# ARTICLE IN PRESS

Molecular Catalysis xxx (xxxx) xxx-xxx



Contents lists available at ScienceDirect

# Molecular Catalysis



journal homepage: www.elsevier.com/locate/mcat

Editor's choice paper

# Dehydration of fructose to HMF in presence of $(H_3O)_xSb_xTe_{(2-x)}O_6$ (x = 1, 1.1, 1.25) in $H_2O$ -MIBK

Sergio F. Mayer<sup>a</sup>, H. Falcón<sup>b,\*</sup>, R. Dipaola<sup>c</sup>, P. Ribota<sup>c</sup>, L. Moyano<sup>d</sup>, S. Morales-delaRosa<sup>e</sup>, R. Mariscal<sup>e</sup>, J.M. Campos-Martín<sup>e</sup>, J.A. Alonso<sup>f</sup>, J.L.G. Fierro<sup>e</sup>

<sup>a</sup> NANOTEC (Centro de Investigación en Nanociencia y Nanotecnología), Universidad Tecnológica Nacional-Facultad Regional Córdoba, Córdoba, Argentina

<sup>b</sup> CITeQ (Centro de Investigación y Tecnología Química), Universidad Tecnológica Nacional-Facultad Regional Córdoba, Córdoba, Argentina

<sup>c</sup> Instituto Superior de Investigación, Desarrollo y Servicios en Alimentos (ISIDSA)-UNC, Córdoba, Argentina

<sup>d</sup> INFIQC, Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Ciudad Universitaria, 5016 Córdoba, Argentina

e Grupo de Energía y Química Sostenible (EQS), Instituto de Catálisis y Petroleoquímica, CSIC, Marie Curie, 2 Cantoblanco, 28049 Madrid, Spain

<sup>f</sup> Instituto de Ciencia de Materiales de Madrid, CSIC, Cantoblanco, E-28049 Madrid, Spain

#### ARTICLE INFO

Keywords: Biomass Biofuels Fructose 5-Hydroxymethyl-furfural (HMF) Pyrochlore

#### ABSTRACT

The pyrochlores  $(H_3O)_xSb_xTe_{(2-x)}O_6$  (x = 1, 1.1 and 1.25) obtained by ion exchange from  $K_xSb_xTe_{(2-x)}O_6$  oxides were used as catalysts for the conversion of fructose to 5-hydroxymethylfurfural (HMF) in  $H_2O$ /Methyl isobutyl ketone (MIBK). The structure of the resulting compounds as well as the location of the  $H_3O^+$  units inside the three-dimensional network, were determined by XRD from powder samples. The effect of factors such as reaction time and temperature on the formation of HMF was studied. A fructose conversion of 99% and a yield of 59% were achieved after 120 min of reaction time and at 150 °C temperature. The percentage of substitution of the cations Sb and Te in the position B of the pyrochlore was determinant to achieve the maximum incorporation of  $H_3O^+$  ions in the pyrochlore structure, which allowed to correlate the density of acidic sites present in the materials and their catalytic activity.

### 1. Introduction

The search for alternatives to fossil fuels has received great interest, as a measure that tends to provide solutions to energy crisis due to the growing demand for transportation fuels that is accelerating the fall of proven oil reserves. In addition, the emission of greenhouse gases produced by combustion engines has attracted increasing interest in the protection of the environment faced with the threat of Global Warming, which makes it imperative finding alternative renewable sources such as biomass [1,2].

Fructose and glucose represent 75% of carbohydrates in the biomass that are renewed annually. For example, acid hydrolysis of polysaccharides can be combined with the dehydration of monosaccharides to obtain platform compounds. Dumesic et al. [3] have described and detailed a variety of chemical processes that can be applied to the transformation of biomass, among which it stand out as primary stages the hydrolysis and dehydration of carbohydrates, as well as other secondary reactions. Various chemicals can be obtained, among which are the furan compounds (for example, 5-hydroxymethylfurfural (HMF), 5ethoxymethylfurfural (EMF), furfural, furfuryl alcohol, Dimethylfuran (DMF), etc.), representing a very important group for the economy of a biorefinery [4–8].

The production of 5-hydroxymethylfurfural (HMF), through the dehydration reaction of sugars, is one of the most important approaches to transform biomass into useful chemicals [9]. HMF is considered an important precursor for the production of high-value polymers, such as polyurethanes and polyamides, as well as biofuels [10].

HMF is produced by the dehydration of hexoses like glucose and fructose. The general agreement is that reaction happens through fructose. Although evidence exists supporting both the open-chain and the cyclic fructofuransyl intermediate pathways [11,12], it is clear that the reaction intermediates and the HMF product degrade by means of processes such as fragmentation, condensation, rehydration, reversion, and/or additional dehydration reactions.

According to van Putten et. Al [13], a proposed pathway of cyclic dehydration of fructose and later rehydration to levulinic acid, formic acid and an alternate way of formation of side-product Humins is presented below (Fig. 1).

E-mail address: hfalcon@frc.utn.edu.ar (H. Falcón).

https://doi.org/10.1016/j.mcat.2018.12.025

Received 6 June 2018; Received in revised form 3 December 2018; Accepted 29 December 2018 2468-8231/ © 2019 Elsevier B.V. All rights reserved.

<sup>\*</sup> Corresponding author. Present address: Centro de Investigación y Tecnología Química (CITeQ), Universidad Tecnológica Nacional-Facultad Regional Córdoba, X5016ZAA Córdoba, Argentina.

# ARTICLE IN PRESS



Fig. 1. Reaction pathway of cyclic dehydration of fructose and later rehydration.

Van Dam et al. [14] found that the reactions performed in the aqueous solution provoke the degradation of 5-HMF and that its polymerization occurs in aqueous media, through removing three water molecules of hexoses in the acid-catalyzed dehydration reaction. In the aqueous system, 5-HMF enters into a consecutive reaction sequence taking up two molecules of water, and forms levulinic and formic acid as semifinal products [15].

The dehydration of sugars by heterogeneous catalysis has fostered the search for suitable catalysts for these processes, being of vital importance because they are more secure and environmentally more sustainable according to the principles of green chemistry. These include heteropoly acids (HPA), the importance of which lies in their unique properties such as well-defined structure, the possibility of modifying their acidity by changing their chemical composition, the ability to accept and release electrons and their high proton mobility [16]. Davis et al. [17] described the combined use of Zeolite Sn-Beta and acidic catalysts, in a biphasic reactor system to synthesize HMF from carbohydrates such as glucose, cellobiose, and also starch, with conversion and selectivity greater than 70% using a process in "one -pot". The key to the process lies in the ability of the Sn-Beta zeolite to isomerize glucose into fructose. On the other hand, sulfated ZrO<sub>2</sub> [18] has also been used in the dehydration reaction of sugars. Other catalysts used for this purpose include, resins [19] and metal oxides such as  $Ta_2O_5$  [20] and  $Nb_2O_5$  [21]. On the other hand, the mesoporous substrates AlSBA-15, allow to incorporate different proportions of Al in the structure, giving rise to a good linear correlation between a moderately strong acidity and the selectivity to HMF [22,23]. Jain et al. [24] also proposed the transformation of carbohydrates into HMF through mesoporous zirconium phosphate (ZrP). Due to the high surface area, this catalyst exhibited excellent catalytic performance for hexose transformation to HMF with high yield. On the other hand, titanium oxides represent another important group of acid catalysts. Porous TiO<sub>2</sub>, with a high surface area and adequate morphology of the particles, can be an efficient catalyst in this reaction [25].

Multiple reaction systems have been reported for the production of HMF using different solvents.  $ZrO_2$  and  $TiO_2$  catalyzed the conversion of p-fructose into HMF in aqueous medium under microwave

irradiation at 200 °C, producing moderate HMF yields (38.1% and 18.6% respectively) [26,27]. Better yields to HMF have been obtained with high-boiling-point aprotic solvents, such as dimethylsulfoxide (DMSO), which suppresses unwanted side reactions and generates high yields of HMF (90%); however, the separation of HMF from even trace amounts of these high-boiling point solvents is difficult and requires energy-intensive isolation procedures [28,29].

Jain et al. studied the catalytic activity of mesoporous ZrP in the conversion of fructose to HMF in water/organic solvent (saturated with NaCl, 1:3, v/v) (40 mL), and at 150 °C for 4 h. The yield of HMF in water-MIBK solvent system was found to be 9% [30]. Carlini and coworkers evaluated the activity of solid acid catalysts. In that report, niobium phosphate could catalyze fructose dehydration with very high HMF selectivity (85-100%), in batch experiments at 100 °C [31]. The selectivity was, however, only obtained at fructose conversions between 25 and 35%. At higher conversions, the selectivity dropped significantly. The highest reported selectivity at 50% conversion was around 60%. Mercadier et al. published a three-part study on fructose dehydration in biphasic water-organic systems, catalyzed by ion-exchange resins [32]. An aqueous fructose solution of about 25 wt % was reacted in the presence of Lewatit SPC 108 and SPC 118 at 88 °C for 5 h. In the absence of extraction solvent, the HMF yield was 10% at 69% conversion, whereas in the presence of 9 eq. MIBK the HMF yield was 28% at 45% conversion. Moreau and co-workers ventured into zeolite catalyzed sugar chemistry [33,34]. In a water/MIBK (1:5 v/v) system, several zeolites were tested: H-Y faujasites and H-mordenite catalysts with diff :erent Si/Al ratios. H-beta, and H-ZSM5. The best result of 69% HMF yield at 76% conversion was obtained after 60 min using Hmordenite with an Si/Al ratio of 11. A recent publication by Ordomsky et al. on zeolite catalyzed dehydration of fructose in water and water/ MIBK systems showed significantly lower selectivity to HMF at comparable conversion with H-mordenite with an Si/Al ration of 11.7, reporting 42% yield at 64% conversion [35]

Interesting candidates as acid catalysts are certain open-framework systems, among them especially oxides with pyrochlore  $(H_3O)B_2O_6$  structure (B = octahedrally coordinated transition or p-block metals) [36–38], which exhibit a remarkable catalytic behavior for the

#### S.F. Mayer et al.

hydrolysis attributable to the reachability of the reactants to the internal acid contents of the solid [39]. The use of open-framework catalysts presents important advantages over conventional ones, due to a better diffusion of reagents and products within the interconnected tunnels or channels present in the structure. It has been reported that HNbMoO<sub>6</sub> has good catalytic activity for the reactions of hydration and hydrolysis [40,41]. Due to strong acid sites in the interlayer, the catalytic activity of HNbMoO<sub>6</sub> is significantly higher than the molecular sieve and niobate in the process of esterification and hydrolysis. The difference of the interlayer proton activity and the laminate negative charges make the layered solid acids have the shape-selectivity for different reactants.

Among this family of oxides, the proton conductors  $(H_3O)_xSb_xTe_{(2-x)}O_3$  (x = 1; 1.1 and 1.25) are very promising acid catalysts, with pyrochlore crystal structure. It is constituted by a covalent network of octahedral  $Sb^VO_6$  and  $Te^{VI}O_6$  units randomly distributed and linked by the vertices, forming large interconnected cavities where  $H_3O^+$  units are located, determined for the first time through Fourier synthesis from neutron diffraction data [20,42].

During the dehydration reaction, water is produced as a by-product, which has a negative impact on the catalyst activity; making a hydrophobic catalyst could be of great help to improve the catalytic activity. In order to increase the stability of these materials in the presence of water, specific microenvironments can be created inside their pores. Increased hydrophobicity of the pores may also decrease the local water concentration, thereby decreasing the tendency to form humins upon the conversion of carbohydrates, as well as increasing the material's resistance to hydrolysis and subsequent loss of functional groups. Hydrophobicity can be conveniently controlled by introduction of stable organic bridging groups between the silicon moieties, creating a hydrophobic microenvironment inside the catalyst pores. Hybrid organic-inorganic periodic mesoporous organosilica (PMO) materials have gained significant attention for application in catalysis [43]. Its synthesis involves the hydrolysis and template-assisted condensation of bis-(trialkoxy)silane-functionalized compounds, by which highly ordered materials can be obtained [44,45].

The above discussion highlights the role of hydrophobic porous framework, which renders them extraordinarily water resistant yet fully retains their intrinsic catalytic activities under heterogeneous systems

The aim of this work is to demonstrate the performance of  $(H_3O)_xSb_xTe_{(2-x)}O_3$  (x = 1; 1.1 and 1.25) oxides as acid catalysts in the dehydration of fructose to HMF, and the study of the influence of the different experimental parameters such as temperature and reaction time in the yield to HMF.

# 2. Experimental

#### 2.1. Catalyst synthesis

The precursor  $K_xSb_xTe_{(2-x)}O_6$  (x = 1; 1.1 and 1.25) pyrochlores were obtained by reaction in solid state, from  $K_2C_2O_4$ ,  $Sb_2O_3$  and  $TeO_2$  (analytical grade). The mixtures were heated in air at 750 °C for 12 h. The ion exchange was carried out with a subsequent treatment of the precursors in concentrated sulfuric acid in excess at 280 °C for 24 h as have been described elsewhere [42].

### 2.2. Characterization

X-ray diffraction of catalysts were measured using a Brucker D8 powder diffractometer with a Cu-K $\alpha$  radiation with Bragg angle between 10° and 120°, in increments of 0.02° and accumulation of 10 s in each step. For the refinement of the X-ray profile the Rietveld method was used [46]. Specific areas were calculated by the BET method from the N<sub>2</sub> adsorption isotherms at -196 °C using a Micrometric ASAP 2000 automatic instrument.

The FTIR spectra were obtained with a Nicolet 5700 spectrometer

#### 2.3. Catalytic activity

corresponding spectrum.

The catalytic measurements were carried out in a glass stirred reactor with a nominal volume of 15 mL and a maximum operational pressure of 10 bar (Ace Pressure Tube, supplied by Sigma-Aldrich). In a typical reaction: 1.5 mL of 5 wt. % fructose in H<sub>2</sub>O solution, 3.5 mL MIBK and 50 mg of catalyst were introduced into the immersed reactor in a heated oil bath, with stirring. Zero time was established when the corresponding temperature was reached. The analysis of the reaction products was carried out in a Shimadzu High Pressure Liquid Chromatograph (HPLC) equipped with a refractive index detector (RID) and a UV detector. The products were separated on a Hi-PlexH ion exchange column (300 × 7.8 mm) (Agilent), using 0.01 M solution of H<sub>2</sub>SO<sub>4</sub> as mobile phase at 65 °C with a flow of 0.6 mL min<sup>-1</sup>.

equipped with a Harris Praying Mantis® as diffuse reflectance accessory

and an environmental chamber for in situ measurements and a high sensitivity MCT-A detector. All spectra were recorded at RT with a

4 cm<sup>-1</sup> resolution, accumulation of 128 scans and presented in units of

Kubelka-Munk. Catalysts were dried at 120 °C for 2 h under helium

flow, and then the catalysts were contacted with pyridine vapor, the

samples were flowed by helium for 30 min to eliminate the pyridine in

the gas phase and physisorbed. The catalysts were outgassed at dif-

ferent temperatures RT, 150 and 200 °C, and cooled down to record the

equipment, equipped with a thermal conductivity detector (TCD). The

samples were dried "in situ" at 120 °C for 2 h under helium flow, then

the temperature was decreased to 100 °C and then the catalysts were

contacted with a flow of NH<sub>3</sub> for 30 min. The physisorbed NH<sub>3</sub> was

eliminated changing the gas flow to helium at 100 °C for 1 h. Then the

TPD were recorded using a heating rate of  $10 \,^{\circ}\text{C} \, \text{min}^{-1}$ .

The TPD-NH<sub>3</sub> tests were carried out in a Micromeritics Autochem II

# 3. Results and discussion

#### 3.1. Structural determination

The samples obtained by ion exchange  $((H_3O)_xSb_xTe_{2-x}O_6, (x = 1; 1.1 and 1.25)$  as well as the precursors counterparts  $(K_xSb_xTe_{2-x}O_6)$  exhibited excellent crystallinity, as was observed by the presence of sharp diffraction peaks in the XRD patterns.

The XRD pattern of (H<sub>3</sub>O)SbTeO<sub>6</sub> (Fig. 2) was indexed with a cubic cell with a = 10.1510 (1) Å, characteristic of a pyrochlore structure [47,48]. For the first refinement with the Rietveld method, a structural model was used in which the atoms of Sb and Te were randomly distributed in the 16d sites, and the O1 oxygens were placed in positions 48f (u, 1/8, 1/8), with u  $\approx$  0.423, reaching an agreement R<sub>Bragg</sub> factor of 7.5%. In the compound with  $H_3O^+$ , the K<sup>+</sup> was replaced by the O belonging to the hydronium ion, since H atoms are invisible by XRD. Fig. 2 (upper panel) illustrates the quality of the Rietveld fit for the pyrochlore structure from XRD data, after final refinement. Fig. 2 (lower panel) shows a simplified structure of the pyrochlore (H<sub>3</sub>O) SbTeO<sub>6</sub> constituted by a randomly distributed network of Sb<sup>V</sup>O<sub>6</sub> and Te<sup>VI</sup>O<sub>6</sub>, joined by their corners with angles (Sb, Te) -O1- (Sb, Te) of 136.2° forming a three-dimensional, strongly covalent subnetwork containing channels or tunnels through which hydronium ions diffuse easily, which gives a strong acid character to this compound. Recently the crystal structure of (H<sub>3</sub>O)SbTeO<sub>6</sub> was determined by neutron powder diffraction (NPD), [49] including the localization of  $H_3O^+$  units in the large cages.

#### 3.2. Acid sites characterization

Infrared (IR) spectroscopy undoubtedly represents one of the most important tools in catalysis research [50]. The pyridine IR spectroscopy adsorbed on a solid is a powerful tool to identify the nature of the acid





Fig. 2. Upper panel) XRD diagrams of (H<sub>3</sub>O)SbTeO<sub>6</sub> refined by the Rietveld method and Lower pannel) Simplified view of the pyrochlore structure. Violet spheres represent the distribution of O from the H<sub>3</sub>O<sup>+</sup> ions in the large cages formed by the octahedral network.

sites. The assignments of the infrared bands are in concert with the wellestablished correlation between the band positions and the type of interaction between the pyridine and the sites on which it is adsorbed. The original work with pyridine adsorbed on solid acids was done by Parry [51]. A compilation of the various band assignments with this technique has been given by Pichat et al. [52]. Liquid pyridine, pyridine hydrogen-bonded to a surface, chemisorbed to a Lewis acid site, and chemisorbed to a Brønsted acid site all show distinctly different regions of absorption in the infrared.

The region of the IR spectrum of pyridine adsorbed between 1400 to 1650 cm<sup>-1</sup> contains the characteristic bands of the different vibrational modes of pyridine. Fig. 3 presents the DRIFTS spectra for the sample



Fig. 3. DRIFT spectra of (H<sub>3</sub>O)<sub>1.25</sub>Sb<sub>1.25</sub>Te<sub>0.75</sub>O<sub>6</sub> with pyridine adsorbed and desorbed at 150 and 200 °C.

Molecular Catalysis xxx (xxxx) xxx-xxx



Fig. 4. TPD of NH<sub>3</sub> adsorbed on  $(H_3O)_xSb_xTe_{2-x}O_6$  (x = 1, 1.1 and 0.75).

 $(\mathrm{H_{3}O})_{1.25}Sb_{1.25}Te_{0.75}O_{6}$  after the adsorption of pyridine and successive heating at 150 and 200 °C. The bands at 1630, 1546 and 1487 cm<sup>-1</sup> are attributed to sites with Brønsted acidity. The first two are due only to Brønsted acid centers, while the latter may be due to both Brønsted and Lewis centers. Based on the published pyridine band assignments it can be concluded that pyridine bands at 1602 cm<sup>-1</sup> is related to Lewis-acidic sites [53]. The intensity of these bands remains unchanged with the thermal treatments, indicating a strong adsorption of pyridine on Brønsted acid sites. These results indicated that the nature of the acid sites are strong Brønsted sites.

Temperature-programmed desorption (TPD) is one of the versatile techniques for the determination of the total acidity and to determine the strength of acid sites present in the catalysts [54]. TPD-NH<sub>3</sub> desorption profiles of studied catalysts  $(H_3O)_xSb_xTe_{2-x}O_6$ , (x = 1; 1.1 and 1.25) are shown in Fig. 4. We detected three desorption regions that correspond to three sites of different strength present on the surface of the solid. The first centers are of a moderate acidity since they retain ammonia that desorb in a relatively low temperature range (T = 150–350 °C). The second centers are associated with a region of moderate-strong acid sites desorption temperatures of 350 to 500 °C. The intensity of the desorption peak in this region depends on the catalyst. The most intense ammonia desorption peak is for the (H<sub>3</sub>O)<sub>1.25</sub>Sb<sub>1.25</sub>Te<sub>0.75</sub>O<sub>6</sub>, clear indication that this catalyst has a higher number of this kind of acid sites on the surface of the solid. The third peak corresponds to the region of highest desorption temperature of temperature higher than 500 °C. These last centers correspond to those of very strong acid sites, and in general, the amount of these acid sites is small for all catalysts.

Semiquantitative data of TPD-NH<sub>3</sub> are compiled in Table 1. Even though all the catalysts desorb in three regions that correspond to acid centers of different strength, differences are observed in the desorbed quantities. In general, it can be seen that the greater the amount of Sb in

Table 1			
Ouantification of TPD of NH3 on	$(H_3O)_xSb_xTe_{2,x}O_6$	(x = 1, 1.1)	and 1.25)

Catalyst	Temperature (°C)	mmol NH <sub>3</sub> /g desorbed
(H <sub>3</sub> O)SbTeO <sub>6</sub>	150 – 350	0.05
	350 - 500	0.11
	> 500	0.05
(H <sub>3</sub> O) <sub>1.1</sub> Sb <sub>1.1</sub> Te <sub>0.9</sub> O <sub>6</sub>	150 - 350	0.13
	350 - 500	0.29
	> 500	0.14
(H <sub>3</sub> O) <sub>1.25</sub> Sb <sub>1.25</sub> Te <sub>0.75</sub> O <sub>6</sub>	150 - 350	0.13
	350 - 500	0.51
	> 500	0.24

#### S.F. Mayer et al.

#### Table 2

BET specific surface area of prepared catalysts  $(H_3O)_xSb_xTe_{2-x}O_6$  (x = 1, 1.1 and 0.75).

Catalyst	BET specific surface area (m <sup>2</sup> /g)
(H <sub>3</sub> O)SbTeO <sub>6</sub> (H <sub>2</sub> O) <sub>2</sub> Sb <sub>2</sub> Te <sub>2</sub> - O	1.9
$(H_3O)_{1.25}Sb_{1.25}Te_{0,75}O_6$	1.8

the composition, the more ammonia is desorbed, which is more evident for the catalyst  $(H_3O)_{1.25}Sb_{1.25}Te_{0.75}O_6$ . This catalyst has a high desorption at moderate temperatures (350–500 °C) that corresponds to medium-strong acid centers. The high-temperature peaks were close to the NH<sub>3</sub> desorption peaks obtained for layered HNbWO<sub>6</sub> (379 °C) and HTaWO<sub>6</sub> (385 °C) [55], which are attributable to strong acid sites formed in the interlayer of layered structures.

# 3.3. Specific surface areas

Specific Surface areas of  $(H_3O)_xSb_xTe_{2-x}O_6$  (x = 1, 1.1 and 0.75) are compiled in Table 2. The values are relatively low and quite similar among them, in consequence, we do not expect any influence of the specific surface area in the catalytic activity.

#### 3.4. Catalytic activity

Since temperature and time are the most critical parameters, they were initially investigated to carry out a systematic evaluation with and without the catalyst (H<sub>3</sub>O)SbTeO<sub>6</sub> to confirm the best conditions of the transformation of fructose to 5-hydroxymethyl-furfural (HMF) in a twophase H<sub>2</sub>O/methyl isobutyl ketone system (MIBK). As shown in Fig. 5, the highest conversion of fructose in the presence of the catalyst was 97.9% and a 47.5% yield was obtained at 170 °C for 120 min. In contrast, a very high yield was obtained below these values in absence of the catalyst. It should be noted that other by-products (furfural, levulinic acid and formic acid) were not considered due to their very low values. It is worth remarking that an important part of the converted fructose yield to the formation of unidentified products. Fig. 6 shows the results of the dehydration of fructose with (H<sub>3</sub>O)SbTeO<sub>6</sub> at different periods, in presence and absence of the catalyst at T = 150 °C. The conversion of fructose (Fig. 6a) was increased when time was extended from 60 to 120 min. to values close to 71%, increasing slightly for 150 min. The yield of HMF (Fig. 6b) increases gradually along with time in the interval from 60 min to 120 min, going from 23.8% to 44.8%, the



range at 140–170 °C. Reaction conditions: 0.050 g of catalyst ( $H_3O$ )SbTeO<sub>6</sub>; 1.5 mL of 5 wt.% dissolution of fructose in water / 3.5 mL MIBK and 120 min.

Molecular Catalysis xxx (xxxx) xxx-xxx



Fig. 6. Conversion of fructose (a) and yield to HMF (b) versus reaction time. Reaction conditions: 0.050 g of catalyst ( $H_3O$ )SbTeO<sub>6</sub>; 1.5 mL of 5 wt.% dissolution of fructose in water / 3.5 mL MIBK and T = 150 °C.



**Fig. 7.** Conversion of fructose (a) and yield to HMF (b) with different catalysts: (A)  $(H_3O)SbTeO_6$ , (B)  $(H_3O)_{1.1}Sb_{1.1}Te_{0.9}O_6$  and (C)  $(H_3O)_{1.25}Sb_{1.25}Te_{0.75}O_6$ . Reaction conditions: 0.050 g of catalyst; 1.5 mL of 5 wt.% dissolution of fructose in water / 3.5 mL MIBK, T = 150 °C and 120 min.

yield decreases for longer reaction time.

From these results, it was then decided to study the effect of the composition variation of Sb and Te,  $(H_3O)_xSb_xTe_{2-x}O_6$  (x = 1, 1.1 and 1.25) on the catalytic activity at 150 °C and 120 min of reaction (Fig. 7). Activity results showed that the conversion of fructose depends on the catalysts composition; the maximum conversion of fructose obtained was for  $(H_3O)_{1.25}Sb_{1.25}Te_{0.75}O_6$  with a 99% (Fig. 7a). The increase in the antimonium contents produces an increase in the yield to HMF (Fig. 7b), the improvement of the HMF yield is clearly higher for the Sb/Te ratio 1.25/0.75 with a yield of 58.6%. This observation is in agreement with previous reports that observed a higher yield to HMF with zeolites with high number of strong acid centers (TPD-NH<sub>3</sub>) [56].

Based on the activity results of the effect of the catalyst composition on the catalytic activity (Fig. 7), it was decided to study the effect of the reaction time with the catalyst  $(H_3O)_{1.25}Sb_{1.25}Te_{0.75}O_6$  on the conversion of fructose and yield of HMF at 150 °C. The effect of reaction time between 60 and 150 min was studied in the presence of the catalyst and in its absence, at T = 150 °C for  $(H_3O)_{1.25}Sb_{1.25}Te_{0.75}O_6$  (Fig. 8).

The conversion to fructose increases with the reaction time. It can be seen that in the presence of a catalyst, for all the times studied, the conversion of fructose is practically complete, except for 60 min., while in the absence of a catalyst the conversion is very low for the whole study. It is observed that an increase in reaction time results in a higher yield to HMF, from 40% to 60 min. at 51% at 120 min, and it is



Fig. 8. Conversion of fructose (a) and yield to HMF (b) in the time range at 60–150 min. Reaction conditions: 0.050 g of catalyst  $(H_3O)_{1.25}Sb_{1.25}Te_{0.75}O_6$ ; 1.5 mL of 5 wt.% dissolution of fructose in water/3.5 mL MIBK and 150 °C.

# Table 3

Yield to HMF from fructose employing some heterogeneous catalysts and H<sub>2</sub>O/ MIBK as solvent.

Catalyst	Reaction Conditions	% Fructose Conversion	% HMF yield	Reference
ZrP	150 °C, 4 h		9	30
Acidic ion-exchange resins	88 °C, 5 h	45	28	32
H-mordenite	165 °C, 1h	76	69	33
H-mordenite/SiO <sub>2</sub>	165°C, 6.5 h	85	53	35
(H <sub>3</sub> O) <sub>1.25</sub> Sb <sub>1.25</sub> Te <sub>0.75</sub> O <sub>6</sub>	150 °C, 2 h	98	59	This work

observed that there is a decrease in the yield to HMF when passing from 120 to 150 min., possibly due to the formation of undesirable byproducts (humic).

In Table 3 we show a comparison of the performance of the pyrochlore oxides compared to literature results for other catalysts. The comparison clearly indicates a good behavior in the fructose dehydration for our pyrochlore oxides, in comparison with other heterogeneous catalysts described in the literature. Pyrochlore oxides help to reach a high conversion rate and HMF yield, among the best described so far in literature.

### 4. Conclusions

Structural characterization confirmed that the pyrochlores  $(H_3O)_xSb_xTe_{(2-x)}O_3$  (x = 1; 1.1 and 1.25) contain cavities formed by interconnected octahedra (Sb,Te)O<sub>6</sub> that lodge hydronium ions  $(H_3O^+)$ . This configuration allows the  $H_3O^+$  to be very mobile, rendering them highly efficient as catalysts in the transformation of fructose to HMF.

There is a correlation between Brønsted acidity, and the number of acid centers with the values of fructose conversion and yield to HMF. The most active catalyst is (H<sub>3</sub>O)<sub>1.25</sub>Sb<sub>1.25</sub>Te<sub>0.75</sub>O<sub>6</sub>, which turns out to have the highest number of acid sites at T = 150 °C for t = 120 min.

# Acknowledgments

The authors acknowledge financial support from Comunidad de Madrid (Spain) (RESTOENE-2-CM S2013/MAE-2882 project) and CSIC (Spain) (201880E029 project). The financial support of Spanish MINEICO to the project MAT2017-84496-R is also acknowledged.

#### References

[1] C. Chatterjee, F. Pong, A. Sen, Green Chem. 17 (2015) 40-71.

- J.C. Escobar, E. Lora, O. Venturini, E. Yañez, E. Castillo, O. Almazan, Renew. [2] Sustain. Energy Rev. 13 (2009) 1275-1287.
- [3] J.N. Chheda, G.W. Huber, J.A. Dumesic, Angew. Chemie Int. Ed. 46 (2007) 7164-7183.
- Y. Roman-Leshkov, C.J. Barrett, Z.Y. Liu, J.A. Dumesic, Nature 447 (2007) 982. [4]
- [5] H. Wang, T. Deng, Y. Wang, Y. Qi, X. Hou, Y. Zhu, Bioresour. Technol. 136 (2013) 394-400
- [6] A. Liu, B. Liu, Y. Wang, R. Ren, Z. Zhang, Fuel 117 (2014) 68-73.
- S. Ma, P. Li, T. Zhu, H. Chang, L. Lin, Chem. Eng. Process. 83 (2014) 71-78. [7]
- J. Marcel, R. Gallo, D. Martin Alonso, M.A. Mellmer, J.A. Dumesic, Green Chem. 15 [8] (2013) 85 - 90
- [9] A.A. Rosatella, S.P. Simeonov, R.F.M. Frade, C.A.M. Afonso, Green Chem, 13 (2011) 754–793.
- [10] R.J. Van Putten, J.G. de Vries, Chem. Rev. 113 (2013) 1499–1597. [11] C. Moreau, et al., Appl. Catal. A Gen. 145 (1996) 211.
- [12] M.J.J. Antal, W.S.L. Mok, G.N. Richards, Carbohydr. Res. 199 (1990) 91.
- J. van Putten, J.C. van der Waal, E. de Jong, C.B. Rasrendra, H.J. Heeres, J.G. de [13] Vries, Chem. Rev. 113 (3) (2013) 1499–1597. [14] H.E. Van Dam, A.P.G. Kieboom, H. Van Bekkum, StarchStarke 38 (1986) 95.
- [15] J. Lewkowski, ChemInform 34 (2) (2003) 17-54.
- [16] Q. Zhao, L. Wang, S. Zhao, X. Wang, S. Wang, Fuel 90 (2011) 2289-2293.
- [17] E. Nikolla, Y. Román-Leshkov, M. Moliner, M.E. Davis, ACS Catal. 1 (2011) 408-410.
- [18] H.X. Qi, M. Watanabe, T.M. Aida, R.L. Smith Jr., Catal. Commun. 10 (2009) 1771e5.
- J. Pérez-Maqueda, I. Arenas-Ligioiz, Ó. López, J.G. Fernández-Bolaños, Chem. Eng. [19] Sci. 109 (2014) 244-250.
- [20] I. Jiménez-Morales, M. Moreno-Recio, J. Santamaría-González, P. Maireles-Torres, A. Jiménez-López, Appl. Catal. B 154–155 (2014) 190–196.
- [21] Y. Zhang, J.W. Xiangcheng, L. Xiaohui, Y. Xia, B. Hu, G. Lu, Y. Wang, Fuel 139 (2015) 301 - 307
- [22] N. Lucas, G. Kokate, A. Nagpure, S. Chilukuri, Microporous Mesoporous Mater. 181 (2013) 38-46.
- [23] W. van der Graaff, K. Garrido Olvera, E. Pidko, E. Hensen, J. Mol. Catal. A Chem. 388-389 (2014) 81-89.
- [24] A. Jain, A.M. Shore, S.C. Jonnalagadda, K.V. Ramanujachary, Amos Mugweru, Appl. Catal. A Gen. 489 (2015) 72–76.
- [25] S. Duttaa, S. Dea, A. Patrab, M. Sasidharanc, A. Bhaumikb, B. Saha, Appl. Catal. A Gen. 409-410 (2011) 133-139.
- [26] M. Watanabe, Y. Aizawa, T. Iida, R. Nishimura, H. Inomata, Appl. Catal, A Gen. 295 (2005) 150-156.
- [27] X. Qi, M. Watanabe, T.M. Aida, R.L. Smith Jr., Catal. Commun. 9 (2008) 2244-2249.
- [28] Y. Nakamura, S. Morikawa, Bull. Chem. Soc. Jpn. 53 (1980) 3705.
- H.E. Van Dam, A.P.G. Kieboom, H. van Bekkum, Starch 38 (1986) 95. [29]
- [30] J. Archana Jain, Andrew M. Shore, Subash C. Jonnalagadda, Kandalam
- V. Ramanujachary, Amos Mugweru, Appl. Catal. A Gen. 489 (2015) 72-76. [31] C. Carlini, M. Giuttari, A.M. Raspolli Galletti, G. Sbrana, T. Armaroli, G. Busca, G. Appl. Catal. A 183 (1999) 295.
- [32] D. Mercadier, L. Rigal, A. Gaset, J.P. Gorrichon, J. Chem. Tech. Biotechnol. 31 (1981) 489.
- [33] C. Moreau, R. Durand, S. Razigade, J. Duhamet, P. Faugeras, P. Rivalier, P. Ros, G. Avignon, Appl. Catal. A Gen. 145 (1996) 211.
- P. Rivalier, J. Duhamet, C. Moreau, R. Durand, Catal. Todav 24 (1995) 165. [34]
- V.V. Ordomsky, J. van der Schaaf, J.C. Schouten, T.A.J. Nijhuis, J. Catal. 287 [35] (2012) 68.
- [36] J. He, Q. Li, Y. Tang, P. Yang, A. Li, R. Li, H.Z. Li, Appl. Catal. A Gen. 443-444 (2012) 145-152.
- [37] Y. Liu, L. Chen, T. Wang, Q. Zhang, C. Wang, J. Yan, L. Ma, Sustain. Chem. Eng. 3 (2015) 1745-1755
- [38] Y. Huang, Y. Fu, Green Chem. 15 (2013) 1095-1111.
- A. Takagaki, S. Furusato, R. Kikuchi, S. Oyama, ChemSusChem. 8 (22) (2015) [39] 3769-3772.
- [40] A. Takagaki, C. Tagusagawa, K. Domen, Chem. Commun. (Camb.) (2008) 5363-5365.
- [41] A. Takagaki, R. Sasaki, C. Tagusagawa, K. Domen, Top. Catal. 52 (2009) 592-596. [42] J.A. Alonso, S. Mayer, H. Falcón, X. Turrillas, M.T. Fernández, Crystals 7 (2017)
- 24 31
- [43] D.E. De Vos, M. Dams, B.F. Sels, P.A. Jacobs, Chem. Rev. 102 (2002) 3615–3640.
  [44] P. Van Der Voort, D. Esquivel, E. De Canck, F. Goethals, I. Van Driessche, F.J. Romero-Salgueroc, Chem. Soc. Rev. 42 (2013) 3913-3955.
- [45] F. Goethals, C. Vercaemst, V. Cloet, S. Hoste, P. Van Der Voort, I. Van Driessche, Microporous Mesoporous Mater. 131 (2010) 68-74.
- [46] H.M. Rietveld, A profile refinement method for nuclear and magnetic structures, J. Appl. Crystallogr. 2 (1969) 65-71.
- M. Subramanian, G. Aravamudan, G.V. Subba Rao, Prog. Solid State Chem. 15 [47] (1983) 55.
- [48] J.A. Alonso, A. Castro, I. Rasines, X.M. Turrillas, J. Mater. Sci. 23 (1988) 4103.
- [49] J.A. Alonso, X. Turrillas, J. Chem. Soc. Dalton Trans. 7 (5) (2005) 865-867.
- J. Ryczkowski, Catalysis 68 (2001) 263-381. [50]
- [51] E.P. Parry, J. Catal. 2 (1963) 371.
- [52] P. Pichat, M.-V. Mathieu, B. Imelik, Bull. Soc. Chim. Fr. 8 (1969) 2611.
- [53] A.I. Osman, J. Meudalc, F. Laffird, J. Thompson, D. Rooney, Appl. Catal. B 212 (2017) 68–79. J.A. Schwarz, J.L. Falconer, Catal. Rev. 25 (1983) 141. [54]
- [55] C. Tagusagawa, A. Takagaki, S. Hayashi, K. Domen, J. Phys. Chem. C 113 (2009)
- 7831. [56] V.V. Ordomsky, J. van der Schaaf, J.C. Schouten, T.A. Nijhuis, J. Catal. 287 (2012)
- 68-75.