## **Supplementary Information**

## IS 1. Method of synthesis and characterization of catalysts Na-Mag, S(x)Sn-Mag and C(x)Sn-Mag

In our previous study,<sup>25</sup> briefly the methodology of synthesis of the materials under study consisted of a reaction mixture of a silica source (Ludox® HS-40, Aldrich), a mineralizing agent (NaOH, Aldrich,  $\geq$ 98.0 %), a source of Sn (Na<sub>2</sub>SnO<sub>3</sub>, Aldrich, 42–45 % of SnO<sub>2</sub> or SnCl<sub>4</sub>·5H<sub>2</sub>O, Aldrich,  $\geq$ 98.0 %) and deionized water. The gels formed were placed in reactors and heated to 150 °C for 72 h, under autogenous pressure. Finally, the materials were characterized by a range of characterization techniques: XRD, N<sub>2</sub> adsorption, TG/DTG, TPD-NH<sub>3</sub>, TPR-H<sub>2</sub>, ICP-OES, FTIR, Raman, DRS (UV-Vis), SEM and TEM. In this study the techniques of Raman spectroscopy and diffuse reflectance spectroscopy in the ultraviolet (200-380 nm) region and visible (380-800 nm) (UV-Vis) were thoroughly analyzed in order to understand the behavior of these catalysts in the fructose conversion.

Raman spectroscopy was performed with a Horiba Scientific Jobin Yvon Xplora instrument (Kyoto, Japan) using a 532 nm laser and 100× objective. The spectra were obtained with 16 acquisitions in 120 s using a spectrometer grid of 600 nm<sup>-1</sup> lines centered at 2000 cm<sup>-1</sup>. UV–Vis diffuse reflectance (DRS) spectra were obtained using a Shimadzu UV-2600 spectrometer with a slit of 5 nm and acquisition range of 0.5 nm. Optical band gaps were estimated using the Tauc ratio,  $(\alpha h \nu)^2$  versus h $\nu$  in eV, where  $\alpha$  is the absorption coefficient, h is the Planck constant (4.135 × 10<sup>-15</sup> eV s), and  $\nu$  is the frequency corresponding to the speed of light divided by wavelength.<sup>41</sup>

## IS 2. Catalytic tests

Catalytic conversion tests of fructose (Aldrich,  $\geq 99$  %) were conducted in glass microreactors, with a capacity of 4 mL each, in an oil bath, controlled temperatures (130, 150 and 170°C) and constant time (4h) in order to evaluate the effect of temperature on the conversion. Thus, in the thermal conversion, 2.0 g of an aqueous solution composed of fructose (0.016 g) and deionized water (2 mL) was added to the microreactors; in catalytic conversions, in addition to 2.0 g of

the aqueous solution described above, a quantity of catalyst (2.69.10<sup>-5</sup> mols) was also added to the microreactors, based on the procedures of Santos et al. (2015).<sup>26</sup> Therefore, the microreactors were removed and the reaction mixture was filtered for further analysis of the products formed by HPLC (Shimadzu, HPLC-RID-20A), at 55°C, injection volume of 20  $\mu$ L, sulfuric acid solution 0.005 mol L<sup>-1</sup> as mobile phase, flow at 0.7 mL min<sup>-1</sup> and analysis time of 30 min. Conversion, yield and selectivity results were obtained by equations 1, 2 and 3, respectively. The error in the conversion of fructose was 5 %.

$$C_{frutose(\%)} = ([]_i - []_f/[]_i) \times 100 \qquad 1$$
C: fructose conversion.  

$$[]_i : \text{ initial concentration of fructose (mol L^{-1}).}$$

$$[]_f : \text{ final concentration of fructose (mol L^{-1}).}$$

$$R_{P(\%)} = ([]_P/[]_i) \times 100 \qquad 2$$
R : yield of determined product P (%).  

$$[]_P : \text{ product P concentration (mol L^{-1}).}$$

 $[]_{i:\text{ initial concentration of fructose (mol L<sup>-1</sup>).}$ 

 $S_{P(\%)} = ([]_P/([]_P + ... + []_{Pn})) \times 100$ 3

S : selectivity of determined product P (%).

 $[]_P$ : product P concentration (mol L<sup>-1</sup>).

 $[]_{Pn}$  concentration of another formed products (mol L<sup>-1</sup>).

Fntry	Samplas	T(°C)	Selectivity (%)								
	Samples	I ( C) -	G	HMF	GLA	PA	LA	HA	AA	FA	
1	Without catalyst		9	24	9	29	-	13	-	8	
2	Na-Mag	130	43	15	5	13	-	11	4	7	
3	S(0.6)Sn-Mag		29	5	9	26	10	7	10	5	
4	S(1.2)Sn-Mag		30	6	9	23	6	8	10	7	
5	S(2.6)Sn-Mag		32	9	6	23	5	10	6	9	
6	C(0.6)Sn-Mag		31	5	9	23	9	9	9	5	
7	C(1.5)Sn-Mag		32	7	6	25	5	9	7	8	
8	C(2.9)Sn-Mag		32	7	6	30	3	9	7	7	
9	Without catalyst		1	65	4	25	-			4	
10	Na-Mag		26	18	12	29	-	7	2	6	
11	S(0.6)Sn-Mag		21	5	10	29	14	9	6	6	
12	S(1.2)Sn-Mag	150	22	13	8	20	14	11	6	5	
13	S(2.6)Sn-Mag	150	20	14	12	12	22	8	6	6	
14	C(0.6)Sn-Mag		21	6	11	26	16	9	6	6	
15	C(1.5)Sn-Mag		30	11	8	20	14	7	6	6	
16	C(2.9)Sn-Mag		26	20	10	8	20	7	3	5	
17	Without catalyst		2	62	4	14	5	7	5	3	
18	Na-Mag		12	39	6	14	8	10	8	4	
19	S(0.6)Sn-Mag		11	8	9	24	16	12	16	6	
20	S(1.2)Sn-Mag	170	14	16	8	11	17	11	18	5	
21	S(2.6)Sn-Mag	170	10	27	7	14	11	9	18	5	
22	C(0.6)Sn-Mag		12	10	8	23	14	12	17	5	
23	C(1.5)Sn-Mag		13	23	7	15	11	10	16	5	
24	C(2.9)Sn-Mag		12	29	6	24	4	8	12	4	

**Table S1** – Selectivity (%) to soluble products identified in the thermal and catalytic conversion of fructose into water at 130, 150 and 170  $^{\circ}$ C, at 4 h of reaction.

G = glucose, GLA = glyceraldehyde, PA = pyruvaldehyde, LA = latic acid, HA = hydroxyacetone, AA = acetic acid, FA = formic acid.

Entry	Catalyst	T (°C)	G	5-HMF	GLA	PA	AL	HA	AA	A	Conversion (%)	Total identified
1	Without catalyst	130	2	4	1,5	7	-	2	-	1	35	18
2	Na-Mag		11	4	1	3	-	3	1	2	43	25
3	S(0,6)Sn-Mag		18	3	5,6	16	6	5	6	3	74	63
4	S(1,2)Sn-Mag		16	3	5	12	3	4	6	4	64	53
5	S(2,6)Sn-Mag		13	4	3	9	2	4	2	4	52	41
6	C(0,6)Sn-Mag		19	3	6	14	6	6	6	3	70	63
7	C(1,5)Sn-Mag		16	4	3	12	2	4	4	4	58	49
8	C(2,9)Sn-Mag		15	4	3	_14	1	_4	3	3	56	47
9	Without catalyst		0,2	24	1,6	9	-	-	-	2	49	37
10	Na-Mag		12	8	5	13	-	3	1	3	64	45
11	S(0,6)Sn-Mag	150	16	4	7	21	11	7	4	4	85	74
12	S(1,2)Sn-Mag		12	7	5	11	8	6	3	3	75	55
13	S(2,6)Sn-Mag		10	7	6	6	12	4	3	3	73	51
14	C(0,6)Sn-Mag		14	4	6	16	10	6	1	4	86	61
15	C(1,5)Sn-Mag		14	6	4	10	7	3	3	3	72	50
_16	C(2,9)Sn-Mag		11	9	5	4	8	_3	4	2	61	46
17	Without catalyst	170	1	42	2,5	9	3	4	3	$^{-2}$	88	67
18	Na-Mag		7	24	3	8	5	6	5	2	86	60
19	S(0,6)Sn-Mag		8	5	6,1	17	11	9	11	4	94	71
20	S(1,2)Sn-Mag		10	11	5	8	12	8	13	4	92	71
21	S(2,6)Sn-Mag		7	18	4	10	7	6	12	3	88	67
22	C(0,6)Sn-Mag		8	7	6	16	10	8	11	4	94	70
23	C(1,5)Sn-Mag		9	16	5	10	8	7	11	3	91	69
24	C(2,9)Sn-Mag		9	21	4	18	3	6	9	3	86	73

Table S2. Yield (%) of soluble products identified in the thermal and catalytic conversion of fructose into water at 130, 150 and 170 °C, at 4 h of reaction.

G = glucose, GLA = glyceraldehyde, PA = pyruvaldehyde, LA = latic acid, HA = hydroxyacetone, AA = acetic acid, FA = formic acid.



Figure S1: Yield values for products from different pathways of fructose conversion.