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Production of 5-HMF from Glucose using TiO₂-ZrO₂ catalysts: Effect of the sol-gel synthesis additive

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Abstract

Different TiO₂-ZrO₂ (50/50 wt%) mixed metal oxide catalysts were synthesized by the solgel method after varying the synthesis additive (e.g., CH₃COOH, HNO₃, NH₄OH and NaOH) to study its effect on the production yield of 5-HMF from the conversion of glucose at 175 °C and 30 bar (Ar) (batch reaction system). Various characterization techniques such as BET, XRD, FTIR, ¹HNMR, NH₃-TPD, TPO, SEM and TEM were employed to study the physicochemical properties of the synthesized materials and to correlate them with the reaction product yields. Highest HMF yield (76%) was obtained over the TiO₂-ZrO₂-C₂H₄O₂ catalyst in a biphasic reaction system with a glucose concentration of 2 wt% and a glucose/catalyst mass ratio of 2.5. From the NH₃-TPD results, highest amount of total acid sites was observed for the TiO₂-ZrO₂ (50/50 wt%) prepared by the sol-gel method using the acetic acid additive, and acidity value was 3 and 2.5 times higher than that of TiO_2 and ZrO_2 alone, respectively. It was concluded that total acid sites density is an important parameter to obtain high 5-HMF product yields. A higher number density of sites can be obtained using the complexing additive of acetic acid in the Sol-Gel method among the other additives investigated.

Keywords: 5-HMF; Glucose conversion; TiO₂-ZrO₂; Additive; Sol-gel.

1. Introduction

The imminent need of oil production and global energy demand stimulate significant efforts to identify carbon renewable sources for the production of fuels and traditional chemical products from sustainable origin, mainly related to biomass [1]. Glucose, the most abundant monosaccharide and the cheapest hexose, appears as a promising raw material to produce 5-hydroxymethylfurfural (5-HMF), which is a prospective platform molecule for the synthesis of polymers and biofuels [2]. The reaction of the production of 5-HMF from glucose can be promoted by a variety of bifunctional catalysts with acid-base characteristics such as TiO₂ [3], ZrO₂ [4] and mixed metal oxides [5]. Conversion of glucose to 5-HMF is believed to follow the mechanism of the isomerization of glucose to fructose (basic sites) followed by dehydration of fructose to 5-HMF (acid sites) as reported by Watanabe et al. [6]. In addition, Osatiashtiani et al. [7] showed that on the SO₄²⁻/ZrO₂ glucose is first isomerized by Lewis acid and base sites of ZrO₂, and the formed fructose was subsequently dehydrated to 5-HMF with Brønsted acid sites offerred by SO₄²⁻ groups followed by rehydration to organic acids (formic acid and levulinic acid) in low concentrations.

However, the use of heterogeneous Lewis acid catalysts can be effective for the HMF production from glucose in water or an organic solvent using TiO₂ as reported by Noma et al. [8]. Thus, it is important to know the nature of the acid sites formed on the surface of these catalysts. Regarding titania (TiO₂) and zirconia (ZrO₂), it has been reported that they both have redox and acid-base properties, which makes them a good choice for being catalysts and catalytic supports. In addition, the catalytic properties of these oxides can be improved by considering both Ti and Zr metals in a mixed oxide matrix. This improvement might be the result of the generation of new surface catalytic sites due to the strong interaction between the individual oxides, which brings forth a mixed oxide with broad

surface acid-base properties and high thermal stability [9]. For example, Zhang et al. [10] prepared sulfated titania-zirconia (SO₄/TiO₂-ZrO₂)in a co-precipitation method and obtained a 26% yield of 5-HMF after 2 h in a biphasic system of (1:1) n-butanol : H₂O. However, He et al. [5] achieved 51.3% yield of 5-HMF after 4 h in a biphasic system of (1:5) H₂O : THF using phosphotungstic acidified titanium-zirconium (HPA/TiO₂-ZrO₂), which was also prepared by a co-precipitation method. In another example, using TiO₂-ZrO₂ with Amberlyst 70 as co-catalyst prepared in sol-gel, Atanda et al. [11] obtained 81% yield to 5-HMF in 3 h in a biphasic system (4:1) THF : H₂O. It is clear from these examples that modifying TiO₂-ZrO₂ is not so helpful in achieving higher yields. It is important to note that even though the use of a co-catalyst helps in improving the product yield, the cost of 5-HMF production increases drastically. On the other hand, sol-gel method is a suitable procedure to produce mixed metal oxides with a homogeneous distribution of metal atoms [12]. However, strict control over the synthesis parameters such as temperature, type of additive, solvent, pH, etc. is necessary to obtain materials with different catalytic properties.

For the sol-gel method, the effect of synthesis additive has been reported using different additives, namely: Complexing acetic acid (CH₃COOH); condensation catalyst Ammonium hydroxide (NH₄OH), and Hydrolysis catalyst nitric acid (HNO₃) [13]. However, these studies focused to observe the modification in the textural and acid-base properties of the supports alone. To the best of our knowledge, the influence of sol-gel synthesis additive for TiO₂- ZrO_2 mixed metal oxides on the conversion of glucose to 5-HMF product is not available in the literature.

This work was focused on the effect of the sol-gel synthesis additive towards TiO_2 -ZrO₂ on their catalytic properties in the 5-HMF production from glucose. For this purpose, TiO_2 -

ZrO₂ was prepared by the sol-gel method and modified using various additives, namely: CH₃COOH, HNO₃, NaOH and NH₄OH.

2. Experimental

2.1. Synthesis of TiO₂-ZrO₂ materials

The synthesis of zirconium oxide (ZrO_2) , titanium oxide (TiO_2) and TiO_2 -ZrO₂ (50/50) wt%) was carried out using the sol-gel method (hydrolysis of zirconium butoxide, Sigma-Aldrich (Zr (OC₄H₉)₄) 80 wt% in 1-butanol) and titanium butoxide (Sigma-Aldrich (Ti (OC₄H₉)₄) 80% wt in 1-butanol) with ultra-pure water and 1-butanol (Sigma-Aldrich, CH₃(CH₂)₃OH) 98%) as solvent medium). The alkoxide/water and water/alcohol molar ratios were 1:16 and 1: 8, respectively. In a typical synthesis, the butoxide/butanol mixture was added to a glass flask and the water was slowly added dropwise for approximately 3 h. The pH of the water was adjusted to 3 for acetic acid [CH₃COOH] and nitric acid [HNO₃] additives, and to 9 for ammonium hydroxide [NH₄OH] and sodium hydroxide [NaOH] additives, and then left in constant agitation for 24 h. After the gel was formed, it was subjected to the extraction of liquids in an oven at 70 °C for 48 h. And finally, the materials were calcined at 500 °C for 12 h with a ramp of 2 °C/min. The materials were labeled according to the type of additive used in the sol-gel synthesis as follows: Mixed oxides TiO₂-ZrO₂ with CH₃COOH, NH₄OH, HNO₃ and NAOH as: TZ5050-C₃H₄O₂, TZ5050-NH₄OH, TZ5050-HNO₃ and TZ5050-NaOH, and reference samples of TiO₂ and ZrO₂ with CH₃COOH as Ti-C₃H₄O₂ and Zr-C₃H₄O₂, respectively.

- 2.2. Catalysts characterization
- 2.2.1. Textural analysis

The determination of specific surface area, pore size and pore volume of the catalysts was carried out by the N_2 physisorption technique using the BET method. Measurements were performed using Micromeritics Tristar 3020 II apparatus at 77 K. In typical measurement, 0.1 g of solid was weighed and degassed in N_2 gas atmosphere (1 bar) during 2 h at 300 ° C to remove adsorbed water and carbon dioxide gases.

2.2.2. X-ray diffraction (XRD)

XRD analysis was carried using Bruker Advance D8 X-ray diffractometer at the following conditions: radiation source of Cu K α at λ =1.790307 Å; 30 kV and 15 mA. Data were collected in the 20 - 80° 2 θ range.

2.2.3. Fourier-transform infrared spectroscopy (FTIR)

FT-IR spectra of solid materials prepared were collected at room temperature and atmospheric pressure by a Shimadzu IRAffinity-1 spectrometer in the frequency range 4000–400 cm⁻¹. In situ FTIR-pyridine adsorption was carried out using a Nicolet 170 SX FTIR equipment. The solid material was pressed into thin wafer and then placed in a glass Pyrex cell with CaF₂ windows coupled to a vacuum line ($1 \times 10-3$ Torr) to be evacuated in situ at 400 °C for 30 min. Subsequently, the temperature was decreased to room temperature and the pyridine was introduced into the cell until adsorption equilibrium was achieved. The excess pyridine was evacuated at the same temperature. Afterwards, the adsorbed pyridine was desorbed from room temperature to 120 °C and spectra were recorded at several desorption temperatures.

2.2.4. Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM)

SEM micrographs of the samples were recorded using a scanning electron microscope (JEOL, model JSM-6010LA). TEM analysis was performed using a JEM-2100 (JEOL, Japan) operating at 200 kV accelerating voltage. The powder was sonicated in isopropanol

to ensure a homogeneous dispersion. A small drop was deposited on the holey carbon films on a 200-mesh copper grid, which was introduced into the TEM analysis chamber after complete solvent evaporation.

2.2.5. Temperature Programmed Desorption of NH₃ (NH₃-TPD)

NH₃-TPD experiments were carried out in a Bel Japan Belcat-B device equipped with a thermal conductivity detector (TCD). Sample was first heated at a heating rate of 10 °C min⁻¹ up to 500 °C for 0.5 h under helium (P = 1 bar). Then, the sample was cooled down to 70 °C in a flow of He (50 mL min⁻¹), followed by NH₃/He adsorption for 30 min. Following adsorption the sample was flushed in He flow (50 mL min⁻¹) for 0.5 h at 70 °C to remove weakly adsorbed NH₃. Then, ammonia was desorbed upon heating to 500 °C in helium flow with a heating rate of 2°C/min, while the evolved gases were analyzed by TCD. The quantification of the acid sites was made by deconvolution (gaussian peak shape) of the area under the ammonia desorption curve from the obtained signal.

2.2.6. Temperature programmed oxidation (TPO)

The TPO study was carried out in a Bel Japan Belcat-B apparatus using a thermal conductivity detector (TCD) and 0.1 g of catalyst sample. The flow rate of the 5%/O₂/95% He gas mixture was 10 mL min⁻¹ and the heating rate was 10 °C min⁻¹. Finally, the TPO traces were recorded from room temperature to 500 °C.

2.3. Catalytic evaluation (Glucose yield to 5-HMF, Conversion and Selectivity)

The glucose conversion reaction to form 5-HMF was carried out in a 50 ml Teflon stainless-steel autoclave equipped with a magnetic stirring system. The reaction was performed with 0.6 g of D-Glucose (Sigma-Adrich 99.5%) in a 30 ml biphasic solution (75:25, THF: H₂O), with a glucose/catalyst mass ratio of 2.5. Finally, an amount of 1.2 g of

NaCl (Sigma-Aldrich 99.5% purity) was added. NaCl was used to separate the reactive aqueous phase from the extractive organic phase, since NaCl increases the partition coefficient in the biphasic system. The reaction was conducted under inert gas conditions with 30 bar of Ar and at the temperature of 175 °C with a constant stirring at 1000 rpm, using similar reaction conditions as reported [11]. Reaction samples from the organic solution were taken every 15 min. The conversion of glucose, yield of 5-HMF and selectivity of reaction to 5-HMF, fructose, formic acid and levulinic acid (FA+LA) was calculated using

the following Eqs. (1)-(4):

$$HMF \ yield \ (\%) = \frac{moles \ of \ 5-HMF \ produced}{moles \ of \ starting \ glucose} x \ 100\%$$
[1]

$$Glucose \ Conversion\ (\%) = \frac{moles\ of\ glucose\ reacted}{moles\ of\ starting\ glucose} x\ 100\ \%$$
[2]

$$S_{5-HMF}(\%) = \frac{\text{moles of 5-HMF produced}}{\text{moles of glucose reacted}} x \ 100 \ \%$$
[3]

$$S_{Fructose,(FA+LA)}(\%) = \frac{moles\ of\ intermedies}{moles\ of\ starting\ glucose} x\ 100\ \%$$
[4]

2.4. Reaction Products Analysis - High Performance Liquid Chromatography (HPLC)

The glucose and fructose were quantified using Shimadzu Prominence HPLC with a Bio-Rad Aminex HPX-87H column made of stainless-steel and measuring 300 mm in height, 7.8 mm of internal diameter and with a RID–10 (refractive index) detector. The HPLC was operated under the following conditions: oven temperature, 50 °C; mobile phase, 5 mM H_2SO_4 ; flow rate, 0.6 mL min⁻¹; injection volume, 20 µL. 5-HMF, formic acid and levulinic

acid were detected using Shimadzu Prominence HPLC with a Restek Model FORCE C18 column made of stainless-steel (measuring 250 mm in height, 4.6 mm of internal diameter and 5 μ m in particle size) and with a Photodiode Array Detector (PDA) at the wavelength of 284 nm (5-HMF) and 210 (formic and levulinic acids). Mobile phase was methanol/water with a ratio of 80/20. The operating conditions of the HPLC were: oven temperature of 30 °C, flow rate of 1 mL min⁻¹ and an injection volume of 15 μ L. The analysis was carried out through the external standard method using 5-HMF (Sigma Aldrich, 99%), glucose (Sigma Aldrich, 99.5%), fructose (Sigma Aldrich, ±99%), formic acid (Sigma Aldrich, ±95%) and levulinic acid (Sigma Aldrich, ±97%) as standard.

2.5. Analysis of the reaction by-products by ¹HNMR Nuclear Magnetic Resonance Spectroscopy

After the reaction, the reactor was cooled to room temperature, the catalyst was filtered and the organic phase was separated by decantation. The collected organic phase was evaporated at room temperature and the crude product was weighed, the products were then measured by ¹H NMR to determine the 5-HMF formation and other possible products generated in the course of the glucose conversion reaction, such as formic acid (AF) and levulinic acid (AL), by means of a Bruker NMR Spectrometer (Progress III 600 MHz), using deuterated methanol (MeOD, 25 °C). The spectra were processed with the MestReNova program(¹H NMR (600 MHz, MeOD)).

3. Results and discussion

3.1. Textural properties

All samples showed (See Fig. S1, ESI) a type-IV isotherm (IUPAC classification) indicating that the catalysts are mesoporous [14]. The hysteresis loop (H2-type) is commonly associated with the presence of ink-bottle shaped pores, which could be due to inter- or intraparticle porosity. Table 1 shows the effects of addition of the different additives on the surface area of TiO₂, ZrO₂ and mixed oxides TZ5050 prepared by the sol-gel method. The results of specific surface area obtained in the simple oxides Ti-C₂H₄O₂ and Zr-C₂H₄O₂, used as reference, are 40 and 41 m²g⁻¹, respectively. However, SSA values for the mixed oxides are 234, 239, 257 and 289 m²g⁻¹ for TZ5050-NH₄OH, TZ5050-HNO₃, TZ5050-NaOH and TZ5050-C₂H₄O₂, respectively. It is clear that highest SSA value was obtained for TZ5050-C₂H₄O₂, e.g. the catalyst synthesized with the complexing additive (CH₃COOH). Also, there was a considerable increase in the SSA from the individual oxides to the mixed metal oxides, with an increase of ~ 7 times.

Average pore size was calculated by the BJH method for the mesoporous solids and the mean pore sizes determined are 5.2 and 7.6 nm for Ti-C₂H₄O₂ and Zr-C₂H₄O₂, respectively. On the other hand, for the mixed metal oxides (TZ5050) the mean pore size varied between 3.1 and 3.6 nm, where the material with the smallest mean pore size was TZ5050-C₂H₄O₂. It is clear that the mean pore size is decreased for the mixed oxides with respect to the single metal oxides. It has been reported [15] that these changes, i.e. the increase in the SSA and decrease in mean pore size, occur due to competition between hydrolysis and condensation reaction steps causing agglomeration of small particles, which agrees with the obtained results by SEM (Fig. S5, ESI) . It is suggested that the formation of the organometallic complex between acetate (CH₃COO-) and the metal ion (Ti and Zr) during

the gelation time is the main reason behind the achievement of the smallest and uniform solid particles when acetic acid is used as additive.

3.2. X ray Diffraction (XRD) analyses

The diffraction patterns of TZ5050 samples with different additives, Ti- C₂H₄O₂ and Zr-C₂H₄O₂ and treated at 500 °C are shown in Fig. S2 (ESI). Ti-C₂H₄O₂ presents only the anatase crystalline phase with its most abundant peak at ~ 25.3° 20 related to the [101] plane (JCPDS No. 86-1157) [16]. In the case of Zr-C₂H₄O₂, the coexistence of two crystalline phases was found, namely tetragonal at 2θ = ~ 30° (JCPDS No. 89-7710) and monoclinic ~ 28° (JCPDS No. 83-0944) [17], where the tetragonal phase exists in greater abundance as compared to the other phase. Regarding TZ5050, these patterns show very poor crystallinity or amorphous form. This is in agreement with the XRD results reported by Anzures et al. [18], and it can be concluded that TiO₂–ZrO₂ mixed metal oxides, prepared by the sol–gel method, do not crystallize at temperatures below 600 °C. Two main broad diffraction peaks between $2\theta = 20^\circ$ - 40° and 40° - 70° are observed, and these are the regions where the main diffraction peaks of monoclinic/tetragonal phases of ZrO₂ and anatase phase of TiO₂ are expected to form [19].

3.3. FTIR studies

Fig. S3 (ESI) shows the IR spectra of the materials prepared in this work. The FTIR spectrum of the TiZr-NH₄OH catalyst before the heat treatment (Fig. 3 (a)), shows a very broad IR band at ~ 3406 cm⁻¹ related to the v-OH stretching vibrational mode, and another small band at 1631 cm⁻¹ corresponding to the δ -OH vibrational mode [20]. The -OH groups

are formed as a result of the dissociative adsorption of H₂O molecules to reduce the coordinative unsaturation of the surface sites [21]. The IR bands at 2961, 2382 and 1381 cm⁻ ¹ represent vibrational modes of -CH group due to the solvent of 1-butanol in reaction, and probably residues of the unreacted butoxide [22]. Besides that, a small band is observed at 1442 cm⁻¹ and it can be related to the NH_4^+ resulted from the synthesis additive [23]. In the case of the catalyst with the complexing additive before calcination, as shown in Fig. S3 (b) (ESI), two IR bands at 1546 and 1449 cm⁻¹ are assigned to the v_{as} -COO⁻ and v_{s} -COO⁻ mode, respectively [24], and are related to the ligands of the acetate (CH₃COO⁻). The separation between these signals is $\Delta v = 97 \text{ cm}^{-1}$ and indicates that CH₃COO⁻ ions act as a bidentate ligand. According to Barboux et al. [25], the acetate may form a chelate attached to a metal or a bridge between the two metals. IR bands at 1118, 1073 and 1032 cm⁻¹ are the characteristic ones of the butoxide groups (OBuⁿ). Also, the v-OH band and v-CH band are observed at around 3232 and 2960-2863 cm⁻¹ respectively. The broad IR band ~ 700 cm⁻¹ is assigned to the v-M-O vibrational mode, i.e. Ti-O-Ti, Zr-O-Zr and/or Ti-O-Zr. It is clear from Fig. S3 (b) (ESI) that there is some kind of linkage between butoxide, acetate and hydroxyl groups: (TiZr (OBun) (OAc)). In materials synthesized at 500 °C, shown in Fig. S3 (c) (ESI), the decrease in v-OH and δ -OH band intensities can be observed with respect to the materials before calcination. The broad IR band between 300 and 900 cm⁻¹ approximately, is observed for all TZ5050 materials as a result of the interaction M-O-M in the Ti-O-Zr network [26]. The signals at 2353 and 1519 cm⁻¹ are assigned to the stretch and bending modes of -CH, respectively, and are observed only in the case of materials prepared at pH=3. For materials synthesized at pH=9, no traces of organic matter are observed after the thermal treatment at 500 °C.

3.3.1. FTIR-pyridine adsorption

The results of the pyridine adsorption by FTIR are shown in Fig. 1. Pyridine adsorption is a valuable method to determine the nature of acid sites. Absorption bands $\sim 1605, 1575,$ 1490 and 1444 cm⁻¹ are characteristic of Lewis acid sites [27]. The Brønsted acid site can be observed at 1540 cm⁻¹ [28]. In the case of Ti-C₂H₄O₂, Zr-C₂H₄O₂ and TZ5050 oxides with different additives show Lewis acid sites at 1603, 1573, 1490 and 1444 cm⁻¹ IR bands (Fig. 1). In the case of TiO_2 , it has been reported [8] that the structure of anatase promotes the formation to Lewis acid sites. In addition, Glorius et al. [29] reported that zirconia-tetragonal can also form Lewis acid sites. These results agree with the analysis of XRD (Fig. S2, ESI). On other hand, the Brønsted acid sites were not observed in any of the samples, simple or mixed metal oxides. The formation of Brønsted acid sites was not reported so far for the TiO₂–ZrO₂ solids under similar experimental conditions [30]. According to the IR intensity shown for the Lewis acid sites of the present metal oxides, the behavior from the highest to the lowest intensity is : TZ5050-C₂H₄O₂> TZ5050-NaOH>TZ5050-HNO3>TZ5050-NH4OH>Ti-C₂H₄O₂> Zr-C₂H₄O₂, where clearly the TZ5050-ACT catalyst showed the highest IR intensity. Similarly, the same behavior was observed from the NH₃-TPD analysis (See Table 1).

3.4. TEM studies

TEM micrographs of TiZr5050-C₂H₄O₂ and TiZr5050-NH₄OH samples treated at 500 °C are presented in the Fig. S4 (ESI). Both samples showed small nanoparticles of spheroid shape with an average particles size ~ 6 nm. The electron diffraction of both samples showed no sign of crystalline phase(s). TiO₂-ZrO₂ treated at 550°C [31] showed similar results.

Furthermore, this result is in agreement with the XRD analysis (Fig. S2, ESI) and confirm that prepared materials are in amorphous phase.

3.5. Acidity measurements - NH₃ TPD

Table 1 presents the amount (μ mol/g) of total acid sites, acid sites density (μ mol/m²) and acid strength distribution calculated from NH₃-TPD profiles of the catalysts synthesized by sol-gel after using different additives. Measured total acid sites for Ti-C₂H₄O₂ and Zr-C₂H₄O₂ are 695 and 700 µmol g⁻¹, respectively. However, mixed metal oxides show relatively high total amount of acid sites, namely: 1301, 1375, 1429 and 1959 µmol g⁻¹ for TZ5050-NH₄OH, TZ5050-HNO₃, TZ5050-NaOH and TZ5050-C₂H₄O₂, respectively. According to these results, highest number of surface acid sites on was observed for the TZ5050-C₂H₄O₂ catalyst. Therefore, it can be confirmed that when the SSA increases, the number of surface acid sites increases. Density of acid sites for Ti-C₂H₄O₂, Zr-C₂H₄O₂, TZ5050-NH₄OH, TZ5050-HNO₃, TZ5050-NaOH and TZ5050-C₂H₄O₂ are: 17.4, 17.1, 5.6, 5.8, 5.6 and 6.8 µmol m⁻², respectively. Density of acid sites is high for individual metal oxides, i.e. Ti-C₂H₄O₂ and Zr-C₂H₄O₂ due to the relatively low specific surface area of these samples when compared to that of mixed metal oxides.

Acid strength distribution for the present solids investigated is shown in Fig. 2. The desorption temperature of ammonia depends on the bonding strength of the acid site with adsorbed ammonia species, thus the surface acidity of the solid samples is classified as weak (100-200 °C), medium (200-300 °C), strong (300-400 °C), and very strong (>400 °C) [32]. From the TPD-NH₃ profiles shown in Fig. S6 (ESI), TZ5050-C₂H₄O₂ displayed a maximum desorption temperature at relatively lower temperature, i.e. 145 °C when compared to that of all other samples. Table 1 shows that the greatest number of weak acid sites is 926 μ mol g⁻

¹, or 47.3% of the total sites available on the surface for the TZ5050-C₂H₄O₂ solid. This value of weak acid sites is higher by at least 2 times when compared to that of any other solid sample, and this might be a key point for the selective yield of 5-HMF observed.

3.6. Catalytic performance studies

Catalytic performance studies of the present metal oxides were focused on the yield of 5-HMF for the model glucose conversion reaction. The reactivity study was conducted with THF/Water as the reaction medium. Fig. 3A shows the evolution of the reaction 5-HMF product with time. It is observed that the production yield of 5-HMF with individual metal oxides, i.e. $Ti-C_2H_4O_2$ and $Zr-C_2H_4O_2$, increases linearly, with reaction rates of 0.1619 and 0.1395 mmol min⁻¹ g⁻¹, respectively. However, the mixed metal oxides display an exponential increase for the transformation to 5-HMF with a reaction rate between 0.2152-0.2938 mmol $min^{-1} g^{-1}$ (See Table 2), where the TZ5050-C₂H₄O₂ catalyst exhibits the highest reaction rate. Table 2 also shows results of glucose conversion, yield to 5-HMF and selectivity to 5-HMF. According to the glucose conversion (Table 2, Fig. 4b) results, the $Ti-C_2H_4O_2$ and $Zr-C_2H_4O_2$ catalysts resulted in 90 and 87% conversion, respectively. In the case of mixed oxides TZ5050, a conversion of $\sim 99\%$ is observed. This result might be the effect of the large amount per gram basis of Lewis acid sites on these materials (Table 1). In the case of the mixed metal oxides, the catalyst TZ5050-C₂H₄O₂ provides the highest performance in the reaction with a production yield of 76%, whereas the materials synthesized with NH₄OH, HNO₃ and NaOH achieved yield values of 67, 63 and 61%, respectively. It is known that acid-base properties are needed to produce 5-HMF, where the Lewis acid sites are more responsible for the isomerization of glucose to fructose, whereas Brønsted acid sites are

responsible for fructose dehydration. In addition, the presence of mannose compound was investigated as a by-product of reaction. Mannose can be generated by an epimerization of glucose by the presence of Lewis acid sites in water [33]. However, in this work the presence of mannose was not found. This can be the result of a rapid and selective isomerization of glucose to fructose with TiO_2 -ZrO₂ catalysts, avoiding the formation of mannose.

Following the above discussion, the number of total surface acid sites coincides with the reaction yield performance for the materials synthesized in this work. More precisely, the simple metal oxides $Ti-C_2H_4O_2$ and $Zr-C_2H_4O_2$ shows the lowest number of total acid sites and therefore exhibit the lowest yield to 5-HMF. Moreover, the mixed metal oxides TZ5050 show better yield as they have more surface acidic sites (1959 - 1301 µmol g⁻¹). Also, the catalyst with the highest number of acid sites, and especially with the highest proportion of weak acid sites, i.e. TZ5050-C₂H₄O₂, provide the highest yield. Therefore, it can be confirmed that the total amount of surface acid sites and the percent of weak acid sites present in the synthesized materials are key factors for a better reaction performance. Also, it is confirmed that it is possible to obtain a greater number of surface acid sites using acetic acid as complexing additive in the sol-gel synthesis of TiO₂-ZrO₂ materials.

Concerning the reaction by-products selectivity, Table 2 presents results for HMF, fructose, levulinic acid (LA) and formic acid. It is noted here that glucose and reaction by-products were analyzed by HPLC and a calibration curve was made in order to quantify their concentration by samples taken during the reaction (the times of response and the conditions of analysis are shown in Fig. S7, ESI). The Ti-C₂H₄O₂ and Zr-C₂H₄O₂ catalysts showed the lowest selectivity to 5-HMF, namely 61 and 63%, respectively. This is due to a non-complete dehydration of fructose to 5-HMF, showing a selectivity to fructose of 8 and 11%, respectively. In the case of TZ5050 catalysts, a lower selectivity to the simple oxides was

observed, between 1-5%, where the TZ5050- $C_2H_4O_2$ catalyst showed the lowest fructose selectivity due to its greater selectivity to 5-HMF.

The presence of acids was analyzed in order to corroborate the existence of a rehydration of 5-HMF to formic and levulinic acids. All the samples showed the presence of levulinic and formic acids with a selectivity value between 22 and 28% likely due to the presence of water in the reaction system.

In addition, to confirm the formation of by-products in the present reaction system, analysis by ¹H NMR of the TZ5050-C₂H₄O₂ catalyst (see Fig. S8, ESI) was conducted. The ¹H NMR spectrum (600 MHz, MeOD) showed the following displacements: the protons of 5-HMF were calculated from integrated values of: (CHOA, $\delta = 9.54$ ppm), (CHB, $\delta = 7.42$ ppm and CHA, $\delta = 6.61$ ppm), and (CH 2 $\delta = 4.64$ ppm). In the case of LA (CH2 $\delta = 2.78$ ppm and CH2 $\delta = 2.55$ ppm), (CH3 $\delta = 2.19$ ppm) and finally of FA (-COOH $\delta = 8.12$ ppm), it was found that after the formation of 5-HMF, levulinic and formic acids are formed, following the reaction pathway presented in Fig. S8 (ESI).

Recycling tests for the TZ5050-C₂H₄O₂ catalyst stability are shown in Fig. 4. The reaction was carried out at 175 ° C and 30 bar of Ar in the THF/H₂O biphasic system, where the yield to 5-HMF was quantified at the end of 1 h of reaction. In each recycle, the catalyst was filtered and washed with methanol several times, and the solvent was evaporated at 120 °C, followed by a heat treatment at 400 °C for 1 h. The results obtained show that the yield of 5-HMF is reduced to ~ 60% after 3 consecutive cycles. This deactivation of catalyst might be due to the stability of the material's surface (amorphous characteristics of the material), which was confirmed by XRD and TEM analyses. The decrease in the yield also could be due to carbon deposits on the mixed metal oxide surface, as a result of the formation of

humic compounds [34]. The latter is supported by the color change from white to dark yellow color after 3 cycles.

The temperature programmed oxidation (TPO) was used to investigate the deactivation of the TZ5050-C₂H₄O₂ catalyst through the evolution of CO₂ from the combustion of carbon deposited on the surface of the catalyst [35]. In Fig. 4 (right-axis), the fresh catalyst shows a carbon amount of 17.5 μ mol as a reference. It was observed that for each recycle, the amount of carbon increased, up to ~ 35.5 μ mol in the third recycle. This is due to carbon deposition in the TiO₂-ZrO₂ active sites. This result corroborates the loss in activity for the production of 5-HMF in the recycle tests over the TZ5050-C₂H₄O₂ catalyst.

4. Conclusions

It was possible to prepare TZ5050 materials by the sol-gel method using different synthesis additives. Acetic acid was the additive that allowed the formation of materials with better textural and surface structural properties. In relation to the results obtained for the glucose transformation reaction, the catalyst TZ5050-C₂H₄O₂ presented the highest yield (ca. 76%) to 5-HMF. Furthermore, selectivity to the reaction by-products was analyzed and the pathway of reaction was corroborated by ¹HNMR analysis, where it was found that besides 5-HMF, levulinic acid and formic acid are formed. However, this selectivity was low over the TZ5050-C₂H₄O₂ catalyst. Recycling tests indicated that the performance of the catalyst was reduced to ~ 60% after 3 cycles. This result generates the need to investigate other calcination temperatures to improve the stability of the material.

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Figure Captions

Figure 1. FTIR-Pyridine adsorption on a) Zr-C₂H₄O₂, b)Ti-C₂H₄O₂, c) TiZr5050-NH₄OH, d) TiZr5050-NaOH, e) TiZr5050-HNO₃, and f) TiZr5050-C₂H₄O₂ solids.

Figure 2. Surface acid strength distribution over the $Ti-C_2H_4O_2$, $Zr-C_2H_4O_2$ and TiZr5050 (C₂H₄O₂, NH₄OH, HNO₃ and NaOH) catalysts synthesized by the sol-gel method.

Figure 3. A) Reaction yield of 5-HMF product from glucose conversion and B) Glucose conversion and selectivity to 5-HMF, fructose and organic acid (FA+LA), where: a) Zr- $C_2H_4O_2$, b)Ti- $C_2H_4O_2$, c) TiZr5050- $C_2H_4O_2$, d) TiZr5050-NH₄OH, e) TiZr5050-HNO₃ and f) TiZr5050-NaOH catalyst. Experimental conditions: 0.6 g of glucose; 0.24 g of catalyst; 30 ml (THF/Water); reaction time of 1 h; reaction T=175 °C; 30 bar Ar.

Figure 4. Catalyst recyclability activity test and TPO analysis for carbon (μ mol/g). (•) 5-HMF yield from glucose conversion on TZ5050-C₃H₄O₂ catalyst. Reaction conditions: glucose/catalyst: 2.5 , 30 mL solvent (Water/THF, 1:4 v/v), 2.1 g NaCl, 60 min reaction time, 175 °C reaction temperature, 30 bar Ar.













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Table 1. Specific surface area (S_{BET}), specific pore volume (Vp), mean pore size (Dp), surface acidity strength distribution, amount of desorbed NH₃ and acid sites density, parameters obtained through BET and TPD-NH₃ measurements.

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Catalysts	Sbet	Vp	Dp TPD-NH ₃	Acid sites density	Acid strength distribution (µmol/g)				
	(m²/g)	(cm ³ /g)	(nm)	(µmol/g)	(µmol/m ²)	Weak	Medium	Strong	Very strong
						(100-200 °C)	(200-300 °C)	(300-400 °C)	(>400 °C)
Ti-C ₂ H ₄ O ₂	41	0.07	5.2	695	17.4	79.4	281.3	154.3	180.3
Zr-C ₂ H ₄ O ₂	40	0.11	7.6	700	17.1	73.8	82.9	292.0	251.7
TZ5050-C ₂ H ₄ O ₂	289	0.22	3.1	1959	6.8	925.5	518.5	330.8	183.3
TZ5050-NH4OH	234	0.24	3.3	1301	5.6	437.8	404.4	275.7	183.2
TZ5050-HNO ₃	239	0.29	3.6	1375	5.8	339.7	440.0	305.9	289.8
TZ5050-NaOH	257	0.29	3.4	1429	5.6	331.5	551.5	304.7	242.1
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Table 2. 5-HMF yield and reaction rate (μ mol/min/g) for the production of 5-HMF from

	Glucose	Yield		Selectivity		
Catalyts	conversion (%)	5-HMF (%)	5-HMF (%)	Fructose (%)	FA+LA (%)	r _A (mmol*min ⁻¹ *g ⁻¹)
Zr-C ₂ H ₄ O ₂	87	53	61	11	28	0.1395
Ti-C ₂ H ₄ O ₂	90	57	63	8	29	0.1619
$TZ5050-C_2H_4O_2$	99	76	77	1	22	0.2938
TZ5050-NH4OH	99	67	69	2	28	0.2699
TZ5050-HNO ₃	99	63	64	2	34	0.2352
TZ5050-NaOH	99	61	62	5	33	0.2152

glucose in a batch reactor system*.

*Reaction conditions: 0.6 g glucose; 0.24 g catalyst; 30 ml (THF/Water); reaction time 1

h; reaction T= 175 °C; 30 bar Ar.

Highlights

- Highest amount of acid sites in TiZr5050 catalyst prepared using acetic acid
- Highest HMF yield (76%) was obtained with TZ5050-C₂H₄O₂ from Glucose (2 wt%)
- Total acid sites are important to obtain high production yields. •
- Lowest selectivity's to Organics Acid using TZ5050-C₂H₄O₂ (1%).

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