 | 53.3 | 6.0 | 10.1 | 0.4 | 0.7 | 0.7 | 1.8 | 2.3 | 76.3 |
| | | | 2 | 0.5 | 36.6 | 13.0 | 17.4 | 0.2 | 0.5 | 0.6 | 1.3 | 2.3 | 72.4 |
| BTA | 190 | 2.69 | 0.5 | 0.6 | 8.7 | 2.1 | 13.8 | nd | nd | 2.2 | 20.1 | 15.3 | 62.9 |
| | | | 1 | 0.6 | 7.5 | 2.0 | 13.4 | nd | nd | 2.0 | 20.7 | 15.8 | 61.9 |
| | | | 2 | 0.6 | 8.4 | 3.3 | 13.4 | nd | nd | 1.3 | 16.4 | 13.5 | 56.9 |
| DBTDL | 190 | 2.69 | 0.5 | 0.7 | 6.9 | 1.8 | 15.0 | nd | nd | 2.8 | 46.8 | 15.6 | 89.6 |
| | | | 1 | 0.6 | 6.1 | 2.2 | 14.2 | nd | nd | 2.3 | 48.7 | 15.3 | 89.3 |
| | | | 2 | 0.3 | 3.7 | 2.3 | 13.0 | nd | nd | 2.2 | 46.2 | 14.6 | 82.2 |
| DBTO | 190 | 2.69 | 0.08 | 1.2 | 6.7 | 0.8 | 0.0 | 12.1 | 20.7 | nd | 18.6 | 6.6 | 66.6 |
| | | | 0.17 | 1.1 | 5.3 | nd | 0.0 | 9.2 | 12.4 | 2.4 | 31.1 | 10.2 | 71.9 |
| | | | 0.25 | 0.9 | 5.9 | 0.9 | 11.2 | 2.3 | 2.8 | 2.1 | 47.4 | 11.0 | 84.4 |
| | | | 0.5 | 1.0 | 7.8 | 1.4 | 11.6 | 2.0 | 1.7 | 2.1 | 47.2 | 12.3 | 87.1 |
| | 190 | 5.38 | 0.5 | 0.6 | 5.2 | 1.9 | 9.7 | nd | nd | 0.3 | 55.2 | 11.8 | 84.6 |
| | 210 | 2.69 | 0.5 | nd | 3.8 | 1.8 | 10.4 | nd | nd | nd | 53.0 | 10.3 | 79.2 |
| | 210 | 5.38 | 0.5 | nd | 3.3 | 1.8 | 11.7 | nd | nd | nd | 63.0 | 12.0 | 91.8 |
| | 190 | 2.69 | 1 | 0.5 | 5.8 | 2.2 | 13.7 | nd | nd | 2.3 | 47.8 | 14.1 | 86.3 |
| | | | 2 | 0.4 | 3.7 | 2.3 | 13.2 | nd | nd | 2.3 | 50.7 | 14.9 | 87.5 |
| | | | 3 | nd | 2.8 | 2.3 | 13.7 | nd | nd | 2.3 | 46.2 | 13.3 | 80.6 |

nd = no detected

**4** *Catal. Sci. Technol.*, [year], **[vol]**, 00–00

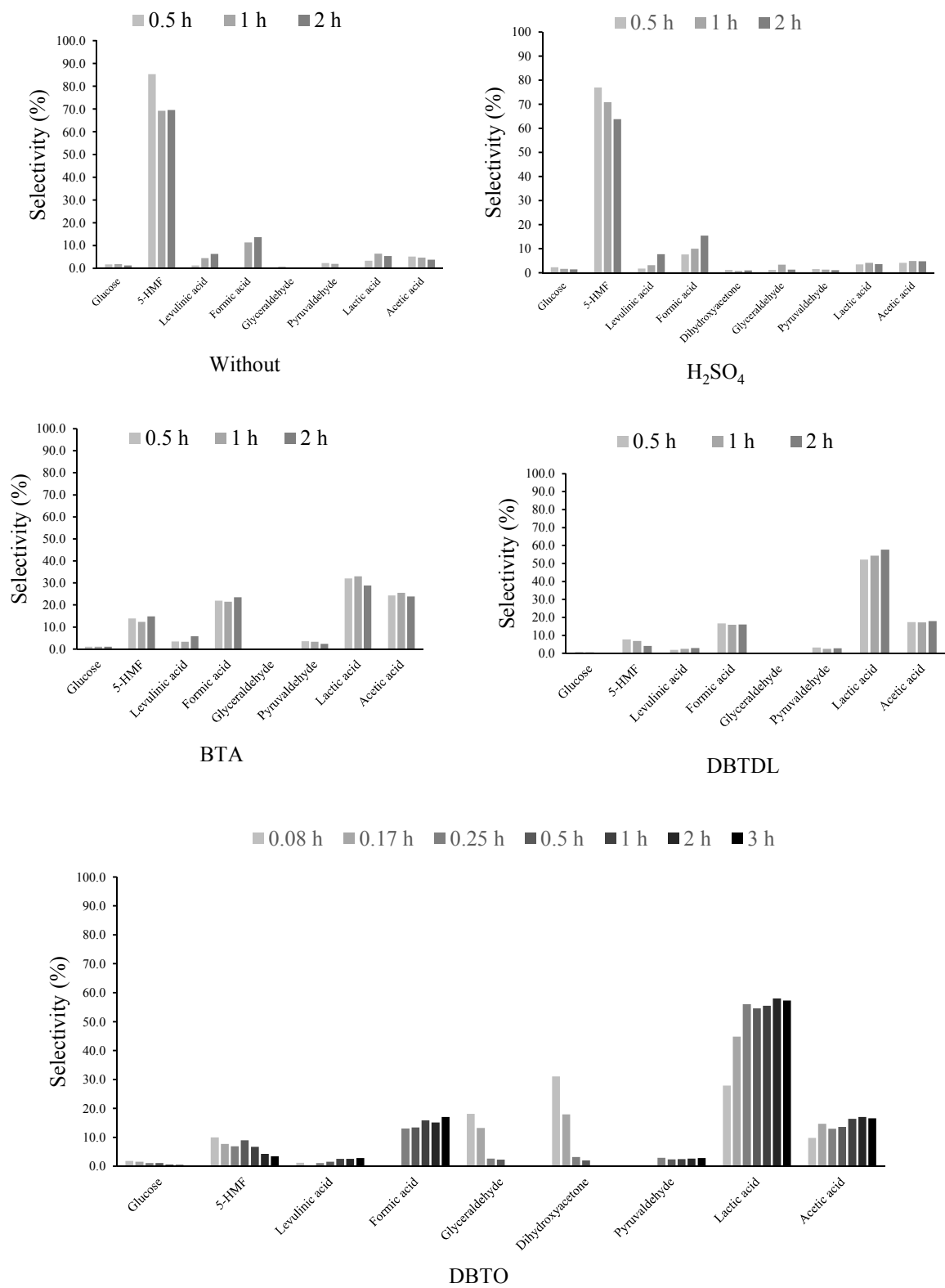This journal is © The Royal Society of Chemistry [year]

Figure 2. Selectivity to soluble products identified from fructose conversion at 190°C, without catalyst and using $H_2SO_4$ and Sn(IV) species ($2.69 \times 10^{-5}$ mol)

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It is important to note that glyceraldehyde, dyhydroxicetone and pyruvaldehyde are detected in significant amounts at 150 °C, and this quantity is reduced at 190 °C. These aldehydes are formed as intermediates to lactic acid formation at lower temperatures[23] and, with increasing temperature, they are transformed into lactic acid. To verify this hypothesis, a reaction was conducted at 110 °C for 2 h using BTA as a catalyst. As a result, 20 % of fructose was converted, and the selectivity was of 24.5 % of pyruvaldehyde, 55.9 % of glyceraldehyde and 19.6 % of dyhydroxicetone. It is important to highlight that just traces of glucose were observed and no lactic acid formation was detected. Despite the lower values of conversion obtained at 110 °C, it is possible confirm that these complexes have a strong tendency to drive the fructose to degrade in this way because the lactic acid was formed at the highest yield at 190 ºC.

Figure 3 presents the selectivity results when the amount of catalyst DBTO and temperature are increased, at 0.5 hour (see yields at Table 2). It is possible to observe no significant modification in terms of selectivity.
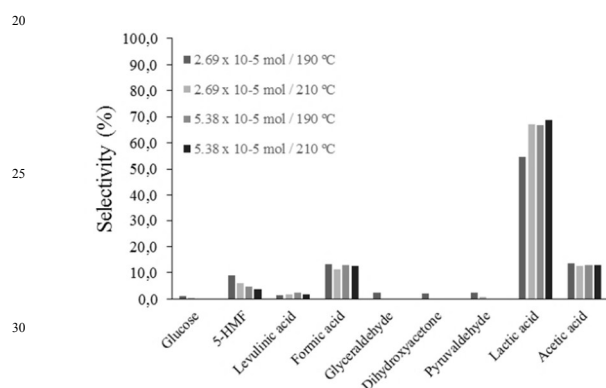


Figure 3. Selectivity to soluble products identified from fructose conversion at 190°C or 210 °C using DBTO ($2.69 \times 10^{-5}$ mol or $5.38 \times 10^{-5}$ mol) at 0.5 h.

The Sn(IV) catalysts investigated here exhibit great potential and performed similarly in terms of conversion of fructose as well as in yield and selectivity in relation to the products formed. Analogous behaviour has been observed in study of cellulose conversion catalysed by these three systems. The hypothesis to justify this behaviour is based on the possibility of oxide or hybrid oxide formation as a hydrolysis product from the Sn(IV) species.[19,24] The higher selectivity to lactic acid observed in the presence of DBTDL and DBTO catalysts, relative to BTA, can be explained by the same number and type of ligands (alkyl and carboxylate) in the molecular catalyst structure of DBTDL and DBTO, leading to species based on similar oxide or hybrid oxide.[19]

To investigate the hypothesis of oxides or hybrid oxide formation as a hydrolysis product of Sn(IV) molecular species, a study of these catalysts was performed in the medium infrared region. For this, spectra of Sn(IV) catalysts were obtained before and after a hydrolysis procedure, as described in the methodology, without the use of an organic substrate (fructose). Indeed, it is verified that the absorption bands related to the presence of organic groups in the structure of the complexes remain in the spectra obtained after the catalysts were subjected to the hydrolysis reaction conditions. Furthermore, increased intensity or the appearance of a broad band in the region between 670 and 550 cm$^{-1}$ confirms the formation of metal oxide or hybrid metal oxide ($\nu_s$ O-Sn-O and $\nu_{as}$ O-Sn-O). (see spectra in supplementary information (Fig. S1), in comparison to SnO$_2$).

In addition, the use of SnO$_2$ as a catalyst was investigated at 190 °C. At reaction times of 0.5, 1 and 2 hours the fructose conversions were 73, 88 and 98 %, respectively. Under the same reaction conditions, these results are comparable to observed for the H$_2$SO$_4$ (see Figure 1B) and, also the product formation profiles were similar to observed when H$_2$SO$_4$ was used, showing more selectivity to HMF formation (see supplementary informations – Table S1 and Fig. S2). This trend suggests the importance of the presence of alkyl substituents in these oxide species, formed during the reaction process from Sn(IV) molecular catalysts, acting to modulate the Lewis acidity of the metal center.

The evolution on pH was measured (Table 3) and, at all conditions, the pH drops to ca. of 3.0. In the presence of DBTO, after 0.25 h of reaction there are no significant changes on pH, conversion, yields and selectivities. Thus, it is possible to infer that this catalytic system is very efficient at short reaction times and the structural changes onto catalyst have occurred at this time (Figure S1 in supplementary informations).

Table 3. Evolution of pH for fructose conversion at 190°C, without catalyst and using H$_2$SO$_4$ and Sn(IV) species ($2.69 \times 10^{-5}$ mol)

| Catalyst | Reaction time (h) | pH before reaction | pH after reaction |
|---|---|---|---|
| Without | 0.5 | 6.7 | 3.0 |
| H$_2$SO$_4$ | 0.5 | 3.4 | 2.9 |
| SnO$_2$ | 0.5 | 6.7 | 3.2 |
| DBTO | 0.08 | | 2.9 |
| | 0.25 | | 2.8 |
| | 0.5 | 6.3 | 3.2 |
| | 2 | | 3.0 |
| | 3 | | 3.0 |

It is important to mention that during the degradation of carbohydrates, such as cellulose, sucrose, or fructose, the production of soluble and insoluble organic products, such as polymeric materials or humins, may occur. Some variables such as high temperatures, long reaction times or even the nature of the catalyst may lead to the formation of such products in large or small amounts. [25,26]

In this study, during the degradation of fructose at 190 °C, regardless of the use of a catalyst, it was found that at the end of the reaction, the reaction mixture had blurred to a dark brown colour, and, after filtration, a solid material was retained in the filter, and the solution exhibits a transparent yellow colour. For the reaction with DBTO at 190 °C for 2 h, the solid obtained after filtration was analysed by scanning electron microscopy (SEM) and X-ray spectroscopy for energy dispersion (EDX) to provide a more detailed study with the objective of investigating the nature of the insoluble materials. Figure 4 presents the image and SEM and EDX micrographs obtained of the solid material. In the case of micrographs, the quantitative EDX data were captured at different regions to determine the presence of carbon, oxygen and tin.

From these results, it is possible to confirm the presence of catalyst residues and significant amounts of carbon and oxygen in the solid, which cannot be related only to the organic residues of catalysts, confirming the formation of organic insoluble materials.

In addition, the filtered solution of some samples was studied by the determination of total organic carbon (TOC). Initially, a TOC analysis of the fructose in water was performed, and the obtained value (3048 ppm) was used as a reference for conversion calculations (Table 4).



A



B
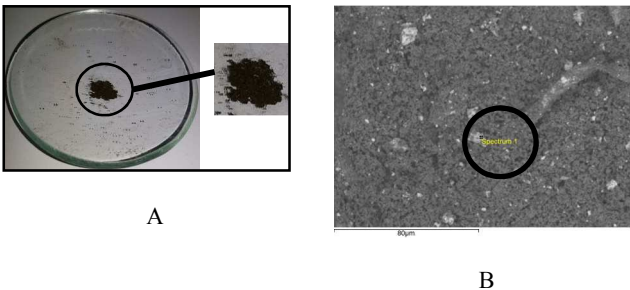
| Element↓ | Spectrum 1 (wt %) |
|---|---|
| Carbon | 51 |
| Oxygen | 15 |
| Tin | 34 |

Figure 4. Image obtained of insoluble products after filtration (A), and micrography from MEV/EDX (B), using DBTO at 190 °C for 2 h.

Table 4. The results of TOC (%) for reactions run using DBTO ($2.69 \times 10^{-5}$ mol or $5.38 \times 10^{-5}$ mol) and without catalyst at 190 °C or 210 °C for several reaction times

| Catalyst | Temp. (°C) | [Catalyst] ($.10^{-5}$ mol) | Time (h) | TOC[a] (ppm) | TOC (soluble products)[b] (%) | TOC (insoluble products)[c] (%) | HPLC conversion[d] |
|---|---|---|---|---|---|---|---|
| Without | 190 | 0 | 0.5 | 2758 | 90.5 | 9.5 | 72 |
| | 210 | | 0.5 | 2241 | 73.5 | 26.5 | 100 |
| | 190 | | 1 | 2524 | 82.8 | 17.2 | 94 |
| | 190 | | 2 | 2287 | 75.0 | 25.0 | 99 |
| DBTO | 190 | 2.69 | 0.08 | 2517 | 82.6 | 17.4 | 91 |
| | | | 0.17 | 2417 | 79.3 | 20.7 | 98 |
| | | | 0.25 | 2237 | 73.4 | 26.6 | 100 |
| | 190 | 2.69 | 0.5 | 2162 | 71.0 | 29.0 | 100 |
| | 190 | 5.38 | 0.5 | 2245 | 73.7 | 26.3 | 100 |
| | 210 | 2.69 | 0.5 | 2146 | 70.4 | 29.6 | 100 |
| | 190 | 2.69 | 1 | 2041 | 67.0 | 33.0 | 100 |
| | | | 2 | 1917 | 63.0 | 37.0 | 100 |
| | | | 3 | 1818 | 59.6 | 40.4 | 100 |

a Determined in the filtered solution after reaction;
b TOC conversion considering soluble products, calculated by the ratio of TOC values after reaction and before reaction (3048 ppm);
c TOC conversion considering insoluble products (obtained by subtraction of soluble products), calculated by ratio of TOC values after reaction and before reaction (3048 ppm);
d Note that for catalyst-free reactions, no full conversion was observed by HPLC; in these reaction conditions, a small part of carbon in the filtrate is due to the presence of fructose.

At 190 °C, with increasing time, there is a decrease in the TOC amount calculated for the soluble products in both reactions

(without catalyst and those performed using DBTO). This trend suggests the increasing amount of insoluble products, which is supported by the analysis of MEV/EDX discussed above. The percentage of insoluble materials probably corresponds to the
5 solid retained in the filter paper (Figure 4).

In the presence of DBTO, doubling the catalyst amount or increasing the temperature (190 to 210 °C) produces no influence observed in the results of TOC, as discussed in terms of yields and selectivity. An evaluation of these results suggests the
10 formation of compounds such as polymers and humin, [25,26] as visual formation of insoluble material occurs, and the results from MEV/EDX analysis indicates a significant presence of organic material, which is not justified by the levels of catalyst employed.

15

## 4. Conclusions

Sn(IV) organometallic catalysts are able to convert fructose into valuable chemical supplies. By comparing the Sn(IV) catalysts tested, the fructose conversion and product formation profiles
20 were found to be quite similar, suggesting that the same type of active species is formed in the reaction medium. The Sn(IV) catalysts are selective to lactic acid, suggesting that these systems follow the route by which fructose can be transformed into glyceraldehyde or dihydroxyacetone (isomers), which can be
25 dehydrated to pyruvaldehyde, which can be hydrated to lactic acid.

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