

Article

From Sugarcane Molasses to Functional Materials: Sustainable Synthesis of Metal Oxide–Carbon Catalysts for HMF Production

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Abstract

Sugarcane molasses (SCM) is an abundant agro-industrial waste and a renewable carbon source for obtaining functional materials and chemicals. This work presents a one-pot strategy for converting SCM into bifunctional metal oxide–carbon catalysts for the production of 5-hydroxymethylfurfural (HMF). Catalysts were synthesised by hydrothermal carbonisation of SCM in the presence of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ or $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, enabling the in situ formation of the carbon support and incorporation of metal oxide phases. The effects of NaOH addition and thermal treatment under N_2 or CO_2 on catalyst structure and performance in the microwave-assisted conversion of sucrose to HMF in water were investigated. Al-containing hydrochars exhibited higher apparent Brønsted acidity ($A_{\text{tot}} = 3.1\text{--}3.4 \text{ mmol H}^+ \cdot \text{g}^{-1}$) than the Sn-containing materials ($A_{\text{tot}} = 2.2\text{--}2.7 \text{ mmol H}^+ \cdot \text{g}^{-1}$), while NH_3 -TPD indicated a higher concentration of accessible acid sites after thermal treatment under CO_2 . NaOH favoured the formation of poorly crystalline or amorphous Al-containing phases, whereas CO_2 activation significantly enhanced the texture of the catalysts. The highest HMF yield (36%) was achieved over the CO_2 -treated, NaOH-derived Al-containing catalyst, demonstrating the importance of controlling catalyst acidity and textural properties for efficient HMF production from sucrose.

Keywords: 5-hydroxymethylfurfural; hydrothermal carbonization; metal oxide–carbon catalyst; sugarcane molasses; sustainable catalyst

1. Introduction

The valorisation of agro-industrial residues is increasingly recognised as a key strategy for supporting low-carbon development and the transition towards a circular bioeconomy [1]. Recent reviews have emphasised the importance of waste valorisation, resource efficiency, and innovative solutions to enhance the sustainability of production systems worldwide [2,3]. Accordingly, the conversion of sugarcane molasses, an abundant by-product of the sugar industry, into functional catalytic materials represents a promising strategy to promote biomass valorisation and support more sustainable chemical processes. Non-edible sugarcane molasses (SCM), a low-cost by-product of the sugar industry rich in sucrose (~50%), is an attractive feedstock for the production of 5-hydroxymethylfurfural (HMF) [4], but it can also serve as a precursor for functional carbon materials with catalytic applications [5,6].

HMF is a key platform chemical for the production of biofuels, bioplastics, and fine chemicals [7]. Its formation from sucrose involves three consecutive steps, as pre-



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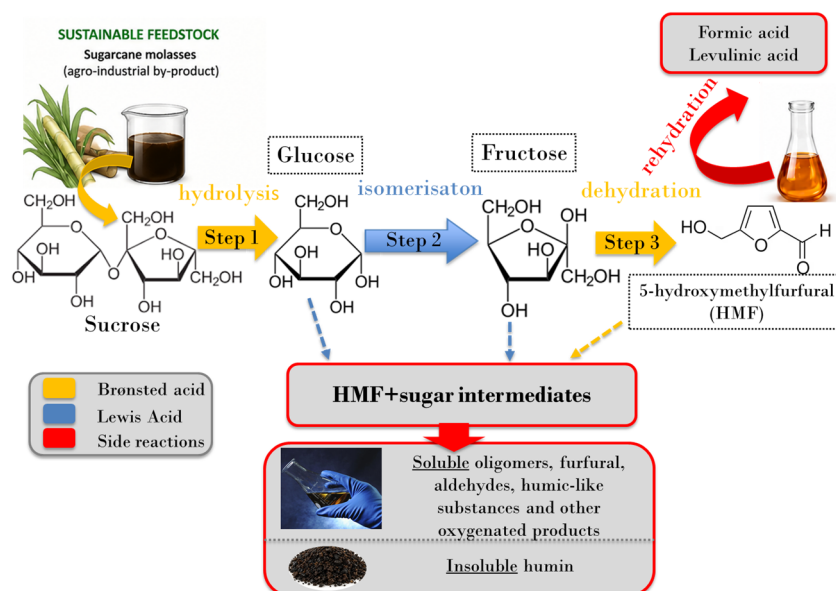
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sented in *Scheme 1*: (i) hydrolysis of sucrose to glucose and fructose accelerated by Brønsted acid (BA) sites, (ii) isomerisation of glucose to fructose over Lewis acid sites, and (iii) dehydration of fructose to HMF promoted by Brønsted acidity [8]. Although sucrose hydrolysis may occur partially through autocatalytic pathways under hydrothermal conditions ($T > 160\text{ }^{\circ}\text{C}$), efficient HMF production generally requires catalysts possessing both Brønsted and Lewis acid functionalities [9].



Scheme 1. Simplified reaction network for the catalytic conversion of sucrose derived from SCM to HMF, including the most common side reactions and highlighting the roles of Brønsted and Lewis acid sites.

Besides the main reaction pathway, there are numerous side reactions, mostly catalysed by strong BA sites, including: (i) rehydration of HMF to form organic acids such as formic and levulinic acid [10] and (ii) formation of soluble polymers or dark-coloured, tarry residue containing insoluble humins, originating from polymerisation or condensation of HMF with sugar-derived intermediates or furanic compounds [11]. In fact, as demonstrated in our previous studies, in aqueous-phase HMF production from sucrose [8], sugarcane molasses [12], and glucose [13] carbon loss was predominantly due to the formation of humin. Importantly, LA sites can also indirectly promote humin formation by generating highly reactive sugar-derived intermediates (see Scheme 1) and by modulating adsorption [14].

Sn- and Al-based oxides are particularly promising for HMF production due to their tunable Lewis and Brønsted acidity, sufficient stability in acidic and basic environments, and low cost. The literature shows that SnO_2 -based systems exhibit strong Lewis acidity associated with Sn^{4+} centres, which efficiently promote glucose–fructose isomerisation (Scheme 1) [15]. In comparison, Al_2O_3 exhibits weaker Lewis acidity arising from Al^{3+} sites. On the other hand, Brønsted acid sites in these oxides arise from surface hydroxyl groups that can donate protons. Importantly, BA sites are less abundant than LA sites in both oxides, and they typically exhibit only weak acidity [16]. Therefore, additional BA sites are generally required to efficiently catalyse the cascade conversion of sucrose to HMF.

Al-based catalysts have been successfully applied in the isomerisation of glucose to fructose. For instance, Yu et al. [17] reported that biochar-supported alumina prepared by one-step pyrolysis of sawdust impregnated with aluminium chloride achieved a fructose selectivity of 73.8% at $160\text{ }^{\circ}\text{C}$ after only 20 min, highlighting the effectiveness of Al species as active Lewis acid sites in this reaction.

Although Al_2O_3 exhibits stronger Brønsted acidity than SnO_2 , which largely depends on the density of surface hydroxyl groups [18], both oxides are often modified to enhance their catalytic activity in cascade production of HMF from sugars. For example, additional Brønsted acidity (in the form of surface P–OH groups) can be created by incorporating phosphate groups on SnO_2 while preserving its intrinsic Lewis sites. This approach was used by Zhang et al., who obtained phosphate-modified SnO_2 by calcinating phosphate-impregnated Sn-MOFs. Under optimised conditions, the catalyst yielded 43.0% HMF from glucose in methyl isobutyl ketone solvent [19].

An alternative strategy for designing bifunctional catalysts for HMF production from sugars involves dispersing metal oxides such as SnO_2 or Al_2O_3 onto carbon supports. In these hybrid systems, the metal oxides provide LA sites for glucose–fructose isomerisation, while the carbon support provides Brønsted acidity through intrinsic surface oxygen groups or introduced functionalities such as $-\text{SO}_3\text{H}$. This approach was adopted by Zhang et al. [20], who developed sucrose-derived sulfonated carbon/ γ - Al_2O_3 catalysts via a three-step impregnation–carbonisation–sulfonation method. The balance among different acid sites in these hybrid catalysts was controlled by the amount of sulfonated carbon added, resulting in HMF yields exceeding 60% from glucose in a DMSO/ H_2O medium.

Hydrothermal carbonisation (HTC) is an attractive route for converting carbohydrate-rich wastes into functional carbon materials [21] because it enables the direct conversion of wet biomass into carbonaceous materials without energy-intensive drying. Furthermore, tailoring the physicochemical properties of hydrochars during synthesis has been identified as an important strategy for producing high-value functional materials with enhanced sustainability [1]. For instance, HTC provides the homogeneous incorporation of metal precursors into the developing carbon material, thereby promoting a uniform dispersion of metal oxide phases and the formation of oxygen-containing surface functionalities, which are commonly associated with Brønsted acidity [12]. This approach was previously demonstrated by Wang et al. [22], who prepared SnO_x -functionalised hydrochars derived from glucose and obtained an HMF yield of 84.1% during glucose conversion in a biphasic system. Despite these advances, the direct and cost-effective one-pot synthesis of bifunctional metal oxide–carbon catalysts from biomass waste featuring Lewis acid sites and tunable Brønsted acidity has not yet been investigated.

We hypothesised that incorporating Sn or Al species during the hydrothermal carbonisation of sugarcane molasses would enable the direct synthesis of bifunctional catalysts featuring Lewis acid sites and tunable Brønsted acidity. We further hypothesised that NaOH addition and thermal treatment under N_2 or CO_2 would tailor the catalyst structure and acidity, thereby influencing HMF production from sucrose in water.

To verify this hypothesis, SnO_2 - and Al_2O_3 -carbon hybrid catalysts were synthesised directly from sugarcane molasses via one-pot hydrothermal carbonisation, followed by thermal treatment under different atmospheres. The effects of the synthesis conditions on the catalyst structure, acidity, and catalytic performance in the microwave-assisted conversion of sucrose to HMF were systematically investigated.

The novelty of this study lies in combining in situ incorporation of metal oxides during HTC with controlled post-treatment under different atmospheres to tailor catalyst acidity and establish structure–performance relationships. Furthermore, the work demonstrates a sustainable route to valorising sugarcane molasses into bifunctional catalysts for various biorefinery processes.

2. Experiment

2.1. Material Preparation

SnO₂- and Al₂O₃-containing carbon hybrid catalysts were prepared via hydrothermal carbonisation of sugarcane molasses in the presence of SnCl₂·2H₂O or Al(NO₃)₃·9H₂O (Merck, Algés, Portugal), enabling the in situ incorporation of metal species into the carbon phase. Selected samples were subsequently thermally treated under N₂ or CO₂ atmospheres. Industrial sugarcane molasses supplied by RAR S.A. (Portugal) was used as the carbon precursor, and its composition has been reported elsewhere [12]. Larger batches of the starting hydrochars were prepared via several independent syntheses using the same experimental protocol, thereby providing sufficient material for all subsequent thermal treatments, characterisations, and catalytic experiments. The hydrochars were then divided and subjected to the different thermal treatments described below. Additional hydrochar batches were synthesised only when extra material was required, following the same preparation procedure. The synthesis method demonstrated good reproducibility, consistently producing materials with comparable properties in independent batches.

2.1.1. Preparation of Tin Oxide–Carbon Catalysts

Carbon–tin oxide (C–SnO₂) hybrid catalysts were prepared following the methodology reported by Wang et al. [22]. Briefly, 40 g of sugarcane molasses was mixed with 40 mL of distilled water and stirred for 30 min. Different amounts of SnCl₂·2H₂O (8.9, 17.8, or 26.7 g) were then added, and the mixtures were stirred for a further 30 min before being subjected to hydrothermal treatment at 180 °C for 8 h in a Teflon-lined stainless-steel autoclave (Parr Instruments Company, Moline, IL, USA). The resulting solids were recovered by filtration, washed thoroughly with water and ethanol, and dried overnight at 80 °C. The hydrothermal carbonisation products were denoted as C-*x*SnO₂-HTC, where *x* represents the relative amount of tin precursor introduced during synthesis (i.e., 8.9 g, etc.).

Sn-containing hydrochars were subsequently thermally treated under N₂ (100 cm³·min^{−1}, 600 °C) or CO₂ (100 cm³·min^{−1}, 750 °C) for 2 h. The thermally treated samples were denoted as C-*x*SnO₂-HTC-G-T, where G represents the treatment atmosphere (N₂ or CO₂) and T the treatment temperature (°C).

For comparison, molasses was subjected to the same HTC procedure and then pyrolysed under identical conditions, without the addition of the Sn precursor. The sample obtained after hydrothermal treatment was denoted C-HTC, while those obtained after subsequent pyrolysis were designated C-HTC-N₂-600 and C-HTC-CO₂-750.

2.1.2. Preparation of Aluminium Oxide–Carbon Catalysts

The methodology for preparing aluminium oxide–carbon hybrid catalysts was developed based on the procedures described by Xue et al. [23] and Bell et al. [24]. In a typical synthesis, 40 g of sugarcane molasses was mixed with 40 mL of deionised water. Al(NO₃)₃·9H₂O (14.8 g) was dissolved separately in 2 mL of water, ultrasonicated for 5 min, and then added to the diluted molasses. After stirring for 10 min, the mixture was transferred to a PTFE-lined stainless-steel autoclave (Parr Instruments Company, USA) and subjected to hydrothermal carbonisation at 180 °C for 20 h. The remaining preparation steps were identical to those described for the Sn-containing composites, including thermal post-treatments. For comparison, a second Al-containing multicomponent material was prepared following the same procedure, with the addition of NaOH (Merck, Portugal, 1.25 g) prior to HTC. The NaOH was introduced to promote the controlled formation of aluminium hydroxide species, precursors of Al₂O₃.

The resulting materials were denoted as C-Al-HTC and C-Al-NaOH-HTC, corresponding to synthesis without and with NaOH, respectively. After thermal treatment, the

samples were designated as C-Al-HTC-G-T or C-Al-NaOH-HTC-G-T, where G represents the treatment atmosphere (N₂ or CO₂) and T the treatment temperature (600 or 750 °C).

Prior to catalytic testing, all materials were sieved, and the fraction with particle size below 100 µm was used.

The apparent material yield (%), was calculated as the ratio of the recovered dry mass (after HTC process) to the sum of the dry mass of molasses (i.e., carbon precursor) and the theoretical metal oxide mass obtained from the amount of metal precursor added to the HTC mixture. The dry mass of molasses was determined to be 30 g after drying the initial feed (40 g) in the laboratory oven overnight at 120 °C.

2.2. Materials Characterisation

The contents of SnO₂ and Al₂O₃ in the selected hybrid catalysts, together with the ash content of the parent hydrochar (C-HTC), were determined by TGA in air using a NETZSCH thermobalance (NETZSCH-Gerätebau GmbH, Selb, Germany). Approximately 10–15 mg of the sample was heated from 50 to 900 °C at 15 °C·min^{−1} under flowing air and held at 900 °C for 10 min until a constant residue mass was obtained.

Since the residual mass obtained after combustion of the hybrid materials comprises both the naturally occurring mineral ash and the introduced metal oxide, the ash content of the metal-free hydrochar (C-HTC) was first determined by TGA in air. The ash was assumed to originate solely from inorganic impurities present in sugarcane molasses. The measured ash content was then normalised to the carbonaceous fraction of each hybrid material and subtracted from the total residue to determine the actual metal oxide (SnO₂ or Al₂O₃) loading, as given by Equation (1).

$$\text{metal oxide (wt\%)} = 100 \times \frac{Ac - Ah}{1 - Ah} \quad (1)$$

where *Ac* is the residual mass fraction of the metal oxide–carbon hybrid after combustion in air, and *Ah* is the ash fraction of the pristine hydrochar (C-HTC).

The apparent material yield was calculated based on Equation (2), given below:

$$\text{Apparent material yield (\%)} = \frac{\text{mass of dry material}}{\text{mass of dry SCM} + \text{theoretical mass of Me}_x\text{O}_y} \quad (2)$$

where SCM is sugarcane molasses, and Me_xO_y is the corresponding metal oxide.

The amount of oxygen-containing surface groups was estimated by TGA under a nitrogen atmosphere. Approximately 10–15 mg of the sample was heated from 50 to 800 °C at 25 °C min^{−1} under an N₂. The mass loss observed was attributed to the thermal decomposition of oxygen-containing surface functionalities. Prior to analysis, the samples were dried at 100 °C for 2 h to remove adsorbed moisture.

The crystallinity and phase composition of the hybrid material were determined by X-ray diffraction (XRD) analysis. The XRD patterns were recorded using a BRUKER D8 Advance X-ray diffractometer equipped with a Johansson monochromator (Cu Kα₁ radiation, λ = 1.5406 Å) and a silicon strip detector LynxEye (Bruker AXS GmbH, Karlsruhe, Germany). The XRD patterns were recorded at room temperature with a step size of 0.05° over the 2θ range of 10–80°.

The total acidity, A_{tot} (mmol H⁺·g^{−1}), of the selected samples was determined by potentiometric back titration after equilibration with 0.01 M NaOH for 20 h. The excess NaOH in the filtrates was quantified using a Cerko Lab microtitration unit (Cerko Sp. z o.o., Gdynia, Poland), as described in our previously established method [6].

The acidity of selected thermally treated samples was characterised by NH₃ temperature-programmed desorption (NH₃-TPD) using a laboratory-built experimental setup comprising

a tubular furnace (Carbolite Gero Ltd., Hope, UK), a quartz reactor, a gas-flow control system, and a thermal conductivity detector (TCD; Gow-Mac Instrument Co., Bethlehem, PA, USA). Approximately 100 mg of the sample was pretreated at a helium flow rate of $100 \text{ cm}^3 \text{ min}^{-1}$ by heating to $500 \text{ }^\circ\text{C}$ at $10 \text{ }^\circ\text{C min}^{-1}$, followed by a 30 min isothermal hold. The sample was then cooled to $100 \text{ }^\circ\text{C}$ under helium ($100 \text{ cm}^3 \text{ min}^{-1}$), after which the carrier gas was switched to NH_3 . The sample was saturated with a 10 vol% NH_3/He gas mixture for 30 min. Subsequently, physisorbed NH_3 was removed by purging with helium at $100 \text{ }^\circ\text{C}$ for 1 h. The NH_3 -TPD profile was recorded by heating the sample from 100 to $500 \text{ }^\circ\text{C}$ at a rate of $10 \text{ }^\circ\text{C min}^{-1}$ under a helium flow of $100 \text{ cm}^3 \cdot \text{min}^{-1}$. The NH_3 desorption peaks were not integrated because the same mass of catalyst was used for all NH_3 -TPD measurements. Therefore, the relative peak areas are directly proportional to the total amount of desorbed ammonia and can be used to qualitatively compare total acidity among the investigated samples.

Textural properties, including specific surface area, pore volume, and pore size distribution, were evaluated by nitrogen adsorption–desorption isotherms at $-196 \text{ }^\circ\text{C}$ using an automated surface area and porosity analyser, Quantachrome Nova 4200e (Quantachrome Instruments, Boynton Beach, FL, USA). Approximately 100 mg of each sample was outgassed for 3 h at $150 \text{ }^\circ\text{C}$ prior to measurement. The apparent surface area (S_{BET}) was determined by using the BET equation, and the micropore volume (V_{micro}) and mesopore surface area (S_{meso}) were calculated using the t-plot method. The total pore volume (V_{tot}) was calculated from the N_2 adsorption branch at a relative pressure close to 0.99.

The surface morphology and microstructure of the materials were analysed by scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) using a FEI Quanta 400 FEG ESEM microscope (FEI Company, Hillsboro, OR, USA) equipped with an EDAX Genesis X4M detector (EDAX Inc., Mahwah, NJ, USA).

2.3. Catalytic Testing

The obtained materials were evaluated as heterogeneous catalysts for the microwave-assisted production of 5-hydroxymethylfurfural (HMF) from sucrose in water. To ensure the reliability and reproducibility of the catalytic results, selected catalytic experiments were performed in duplicate, and the variability observed between these duplicate experiments was represented by the error bars in the respective figure. The experimental error did not exceed 1.5%.

In a typical experiment, 10 mL of a 5 wt% aqueous sucrose solution and 0.06 g of catalyst were introduced into a sealed microwave vial and heated in an Anton Paar Monowave 200 microwave reactor. The reaction mixture was rapidly heated to $190 \text{ }^\circ\text{C}$ ($\approx 90 \text{ s}$), after which stirring was initiated at 650 rpm and maintained for 30 or 60 min. Upon completion, the reaction mixture was rapidly cooled to room temperature ($\approx 2 \text{ min}$) using compressed air.

The liquid products were diluted with ultrapure water and analysed quantitatively by HPLC using a Shimadzu LC-20AD system with a SIL-20A autosampler (Shimadzu Corporation, Kyoto, Japan). Sucrose, glucose, and fructose concentrations were determined using an Alltech OA-1000 organic sugar column (Alltech Associates, Inc., Deerfield, IL, USA) coupled to a refractive index detector (RID-20A, Shimadzu Corporation, Kyoto, Japan) under isocratic conditions with 5 mM H_2SO_4 as the eluent at a flow rate of 0.5 mL min^{-1} . The total run time is 15 min. The retention times were 7.4, 8.4, and 9.4 min for sucrose, glucose, and fructose, respectively.

HMF was quantified separately using a Hydrosphere C18 column ($250 \times 4.6 \text{ mm}$, $5 \text{ }\mu\text{m}$; YMC Co., Ltd., Kyoto, Japan) under isocratic conditions with 40 vol% methanol in water as the mobile phase, a flow rate of 0.4 mL min^{-1} , and UV detection (SPD-20AV

UV-Vis detector from Shimadzu Corporation, Kyoto, Japan) at 254 nm. The analysis had a total runtime of 13 min, and the HMF retention time was 10.3 min. Quantification was performed using external calibration curves with at least six calibration points prepared from authentic standards of sucrose, glucose, fructose, and 5-hydroxymethylfurfural (Sigma-Aldrich, Merck KGaA, Darmstadt, Germany). The calibration ranges were 6–54 g L^{−1} for sucrose, 2–18 g L^{−1} for glucose and fructose, and 2–15 g L^{−1} for 5-hydroxymethylfurfural (HMF), covering the concentration ranges encountered in the analysed reaction mixtures. The limits of detection (LOD) and quantification (LOQ) were not experimentally determined, as the method was developed for quantitative analysis within the expected concentration range of the reaction products. The calibration curve showed a linear response over the investigated concentration range, with a coefficient of determination (R^2) ≥ 0.98 . Sucrose conversion, product selectivities, and HMF yields were calculated according to Equations (3) and (4).

$$\text{Conversion of sucrose (\%)} = \frac{\text{Moles of sucrose converted}}{\text{Moles of sucrose initially used}} \times 100\% \quad (3)$$

$$\text{Selectivity to products (\%)} = \frac{\text{Moles of product formed}}{\text{Moles of sucrose converted}} \times 100\% \quad (4)$$

3. Results and Discussion

3.1. Results from Material Characterisation

3.1.1. Thermogravimetric Analysis, Material Yields, and Oxide Loading

The amount of metal oxides present in the selected samples was determined by thermogravimetric analysis (TGA), and the results are shown in Figure 1a. The calculated metal oxide loadings (as described in the experimental part) are reported in Table 1.

Table 1. The ash content and metal oxide loading in the samples determined from TG analyses performed in air.

Sample	Ashes (wt%)	Metal Oxide (wt%)
C-HTC	2.2	2.2
C-8.9SnO ₂ -HTC	30.6	29.0
C-17.3SnO ₂ -HTC	38.8	37.4
C-26.7SnO ₂ -HTC	44.7	43.5
C-Al-HTC	7.3	5.2

The TG results in Figure 1a confirmed that hybrid catalysts with varying SnO₂ contents were successfully produced using one-pot hydrothermal carbonisation of sugarcane molasses in the presence of metal salts. The results also demonstrated a non-linear relationship between the amount of Sn precursor (SnCl₂·2H₂O) used during synthesis and the resulting SnO₂ loading in the materials. While a twofold increase in precursor amount increased the oxide content by only 8.4 wt% (from 29.0 to 37.4 wt%), a threefold increase resulted in a total increase of just 14.5 wt% (Table 1).

All hybrid catalysts exhibited two overlapping DTG peaks with minima at 320–336 °C and 423–442 °C, indicating a two-step oxidation process involving less-stable, oxygen-rich carbon species and more-condensed carbon domains, respectively. Similar behaviour has been reported for grape-derived hydrochars [25]. Compared with pristine hydrochar, the shift in these peaks to lower temperatures suggests that SnO₂ and Al₂O₃ catalysed the oxidation of the carbon phase, indicating good dispersion and strong interaction between the metal oxide phases and the carbonaceous structure [26]. In contrast, C-HTC displayed

a broad DTG peak centred at $\sim 580^\circ\text{C}$, reflecting the heterogeneous nature of the hydrochar support, which comprises domains with varying resistance to oxidation (Figure 1a).

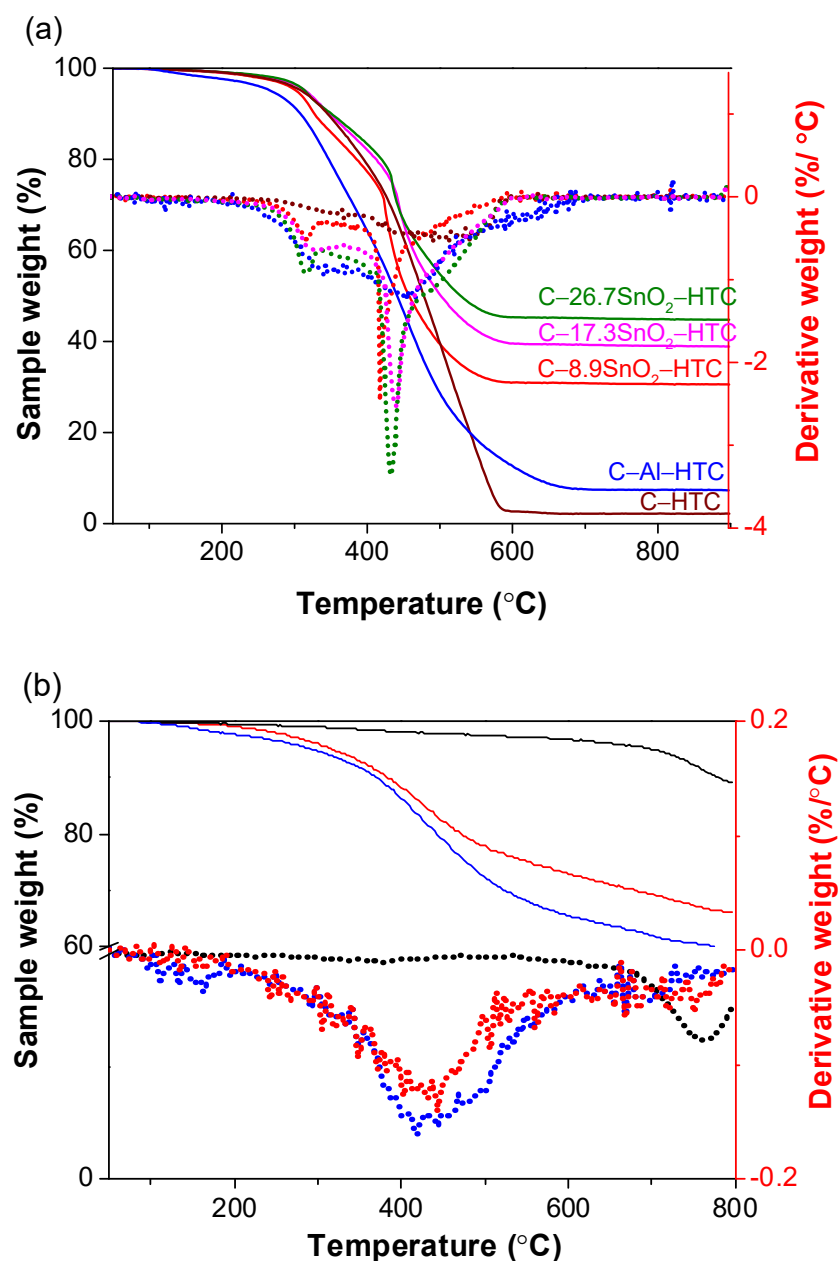


Figure 1. Thermogravimetric (TG) and derivative thermogravimetric (DTG) curves of selected samples recorded under air (a) and N_2 (b) atmospheres. TG curves are represented by solid lines, whereas DTG curves are shown by dotted lines. The legend shown in panel (a) applies to both panels; the samples are represented by the same colours in panel (b).

The apparent catalyst yield, the actual composition of the materials, and the metal retention (%) in the samples were determined from the dry masses of the materials obtained after hydrothermal carbonisation (HTC). The results are gathered in Table 2.

As demonstrated in Table 2, the apparent yield of the Sn-containing catalysts increased with Sn loading, likely due to the catalytic effect of Sn species on carbon formation during HTC. The resulting increase in carbonaceous material may explain the less-than-proportional rise in SnO_2 loading. At the same time, the decrease in Sn retention efficiency suggests a limited capacity of the hydrochar matrix to stabilise Sn species at higher precursor loadings. As a result, saturation of available anchoring sites may occur at elevated

precursor concentrations, leading to the formation of aggregated or weakly bound SnO_2 domains that are more prone to loss during subsequent processing steps.

Table 2. TGA-derived material yields, metal oxide loadings, and metal retention values.

Sample	Dry Mass of the Material (g) ^a	Theoretical Amount of MeOx (g) ^b	Apparent Material Yield (%) ^c	Actual Mass of Oxide in the Catalyst (g) ^d	Carbonaceous Fraction (g)	Metal Retention (%)
C-HTC	9.6	0.0	32.0	0.0	9.6	n.a
C-8.9SnO ₂ -HTC	15.3	5.9	42.6	4.4	10.9	66.1
C-17.3SnO ₂ -HTC	19.0	11.9	45.3	7.2	11.8	54.7
C-26.7SnO ₂ -HTC	23.1	17.8	48.3	10.0	13.1	53.3
C-Al-HTC	10.5	2.0	32.8	0.5	10.0	26.1

^a Dry mass of the material, weighed after drying in a laboratory oven. ^b Theoretical amount of metal oxide (Me_xO_y) calculated from the initial mass of precursor assuming complete conversion of the metal species to the corresponding oxide (e.g., $\text{Sn} \rightarrow \text{SnO}_2$, $\text{Al} \rightarrow \text{Al}_2\text{O}_3$). ^c Apparent material yield calculated according to Equation (2) shown in the Experimental Part. ^d Actual mass of Me_xO_y in the dry material, calculated from the metal oxide content (in wt%) determined by TG analysis in air, listed in Table 1.

In contrast, comparable apparent yields were obtained for C-HTC and C-Al-HTC, suggesting that the presence of Al species did not significantly influence the amount of material produced during HTC. It should be pointed out that although the XRD analysis of the as-prepared C-Al-HTC sample (discussed below) indicated the presence of aluminium hydroxide and oxyhydroxide species, these phases undergo thermal decomposition and transformation into Al_2O_3 during TG analysis in air [27,28]. Therefore, the remaining ashes after TG analysis of this sample in air are reported as Al_2O_3 equivalents. With this in mind, the estimated loading of Al_2O_3 in C-Al-HTC derived from TGA (5.2 wt%) was markedly lower than the theoretical value of Al_2O_3 expected (~14 wt%), pointing to strongly limited incorporation of aluminium species into the hydrochar matrix. Moreover, significantly lower metal retention was observed for C-Al-HTC than for the Sn-based materials (26.1% vs. 53–66%, Table 2). This difference in metal retention can be attributed to the distinct hydrolysis and coordination chemistry of the respective precursors. Aluminium species derived from $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ are known to remain highly soluble and mobile under hydrothermal conditions [29], forming stable hydrated complexes. These Al-rich phases appeared to interact less effectively with the developing hydrochar matrix during HTC and were therefore more susceptible to removal during the subsequent washing and filtration steps.

The thermal stability of the selected samples was studied by performing the TG analyses in N_2 flow, and the results are shown in Figure 1b. The amount of volatile species released during heating under an inert atmosphere can be associated with the number of oxygen functionalities on the carbonaceous phase [30], while the mass of the inorganic phase remains largely intact. As shown, the mass of the materials decreased gradually and continuously with increasing temperature. The TG profiles exhibited a multistep mass-loss pattern. The mass loss at lower temperatures ($T < 150^\circ\text{C}$) is associated with the removal of moisture and physisorbed water. This contribution is more pronounced in C-Al-HTC than in the Sn-derived counterparts. This is most likely due to the higher proportion of hydrochar in this sample, which demonstrates a hygroscopic behaviour [21]. Subsequently, a gradual mass decrease can be observed in the range of 150–400 $^\circ\text{C}$ related to the decomposition of labile oxygen-containing surface groups (e.g., carboxylic and anhydrides) [31], and residual low-molecular-weight organic species originating from incomplete carbonisation of sugarcane molasses. Importantly, a more pronounced mass loss in this temperature range is observed for the composites containing hydrochars (C-8.9-SnO₂-HTC and C-Al-HTC) compared to the carbonised sample (i.e., C-8.9-SnO₂-N₂-600), reflecting their higher content of labile oxygen-containing functionalities and lower degree of carbon condensation. The minima in the DTG curves (Figure 1b) indicated the temperatures at which the rate of mass

loss (i.e., thermal degradation) of the material is the highest. For the hydrochar-containing samples, the maximum degradation rate occurred at approximately 430 °C, corresponding to the decomposition of residual polysaccharides and furanic structures formed during HTC. The DTG minimum was observed at 427 °C for C-Al-HTC and 435 °C for C-8.9SnO₂-HTC, indicating slightly higher thermal stability of the Sn-containing hydrochar. At higher temperatures (≈400–800 °C), gradual mass loss was associated with carbon restructuring and the decomposition of stable oxygen-containing functionalities [6,32]. In contrast, C-8.9SnO₂-N₂-600 exhibited much lower mass loss between 150 and 700 °C, indicating a more stable carbon structure and lower oxygen functionality content. Therefore, C-8.9SnO₂-N₂-600 exhibited its maximum weight loss above 550 °C, with the highest degradation rate at 760 °C, reflecting continued carbon restructuring and the removal of residual thermally stable oxygen-containing groups.

The total mass loss under N₂ decreased in the order C-Al₂O₃-HTC (40.4 wt%) > C-8.9SnO₂-HTC (34.7 wt%) > C-8.9SnO₂-N₂-600 (11.0 wt%). These results indicated that the untreated hybrid material contained a high concentration of oxygen-rich surface functionalities, including carboxylic, lactonic/anhydride, and hydroxyl groups, which acted as Brønsted acid sites. However, most of these groups were removed during thermal treatment at 600 °C.

3.1.2. XRD Analysis

The crystal structure of the catalysts was analysed by X-ray diffraction (XRD), and the results are shown in Figure 2. The XRD patterns of C-8.9SnO₂-HTC and C-26.7SnO₂-HTC (Figure 2a) exhibited broad reflections at $2\theta \approx 27^\circ, 34^\circ, 38^\circ, 52^\circ, 55^\circ, 62^\circ$, and 66° , characteristic of tetragonal rutile SnO₂ (JCPDS 21-1250) [33]. These results confirm the successful formation and incorporation of SnO₂ into the hydrochar matrix during the one-pot hydrothermal synthesis. The absence of distinct carbon-related diffraction peaks is consistent with the predominantly amorphous nature of the hydrochar and its low degree of structural ordering [34].

The pronounced structural changes were observed after thermal post-treatment of C-8.9SnO₂-HTC, as evidenced by the appearance of new diffraction peaks in the respective XRD patterns. Regardless of the conditions used during the post-treatments, new reflections corresponding to metallic Sn and SnO phases were detected, indicating the partial reduction of SnO₂ at elevated temperatures (reactions 5–7 below) [35]. Furthermore, the diffraction peaks attributed to SnO₂ became sharper as compared to those observed for C-8.9SnO₂-HTC, indicating enhanced crystallinity or increased domain size. However, no clear evidence of agglomeration was observed in the SEM images, as discussed below.



Interestingly, the sample treated under N₂ at 600 °C exhibited greater peak overlap and more intense reflections associated with SnO_x phases, indicating the presence of multiple intermediate non-stoichiometric tin oxide phases likely formed under an inert atmosphere. In contrast, the material treated under CO₂ at 750 °C displayed sharper, better-defined diffraction peaks with significantly less overlap, primarily corresponding to the SnO₂ and Sn phases. The increased intensity and definition of the XRD reflections following CO₂ treatment indicated enhanced crystallinity of the Sn-containing phases, which may facilitate the exposure of active sites at the oxide surface. These changes can be attributed to the combined effect of thermal treatment and CO₂ gasification during pyrolysis. In

contrast, thermal treatment in N_2 at 600 °C likely limited the extent of reduction and phase segregation, favouring the formation of intermediate and/or poorly crystalline SnO_x phases containing mixed tin oxidation states.

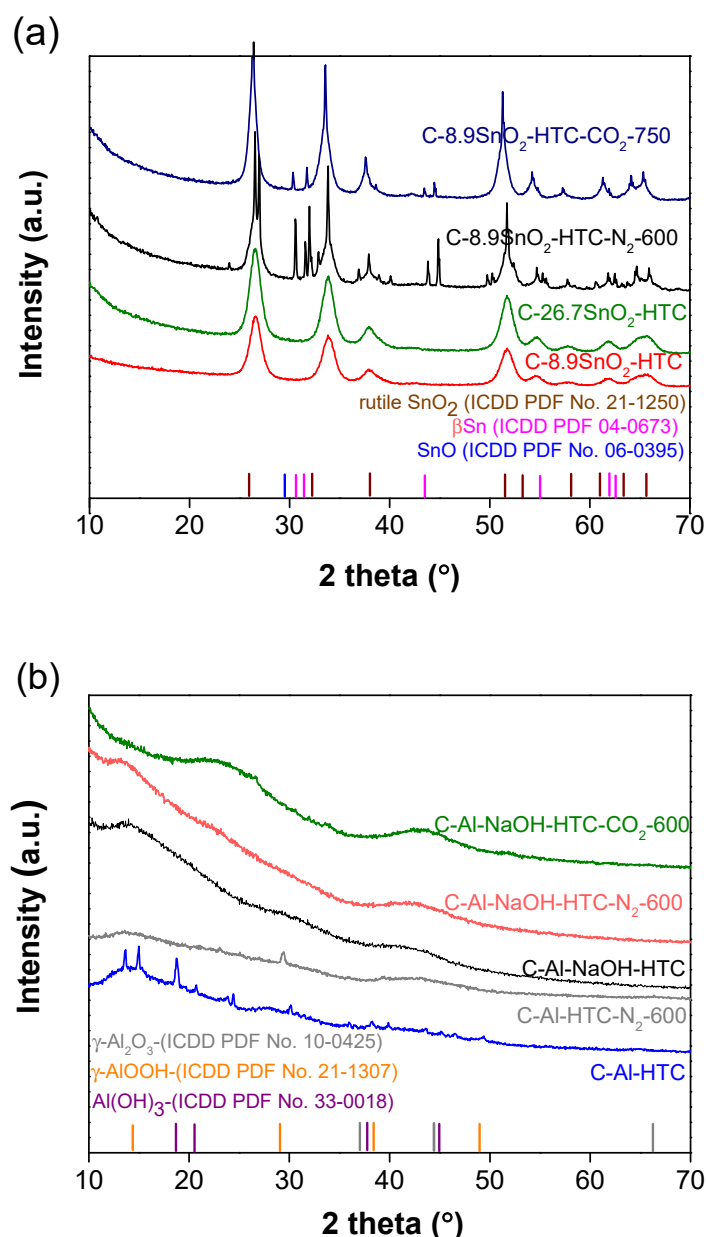


Figure 2. XRD patterns of the selected (a) SnO_2 -C and Al-C samples (b). Reference diffraction stick patterns (PDF/JCPDS cards) of the identified crystalline phases are shown in the experimental diffractograms.

As described in the Experiment Section 2.1.2, the Al-containing materials were synthesised both with and without the addition of NaOH (samples Al-HTC and Al-NaOH-HTC, respectively). Interestingly, Al-NaOH-HTC appeared as a brown powder (Figure 3a), whereas the sample prepared without NaOH formed a black solid typical of sugar-derived hydrochars (Figure 3b). The lighter colour of Al-NaOH-HTC may be attributed to altered hydrothermal carbonisation pathways under alkaline conditions, resulting in a lower degree of aromatisation and/or greater retention of oxygen-containing functionalities [36].

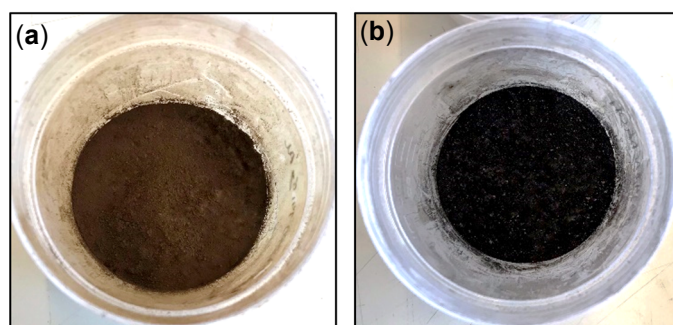


Figure 3. Differences between obtained samples: (a) the reaction with the addition of NaOH (sample Al-NaOH-HTC) and (b) HTC performed without the addition of NaOH (sample Al-HTC).

The XRD patterns of the representative Al-containing catalysts are shown in Figure 2b. The diffraction features observed for Al-HTC were strongly suggestive of boehmite (AlOOH), although weak reflections attributable to $\text{Al}(\text{OH})_3$ and Al_2O_3 were also detected [24,37,38]. According to Mishra, crystalline boehmite forms rapidly under acidic hydrothermal conditions at temperatures $\geq 180^\circ\text{C}$ [39]; therefore, it was expected to be present in both Al-containing hydrochars. The weak but distinguishable reflections observed for Al-HTC indicate that part of the Al phase was present in a structurally defined form.

In contrast, Al-NaOH-HTC exhibited only a broad halo characteristic of amorphous carbon, with no distinct diffraction peaks associated with crystalline aluminium phases. These differences are likely related to the synthesis pH. Under acidic conditions, interactions between humic substances and aluminium hydroxides may promote the formation of more ordered Al-containing domains, whereas alkaline conditions favour rapid precipitation of highly dispersed or amorphous aluminium hydroxide/oxyhydroxide species [40]. This may explain the small but distinguishable XRD peaks observed for C-Al-HTC. Consequently, the absence of distinct Al-related reflections in Al-NaOH-HTC is likely associated with the formation of amorphous and/or highly dispersed Al species embedded within the carbon matrix rather than the absence of Al-containing phases. Similar XRD patterns have been reported for biochar-supported amorphous alumina [41].

After thermal treatment under N_2 (Al-HTC- N_2 -600), the diffraction peaks assigned to AlOOH , $\text{Al}(\text{OH})_3$, and Al_2O_3 largely disappeared, indicating substantial structural rearrangement of the Al-containing phases. This behaviour can be attributed to the dehydroxylation of $\text{AlOOH}/\text{Al}(\text{OH})_3$ [27] and the formation of poorly crystalline transition aluminas, whose broad reflections may be masked by the carbon matrix. The occurrence of dehydroxylation is further supported by the significant decrease in total acidity (A_{tot}) after thermal treatment (Table 3), as discussed below.

Table 3. Total acidity (A_{tot}) values for the selected hydrochar-based materials.

Sample	Total Acidity, A_{tot} ($\text{mmol H}^+ \cdot \text{g}^{-1}$)
C-HTC	1.5
C-8.9SnO ₂ -HTC	2.7
C-26.7SnO ₂ -HTC	2.2
C-8.9SnO ₂ -HTC- N_2 -600	0.1
C-Al-HTC	3.1
C-Al-NaOH-HTC	3.4
C-Al-HTC- N_2 -600	0.0
C-Al-NaOH-HTC-CO ₂ -750	0.8

Likewise, thermal treatment did not result in the appearance of distinct crystalline Al-containing phases in Al-NaOH-HTC, suggesting that the Al species remained highly dispersed and poorly crystalline within the carbon matrix. This observation agrees with the findings of Hu et al. [28], who reported that Al species derived from aluminium nitrate nonahydrate remained amorphous or poorly crystalline up to 800 °C. However, the CO₂-treated sample (C-Al-NaOH-CO₂-750) exhibited slightly more pronounced diffraction features than its N₂-treated counterpart, likely due to partial gasification of the carbon matrix, which exposed Al-containing domains previously masked by amorphous carbon. This interpretation is consistent with the NH₃-TPD results, which revealed the highest concentration of accessible acid sites for the corresponding CO₂-treated Al-containing catalyst.

3.1.3. Total Brønsted Acidity (A_{tot})

The acid–base titration method used in this work has been widely applied to determine the total Brønsted acidity (A_{tot}) of hydrochars [8,12,42]. However, hydrochars may release soluble organic and inorganic species during the titration procedure [43]. Accordingly, yellow to brown filtrates were observed in this work after equilibration of the Sn- and Al-containing hydrochars with NaOH, and the presence of dissolved species was confirmed by UV–Vis spectroscopy at 254 nm. The darker and more intense colouration of the Al-containing samples suggests that Al species promote the formation of partially soluble products during HTC. As these species may also consume NaOH, the A_{tot} values reported here should be regarded as apparent acidity values.

As shown in Table 3, the total Brønsted acidity was strongly influenced by both the incorporated metal species and the post-treatment conditions. The reference hydrochar (C-HTC) exhibited a moderate acidity of 1.5 mmol H⁺·g^{−1}, consistent with values reported for sugar-derived hydrochars [8,12]. The incorporation of Sn or Al species increased the acidity to 2.7–3.4 mmol H⁺·g^{−1}. Notably, Al-containing composites exhibited higher acidity despite their significantly lower metal loading compared to the Sn-containing materials (Table 3). This observation suggests that Al-containing phases promote the formation and/or stabilisation of acidic surface functionalities more effectively than SnO_x species. The higher A_{tot} observed for the Al-containing hydrochars may be associated with their predominantly amorphous character and the formation of poorly crystalline or amorphous boehmite-like domains, as evidenced by the XRD results and their rich surface hydroxyl groups (see Figure 2b). Additionally, the hydroxyl groups on the Al-containing phases may contribute to the Brønsted acidity of the hybrid catalyst [44].

In contrast, the Sn-containing hydrochars were dominated by SnO₂/SnO_x phases, as confirmed by the XRD results (Figure 2a). These phases, according to the literature [36], are known to exhibit mainly Lewis acidity and only a limited number of Brønsted-acidic sites. Consequently, the measured A_{tot} is primarily associated with oxygen-containing surface functionalities of the hydrochar matrix rather than the SnO₂/SnO_x phases themselves.

It is also worth noting that the A_{tot} values for the Sn-containing hybrid catalysts decreased from 2.7 to 2.2 mmol H⁺·g^{−1} as the amount of Sn precursor increased. This result is most likely associated with the progressive coverage of the carbon surface by Sn-containing phases, as well as changes in the hydrothermal carbonisation pathways induced by the metal precursor. These conclusions are consistent with the non-proportional increase in SnO₂ loading observed despite the increasing amounts of Sn precursor used (see Tables 1 and 2).

Notably, thermal treatment under N₂ at 600 °C of Sn- and Al-containing hydrochars almost completely removed the Brønsted acidity from both samples, as shown by the

values of 0.1 and 0.0 mmol $\text{H}^+ \cdot \text{g}^{-1}$ for C-8.9SnO₂-HTC-N₂-600 and C-Al-HTC-N₂-600, which agrees with our TG results.

Interestingly, the sample treated under CO₂ (sample C-Al-NaOH-HTC-CO₂-750) exhibited significantly higher Brønsted acidity (0.8 mmol $\text{H}^+ \cdot \text{g}^{-1}$) despite the partial dehydroxylation of Al-containing species expected at elevated temperatures [17,27]. This observation is consistent with the XRD results (Figure 2b), which showed more pronounced diffraction features in this material, suggesting increased exposure of Al-containing domains due to partial gasification of the amorphous carbon matrix. In addition, the literature shows that CO₂ activation can promote the formation and exposure of oxygen-containing surface functionalities on carbon materials [17], which may also contribute to the increased acidity of this sample.

To complement the potentiometric titration results and evaluate total acidity alongside the acid-strength distribution, representative thermally treated catalysts were further characterised by NH₃ temperature-programmed desorption (NH₃-TPD). The corresponding results are discussed in the following section.

3.1.4. NH₃-TPD Analysis

Ammonia is an excellent probe molecule for characterising the acidic properties of solid catalysts, as its strong basicity and small molecular size allow the detection of acid sites even within very narrow pores [45,46]. According to the commonly accepted classification, acid sites are categorised as weak (<200 °C), medium (200–400 °C), and strong (>400 °C) based on the NH₃ desorption temperature [46]. Importantly, NH₃-TPD provides only information on the total acidity and the acid-strength distribution of the catalyst surface and does not distinguish between Brønsted and Lewis acid sites [45].

The NH₃-TPD profiles of the selected thermally treated catalysts are presented in Figure 4. The desorption profiles revealed clear differences in both the amount and strength distribution of acid sites among the investigated materials. The C-Al-HTC-NaOH-CO₂-750 catalyst exhibited the highest NH₃ desorption intensity over a broad temperature range (approximately 150–430 °C), indicating the highest concentration of accessible acid sites. Two desorption maxima were observed at approximately 160 °C and 210 °C, corresponding to weak and medium-strength acid sites, respectively, followed by a broad desorption shoulder extending to approximately 450 °C. This broad desorption profile indicates a wide distribution of acid sites with different strengths, extending from weak to medium and strong acidity [47].

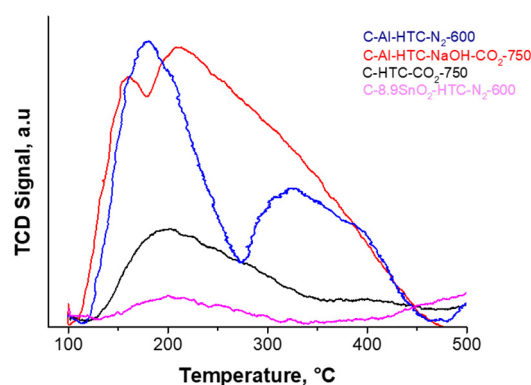


Figure 4. NH₃-temperature programmed desorption (NH₃-TPD) profiles of selected thermally treated carbon-based catalysts. The TCD signal recorded during NH₃ desorption reflects the total acidity and the distribution of acid strengths of the investigated catalysts.

Similarly, C-Al-HTC-N₂-600 exhibited a pronounced NH₃ desorption profile with a major peak centred at approximately 180 °C, accompanied by a broader overlapping

desorption band with a maximum at approximately 325 °C and a tail extending towards higher temperatures. This profile indicates the presence of weak and medium-strength acid sites, together with a smaller contribution of strong acid sites associated with the high-temperature desorption tail. However, compared with C-Al-HTC-NaOH-CO₂-750, the contribution of medium- and strong-acid sites was considerably lower, suggesting that weak acid sites predominated in C-Al-HTC-N₂-600.

In contrast, C-HTC-CO₂-750, prepared without the addition of metal species, exhibited a considerably lower NH₃ desorption intensity, with a broad maximum centred at approximately 200 °C, indicating a lower concentration of accessible weak- and medium-strength acid sites. These results demonstrate that the incorporation of aluminium species increased the total acidity of the catalysts, consistent with the higher apparent Brønsted acidity (A_{tot}) determined by potentiometric titration (Table 3). Furthermore, the NH₃-TPD profiles of the Al-containing catalysts indicate a broader distribution of acid strengths, leading to a greater contribution from medium-strength acid sites. Combined with the XRD results, these findings suggest that the aluminium-containing phases contributed to this behaviour.

Comparison of the NH₃-TPD profiles of the Al-containing catalysts demonstrates that both the addition of NaOH during hydrothermal carbonisation and the subsequent thermal treatment atmosphere significantly influenced the distribution of acid sites. In particular, the NaOH-derived catalyst activated under CO₂ exhibited a broader desorption profile extending towards higher temperatures, indicating a greater contribution of medium-strength acid sites than the catalyst thermally treated under N₂.

On the other hand, C-8.9SnO₂-HTC-N₂-600 displayed only a weak and broad desorption profile with a maximum at approximately 200 °C and a shoulder extending to around 330 °C, consistent with its low total acidity (A_{tot} , Table 3). This behaviour is consistent with the partial reduction of Sn oxide species observed by XRD (Figure 2a), which may decrease the number of accessible acidic surface sites. Similar NH₃-TPD profiles have previously been reported for SnO₂–carbon composites prepared by hydrothermal carbonisation [22].

Overall, the NH₃-TPD results complement the potentiometric titration data by demonstrating that the catalysts differ not only in the total amount of acidity but also in the distribution of acid strengths. The combination of a higher concentration of accessible medium-strength acid sites together with the well-developed porous structure of C-Al-HTC-NaOH-CO₂-750 is likely to contribute to its superior catalytic performance in the conversion of sucrose to HMF.

3.1.5. Textural Analysis

The textural properties of the samples are summarised in Table 4. All thermally treated materials exhibited both micro- and mesoporosity. The reference hydrochar treated under N₂ at 600 °C showed a very low surface area (22 m²·g^{−1}), whereas CO₂ treatment at 750 °C increased the S_{BET} to 384 m²·g^{−1} due to the activating effect of CO₂ and the Boudouard reaction [17]. The ratio of micropore volume to total pore volume ($V_{\text{micro}}/V_{\text{tot}}$) was calculated and included in Table 4 to evaluate the relative contribution of microporosity to the overall pore structure. As shown by this data, most CO₂-treated samples exhibited higher micropore fractions (0.37–0.71) than their N₂-treated counterparts (0.04–0.55), indicating that CO₂ activation preferentially promoted microporosity development while preserving a significant mesoporous network.

Increasing the Sn loading slightly enhanced the S_{BET} and V_{meso} of the N₂-treated materials, likely due to Sn species influencing the carbonisation process and the development of interparticle mesoporosity. Overall, the incorporation of Sn and Al species significantly improved pore development, with most N₂-treated samples exhibiting S_{BET} values above 300 m²·g^{−1}. Al-containing materials exhibited significantly enhanced meso-

porosity, particularly Al-HTC-N₂-600, which showed an estimated mesopore volume of 0.184 cm³·g^{−1}. The presence of alumina species in carbon-based hybrid catalysts has previously been linked with the development of porosity [48]. The highest micropore volume, 0.148 cm³·g^{−1}, was observed for Al-NaOH-HTC-CO₂-750, probably due to the combined effect of NaOH-promoted hydrochar restructuring and CO₂ activation of the sample. The improved pore structure was also reflected in the NH₃-TPD results (see Figure 4), with the CO₂-treated catalyst exhibiting the highest NH₃ desorption intensity, suggesting that increased surface area and porosity enhanced access to acid sites. In contrast, the very low S_{BET} and V_{micro} values of C-Al-NaOH-HTC-N₂-600 indicate that thermal treatment under N₂ alone was insufficient to develop a well-developed pore structure. This interpretation is consistent with the XRD results (Figure 2b), in which the Al-containing phases exhibited only weak diffraction features, suggesting they remained largely embedded within the carbon matrix.

Table 4. Textural properties of the selected materials.

Catalyst	S _{BET} (m ² ·g ^{−1})	S _{meso} (m ² ·g ^{−1})	V _{micro} (cm ³ ·g ^{−1})	V _{meso} (cm ³ ·g ^{−1})	V _{tot} (cm ³ ·g ^{−1})	V _{micro} /V _{tot}
HTC-N ₂ -600	22	16	0.002	0.018	0.02	0.10
HTC-CO ₂ -750	384	103	0.124	0.076	0.20	0.62
C-8.9SnO ₂ -HTC-N ₂ -600	358	96	0.115	0.095	0.21	0.55
C-8.9SnO ₂ -HTC-CO ₂ -750	380	68	0.135	0.055	0.19	0.71
C-26.7SnO ₂ -HTC-N ₂ -600	371	99	0.114	0.126	0.24	0.48
C-26.7SnO ₂ -HTC-CO ₂ -750	390	126	0.122	0.168	0.29	0.42
C-Al-HTC-N ₂ -600	314	95	0.086	0.184	0.27	0.32
C-Al-HTC-CO ₂ -750	335	96	0.099	0.171	0.27	0.37
C-Al-NaOH-HTC-N ₂ -600	25	22	0.002	0.048	0.05	0.04
C-Al-NaOH-HTC-CO ₂ -750	420	50	0.148	0.062	0.21	0.71

3.1.6. Scanning Electron Microscopy and Energy Dispersive Spectroscopy (SEM-EDS)

The morphology of the CO₂-treated hydrochar prepared without a metal precursor (Figure 5a) consisted of irregular particles and aggregated carbon spheres typical of HTC products [6,8]. Large cavities (~20 µm) and Ca-rich inorganic residues originating from sugarcane molasses were also observed.

Similarly, C-8.9SnO₂-HTC (Figure 5b) was mainly composed of aggregated spherical particles, although the addition of Sn resulted in the formation of smaller, more regular particles and a few rod-like structures. EDS analysis (Table 5) revealed that the spheres were predominantly carbonaceous (6.9 wt% Sn), while the rods were highly enriched in Sn (75.8 wt%), indicating the formation of distinct Sn-rich domains during HTC.

Table 5. Elemental composition of the selected samples determined by energy-dispersive X-ray spectroscopy (EDS). Results are expressed in wt% and correspond to the average composition obtained from the analysed regions.

Sample	Zone	C wt%	O wt%	Sn/Al wt%
C-8.9SnO ₂ -HTC	Z1	67.2	22.9	6.9
	Z2	13.4	7.8	75.8
C-8.9SnO ₂ -CO ₂ -750	Z3	19.4	6.7	74.0
	Z4	71.6	15.7	12.7
	Z5	40.4	16.3	43.3
C-8.9SnO ₂ -N ₂ -600	Z6	41.7	15.1	43.2
	Z7	49.2	15.3	35.6
C-Al-HTC	Z8	64.3	24.9	10.8
	Z9	62.6	32.8	4.7
C-Al-NaOH-HTC	Z10	54.5	37.8	7.7
	Z11	36.9	40.3	22.8

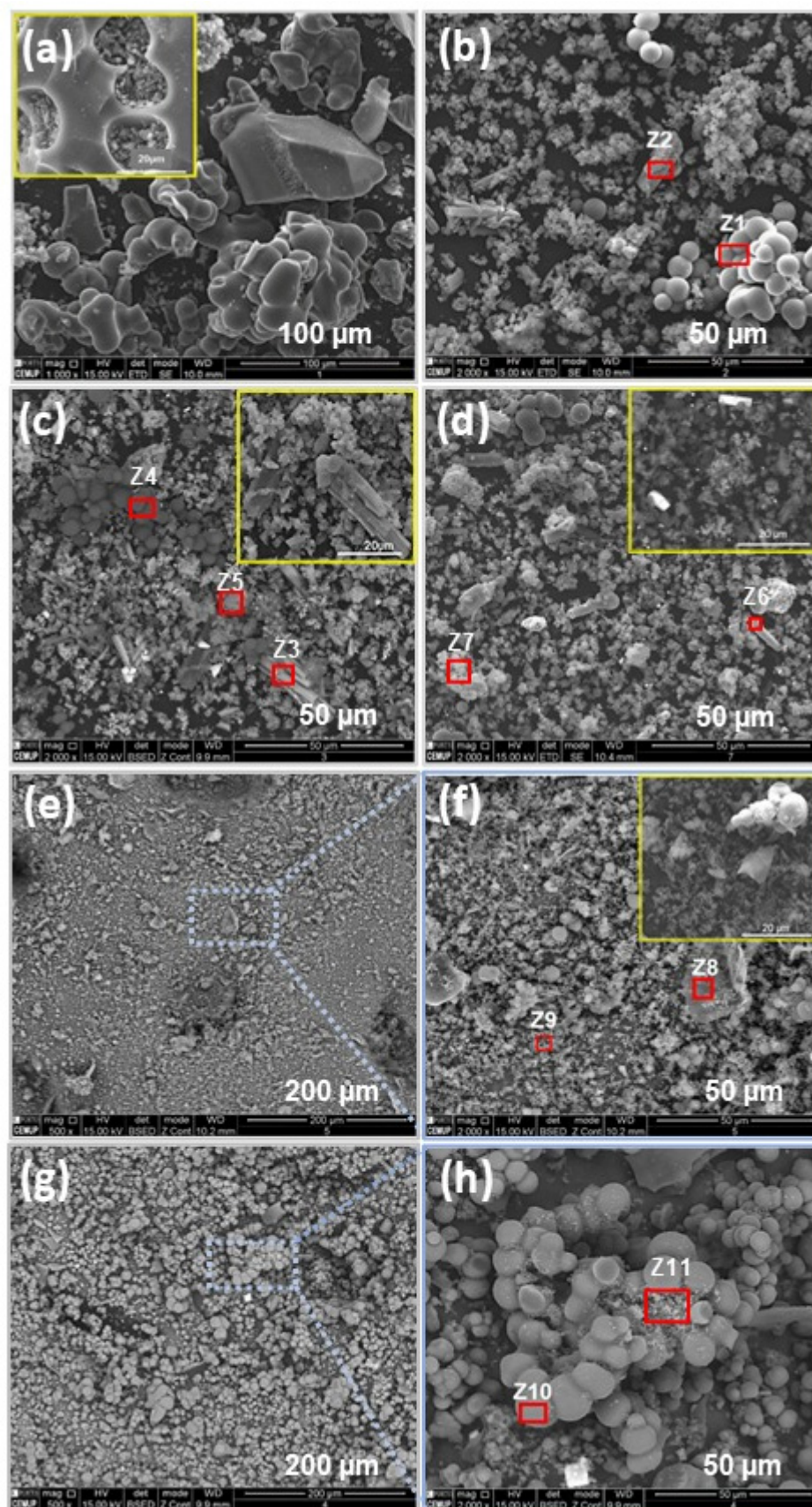


Figure 5. SEM images of the prepared carbon materials with marked EDS analysis regions (a) C-CO₂-750, (b) C-8.9SnO₂-HTC, (c) C-8.9SnO₂-HTC-CO₂-750, (d) C-8.9SnO₂-HTC-N₂-600, (e,f) C-Al-HTC, (g,h) C-Al-NaOH-HTC.

No significant changes in morphology were observed after thermal treatment of Sn-containing hybrid materials under CO₂ or N₂ (Figure 5c,d). EDS analysis confirmed the presence of C, O, and Sn, while the absence of chlorine suggested a complete conversion of the precursor into SnO₂/SnO_x phases. EDS results demonstrated that in the CO₂-treated sample, carbon-rich and Sn-rich domains coexisted, whereas regions analysed in the N₂-treated sample exhibited similar compositions despite differences in morphology.

SEM images revealed that the addition of NaOH strongly influenced the morphology of the Al-containing hydrochars. C-Al-HTC prepared without NaOH (Figure 5e,f) exhibited a heterogeneous morphology composed of irregular agglomerates, fused spherical particles, and nanosheet-like structures. In contrast, C-Al-NaOH-HTC (Figure 5g,h) exhibited predominantly spherical particles with a broad size distribution partially fused into larger aggregates, consistent with the alkaline precipitation and growth of Al hydroxide/oxyhydroxide species during hydrothermal carbonisation. Plate-like domains were also observed, which is a typical morphology for boehmite or aluminium hydroxides formed under hydrothermal conditions [39].

3.2. Catalytic Results

The prepared Sn- and Al-carbon catalysts were evaluated in the conversion of sucrose to 5-hydroxymethylfurfural (HMF) in water without co-solvents. Complete sucrose conversion was achieved in all experiments; therefore, selectivities were equivalent to product yields. As shown in Scheme 1, HMF formation is normally accompanied by side reactions, including rehydration to organic acids and polymerisation/condensation into soluble oligomers and insoluble humins [14]. Thus, the development of catalysts for HMF production from sucrose requires that the active sites be tailored to facilitate the desired intermediate reaction steps (hydrolysis, isomerisation, and dehydration) while limiting competing side reactions, especially humin formation.

3.2.1. Influence of the Catalyst, Reaction Time and the Type of Metal Oxide

Figure 6 compares the catalytic performance of representative Sn- and Al-containing hydrochars (C-8.9SnO₂-HTC and C-Al-HTC) with that of the blank reaction in the conversion of sucrose to HMF as a function of reaction time. After 30 min, C-8.9SnO₂-HTC produced approximately 23% glucose, 0.7% fructose, and 23.9% HMF, whereas C-Al-HTC yielded 11.6% glucose, 7.8% fructose, and 33.3% HMF. Extending the reaction time to 1 h decreased the yields of C6 sugars and HMF for both catalysts, likely due to secondary reactions such as humin formation and HMF rehydration (Scheme 1). Interestingly, the blank experiment, conducted under identical reaction conditions in the absence of a catalyst, also resulted in complete conversion of sucrose, yielding 49.2% glucose, 3.1% fructose, and 26.1% HMF after 30 min. These results indicate that hot-compressed water at temperatures above 160 °C promotes sucrose hydrolysis and subsequent sugar transformations, as discussed in the Introduction. Nevertheless, the high glucose and low fructose yields in the blank experiment indicated that, in the absence of a catalyst, fructose is preferentially dehydrated to HMF, whereas the more stable glucose largely remains unconverted due to the lack of catalytic isomerisation. The results further demonstrated that the catalysts significantly altered the product distribution. In particular, C-Al-HTC increased the HMF yield while markedly reducing the glucose concentration, indicating more efficient glucose isomerisation and fructose dehydration. This behaviour can be attributed to the combined presence of Lewis-acidic Al-containing domains [17] and Brønsted-acidic oxygen-containing surface functionalities, as evidenced by the XRD, TG, NH₃-TPD and A_{tot} obtained from potentiometric titration. In contrast, C-8.9SnO₂-HTC afforded a lower HMF yield, suggesting that

competing reaction pathways limited fructose dehydration, or that further conversion of HMF was occurring on the surface of this catalyst.

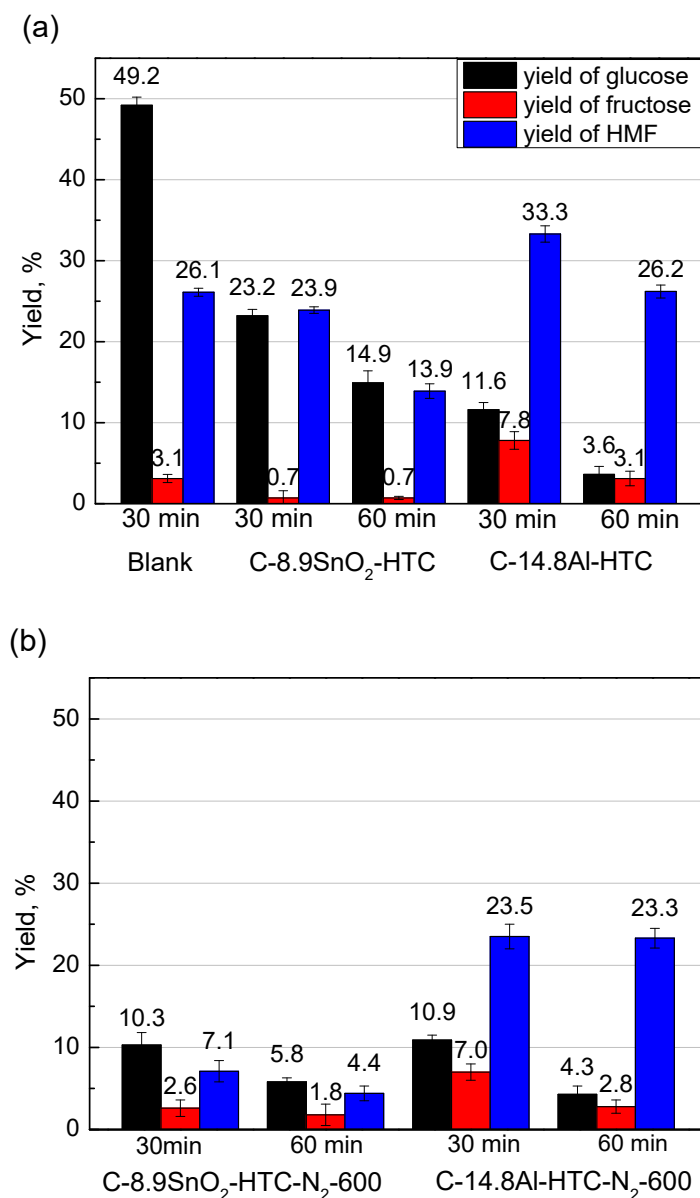


Figure 6. Influence of reaction time and the type of metal oxide on the catalytic performance in sucrose transformation of selected hydrochars before (a) and after thermal treatment under N₂ flow at 600 °C, (b) reaction conditions: T = 190 °C, 5% sucrose in water, 0.06 g catalyst, t = 30 or 60 min, stirring speed = 650 rpm. Blank is the experiment carried out in the absence of a catalyst. Error bars indicate the standard deviation of duplicate experiments for the corresponding data points. The colour coding shown in the legend of panel (a) also applies to panel (b).

Overall, the presence of the catalyst had no effect on sucrose conversion, which was complete in all experiments, but it altered the reaction pathway by promoting the Lewis acid-catalysed isomerisation of the more stable glucose into fructose, and further dehydration of fructose to HMF. The presence of the catalyst also appeared to limit competing side reactions, including humin formation, as indicated by the lower amount of dark insoluble deposits compared with the blank reaction.

In fact, the formation of humins was observed in all reactions, but it was particularly evident in the blank experiment performed without a catalyst. In this case, a dark, sticky, insoluble solid was visibly deposited on the walls of the reaction vial and on the

magnetic stirrer, indicating extensive humin formation. In the catalytic experiments, the recovered catalysts showed an increase in mass after the reaction, suggesting that a fraction of the humins was deposited on the catalyst surface, in addition to the free insoluble material remaining on the reactor walls. Therefore, the difference between the quantified amounts of sugars and HMF in the carbon balance can most likely be attributed to the formation of humins, which are well-known by-products of acid-catalysed carbohydrate dehydration [12,49]. However, accurate quantification of humins is particularly challenging because they are distributed among several fractions, including insoluble deposits on the reactor walls, species adsorbed on the catalyst surface, and soluble humin-like oligomers remaining in the liquid phase [50,51]. Consequently, a complete and accurate carbon balance could not be established within the scope of this work.

The consistently low fructose yields observed over C-8.9SnO₂-HTC, irrespective of reaction time, suggest that fructose did not accumulate in the reaction medium because it was rapidly converted into HMF and/or secondary products. The evolution of product yields revealed distinct reaction pathways for the two hydrochars. For C-Al-HTC, the simultaneous decrease in glucose and fructose yields indicates that both monosaccharides were readily consumed in subsequent reactions. Conversely, over C-8.9SnO₂-HTC, fructose was preferentially consumed while glucose accumulated, suggesting less efficient glucose isomerisation.

The influence of reaction time was also investigated using the N₂-treated catalysts, and the results are shown in Figure 6b. Overall, thermal treatment significantly reduced catalytic activity compared with the parent hydrochars. The HMF yield over the Sn-containing catalyst decreased from 23.9% to 7.0%, whereas a less pronounced reduction was observed for the Al-containing counterpart (from 33.3% to 23.5%). Similar to the parent hydrochars, increasing the reaction time from 30 to 60 min resulted in lower yields of intermediates and HMF. However, the decline in HMF yield was less pronounced for the thermally treated materials, suggesting a reduced tendency to promote secondary HMF degradation reactions and, consequently, greater HMF accumulation in the reaction medium.

Importantly, the thermally treated catalysts exhibited almost no apparent Brønsted acidity (Table 3). Consequently, fructose dehydration was likely promoted mainly by H₃O⁺ ions generated under hydrothermal conditions [9], while the remaining catalyst acidity revealed by NH₃-TPD of sample C-Al-HTC-N₂-600. However, this assignment remains only tentative because NH₃-TPD does not distinguish between Brønsted and Lewis acidity. Thus, the marked decrease in HMF yield after thermal treatments might be attributed to the removal of carboxylic and most phenolic groups from the hydrochar surface, or hydroxyl groups from the metal oxide phases, all of which contributed to the BA sites. These results indicated that BA sites play an important role in the dehydration of fructose to HMF. Meanwhile, these sites were also involved in the secondary degradation reactions of HMF and C6 sugars. At the same time, the improved stability of HMF observed over the thermally treated catalysts indicated that the removed Brønsted acidic functionalities were also involved in secondary HMF degradation reactions. Additionally, the higher degree of carbonisation and the improved porosity of the thermally treated materials, as shown by results in Table 4, could have facilitated diffusion of intermediates and desorption of HMF from the catalyst surface, limiting its prolonged contact with the remaining active sites and thus suppressing secondary reactions, including humin formation, as previously discussed in the literature [17,52].

Comparison of the results shown in Figure 6 revealed clear differences in the catalytic performance of the Sn- and Al-containing catalysts, which could be attributed to the nature of Lewis acid sites present in these materials. While both catalysts produced similar glucose

yields ($\approx 10\%$), C-Al-HTC-N₂-600 exhibited substantially higher fructose (7%) and HMF (23%) yields than its Sn-containing counterpart (2.6% fructose and 7.1% HMF, respectively).

According to the XRD results (Figure 2b), C-Al-HTC-N₂-600 mainly contained amorphous partially dehydroxylated AlOOH/Al(OH)₃ domains. Such poorly ordered AlO_x species can expose more accessible coordinatively unsaturated Lewis acid sites. These species were previously reported to be highly active in glucose isomerisation via a Lewis acid-driven 1,2-hydride shift mechanism [17,53]. Interestingly, despite exhibiting negligible apparent Brønsted acidity according to potentiometric titration (see A_{tot} in Table 3), C-Al-HTC-N₂-600 showed a pronounced NH₃-TPD profile (Figure 4). Since NH₃-TPD measures the total acidity without distinguishing between Brønsted and Lewis acid sites, these results suggest that the remaining acidity is likely associated predominantly with Lewis acid sites originating from the Al-containing phases, whereas the Brønsted acid sites were largely removed during thermal treatment at 600 °C. In contrast, C-8.9SnO₂-HTC-N₂-600 contained crystalline SnO₂ together with Sn and SnO species (Figure 2a). This sample exhibited very low apparent Brønsted acidity ($A_{\text{tot}} = 0.1 \text{ mmol H}^+ \text{ g}^{-1}$, see results in Table 3) and only a weak, broad NH₃-TPD profile (Figure 4), indicating a low concentration of accessible acid sites after thermal treatment. The residual acidity could be associated predominantly with Lewis-acidic SnO_x species, while the partial reduction of SnO₂ to SnO and metallic Sn, discussed previously, may have further decreased the number of accessible acidic Sn centres.

In general, Lewis acidity decreases with decreasing oxidation state of the metal cation [54], due to lower charge density and weaker electron-accepting ability of lower-valence metal species. Thus, the presence of reduced Sn species likely decreased the overall Lewis acidity of the sample, resulting in lower activity in the glucose isomerisation step. This is consistent with Wang et al. [22], who reported that partial reduction of SnO₂ in SnO_x-C catalysts resulted in significantly lower catalytic performance and HMF selectivity.

3.2.2. The Effect of Metal Oxide Loading on the Catalytic Performance

As confirmed by the TGA results presented in Table 1, Sn-containing hydrochars with different SnO₂ contents (29.0, 37.5, and 43.5 wt%) were successfully prepared via a one-step hydrothermal synthesis using SnCl₂·2H₂O as the metal precursor. The influence of SnO₂ loading on the catalytic performance of these materials is shown in Figure 7a. The results demonstrated that increasing the tin oxide content did not enhance the performance of the SnO₂-C catalysts towards HMF production. Although a gradual decrease in glucose yield was observed with increasing SnO₂ loading, this did not translate into higher yields of the desired product. On the contrary, the HMF yield decreased progressively with increasing SnO₂ content, while fructose yields remained at trace levels (0.7–1.0%).

Based on these observations, it can be concluded that the additional Lewis acid sites introduced by the higher SnO₂ loadings promoted glucose isomerisation to fructose and that, once formed, fructose was rapidly consumed. However, the decreasing HMF yield suggests that the subsequent reaction pathway proceeded predominantly through non-selective degradation and condensation reactions rather than selective dehydration to HMF. Therefore, it can be speculated that increasing SnO₂ loading partially blocked or altered the accessibility and/or strength of the Brønsted acid sites responsible for fructose dehydration. Alternatively, the higher concentration of the Sn precursor in a mixture during hydrothermal synthesis may have promoted dehydration and condensation reactions, leading to a lower abundance of oxygen-containing surface functionalities in the resulting hydrochars. This interpretation is consistent with the gradual decrease in total acidity (A_{tot}) observed with increasing SnO₂ loading (Table 3). Consequently, while higher SnO₂ contents may increase the density of Lewis acid sites available for glucose isomerisation,

the simultaneous reduction in Brønsted acidity appears to limit the efficient conversion of fructose into HMF.

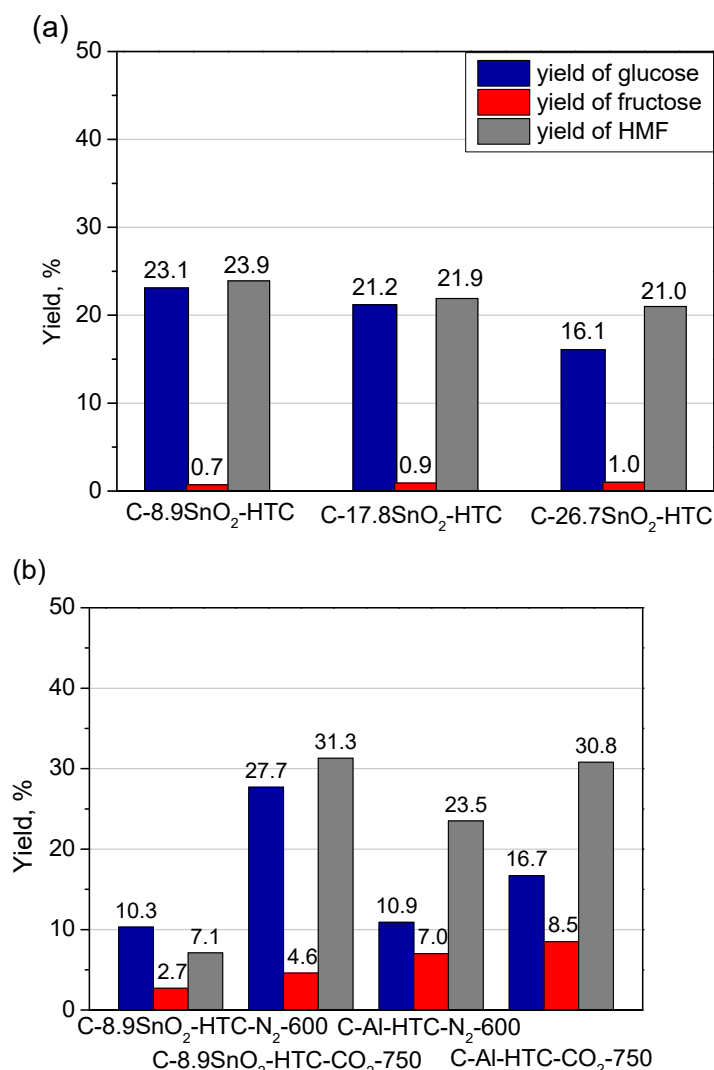


Figure 7. Influence of SnO₂ loading in the catalysts (a) and thermal post-treatment atmosphere (b) on the catalytic performance in sucrose conversion to HMF. Reaction conditions: T = 190 °C, 5 wt.% sucrose in water, catalyst mass = 0.06 g, reaction time = 30 min, stirring speed = 650 rpm. The colour legend shown in panel (a) also applies to panel (b).

3.2.3. The Effect of the Post-Treatment Atmosphere (CO₂ vs. N₂)

The comparison of the catalytic performance of Sn- and Al-containing hybrid catalysts treated in N₂ or CO₂ in HMF production from sucrose is shown in Figure 7b. The atmosphere during thermal post-treatment had a pronounced effect on the catalytic performance of the metal oxide–carbon catalysts for HMF production. For both Sn- and Al-containing materials, post-treatment under CO₂ resulted in substantially higher HMF yields compared to the corresponding materials treated under N₂. In particular, the HMF yield over the Sn-containing catalyst increased from 7.1% for C-8.9SnO₂-HTC-N₂-600 to 31.3% for C-8.9SnO₂-HTC-CO₂-750, while for the Al-containing catalyst, the HMF yield increased from 23.5% to 30.8% after treatment under CO₂.

At the same time, both CO₂-treated catalysts showed higher fructose yields than their N₂-treated counterparts, suggesting enhanced glucose isomerisation activity or reduced fructose side reactions. These results indicated that thermal treatment under CO₂ generated more active catalytic surfaces for both isomerisation and dehydration reactions.

As discussed previously, CO₂ activation preferentially promoted the development of microporosity, as reflected by the higher $V_{\text{micro}}/V_{\text{tot}}$ values (Table 4), while maintaining a significant mesoporous volume and consequently producing a hierarchical pore structure. Considering the molecular dimensions of glucose and fructose ($\approx 0.8\text{--}0.9$ nm) and HMF (≈ 0.6 nm) [55], both pore systems remain accessible to the reactants and products. The coexistence of micropores and mesopores is likely beneficial for catalysis. While micropores provide a high density of acid sites, mesopores facilitate molecular diffusion and the rapid desorption of HMF, thereby reducing secondary reactions. In addition, CO₂ treatment may have promoted the formation and exposure of oxygen-containing surface functionalities and more accessible Lewis acid sites, contributing to the enhanced catalytic performance. In fact, more pronounced diffractions of Al-domains were observed in the XRD pattern of C-Al-HTC-CO₂-750 as compared to its N₂-treated counterpart (Figure 2b). Consistent with this interpretation, the NH₃-TPD results showed higher NH₃ desorption intensities for the CO₂-treated catalyst, suggesting improved accessibility of the acid sites.

Interestingly, the improvement induced by CO₂ treatment was particularly pronounced for the Sn-containing catalyst, suggesting that the oxidative atmosphere favoured the formation and stabilisation of catalytically active SnO₂/SnO_x domains. This interpretation is supported by the XRD results, which revealed sharper and more distinct diffraction features for C-8.9SnO₂-HTC-CO₂-750, whereas the pattern of C-8.9SnO₂-HTC-N₂-600 exhibited significant peak overlap associated with the coexistence of multiple SnO_x phases. The more defined diffraction peaks observed after CO₂ treatment indicate a higher degree of phase segregation and crystallinity, potentially resulting in greater exposure and accessibility of surface Sn⁴⁺ Lewis acid sites. Such sites are widely reported in the literature as being highly active for glucose isomerisation in carbohydrate conversion reactions [22]. Therefore, the enhanced catalytic performance of C-8.9SnO₂-HTC-CO₂-750 can be attributed to the combined effects of CO₂-induced carbon gasification, improved accessibility of the metal oxide domains, and the formation of more crystalline Sn-containing phases exposing a higher density of catalytically active surface sites.

Overall, the different catalytic performances of the Sn- and Al-containing catalysts (Figure 7b), despite their comparable micropore fractions (C-8.9SnO₂-HTC-CO₂-750 and C-Al-NaOH-HTC-CO₂-750; Table 4), suggest that high HMF yields result from the synergistic interplay between pore architecture and the strength and accessibility of acid sites. These findings are consistent with those of Kruger et al. [55], who reported a scattered relationship between pore diameter and furan selectivity, suggesting that catalytic performance results from the combined influence of pore structure and other physicochemical properties, particularly the nature of the active sites.

3.2.4. Influence of Al Species and NaOH on the Catalytic Performance of Al-Containing Hybrid Catalysts

The catalytic performance of the Al-containing materials synthesised via different preparation routes is summarised in Figure 8. Significant differences were observed between the materials prepared using aluminium nitrate alone and those synthesised in the presence of NaOH. As shown by the characterisation data presented above, the addition of NaOH during hydrothermal carbonisation, followed by thermal treatment, strongly influenced the surface chemistry and structural properties of the resulting composites, leading to distinct catalytic performances in the conversion of sucrose to HMF.

C-Al-HTC hydrochar produced a higher HMF yield (33.3%), accompanied by higher yields of glucose (11.6%) and fructose (7.8%), whereas C-Al-NaOH-HTC yielded lower amounts of HMF (29.0%), glucose (4.4%), and fructose (2.8%). The lower concentrations of glucose and fructose observed for C-Al-NaOH-HTC suggest that these intermediates were converted more rapidly, indicating enhanced catalytic activity in the subsequent

reaction steps. This behaviour can be linked to the material's distinct physicochemical properties, which arise from the alkaline synthesis conditions. As discussed previously, the absence of discernible Al hydroxide/oxyhydroxide diffraction peaks in the XRD pattern of C-Al-NaOH-HTC (Figure 2b) suggests the presence of highly dispersed and/or amorphous Al-containing domains. In addition, SEM analysis revealed a predominantly spherical morphology in the NaOH-assisted sample (Figure 5g,h). These characteristics are consistent with a more homogeneous distribution of Al species and improved accessibility of Lewis acid sites compared with C-Al-HTC, which may explain the more efficient consumption of glucose and fructose over C-Al-NaOH-HTC. Furthermore, C-Al-NaOH-HTC exhibited a slightly higher total acidity ($A_{\text{tot}} = 3.4 \text{ mmol H}^+ \text{ g}^{-1}$) than C-Al-HTC ($3.1 \text{ mmol H}^+ \text{ g}^{-1}$). Together with its lighter brown colour (Figure 3), this finding suggests a higher abundance of oxygen-containing surface functionalities, which may have contributed to both fructose dehydration and subsequent HMF degradation reactions. As a result, despite the enhanced conversion of reaction intermediates, the final HMF yield remained lower than that obtained with C-Al-HTC.

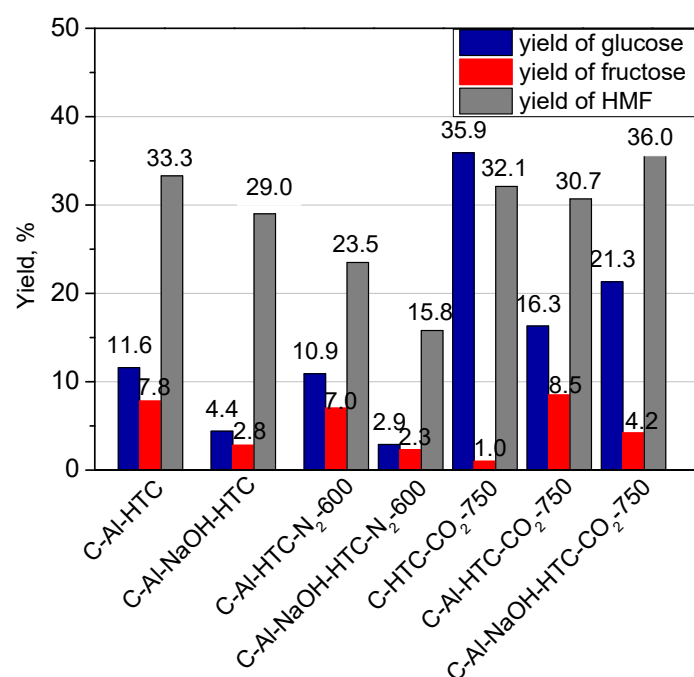


Figure 8. Comparison of the catalytic performance of C-HTC-CO₂-750 and Al-containing materials prepared via hydrothermal carbonisation with and without the NaOH addition in sucrose conversion to HMF. Reaction conditions: $T = 190^\circ\text{C}$, 5 wt.% sucrose in water, catalyst mass = 0.06 g, reaction time = 30 min, stirring speed = 650 rpm.

The impact of NaOH addition changed markedly after thermal treatment. Interestingly, C-Al-NaOH-HTC-N₂-600 exhibited the poorest catalytic performance, producing only 15.0% HMF compared with 23.5% obtained for C-Al-HTC-N₂-600. This deterioration is consistent with the extremely low surface area of C-Al-NaOH-HTC-N₂-600 ($S_{\text{BET}} \approx 25 \text{ m}^2 \cdot \text{g}^{-1}$), suggesting limited accessibility of active sites due to poor pore development and possible blockage by residual inorganic species and/or carbonaceous deposits.

In contrast, C-Al-NaOH-HTC-CO₂-750 exhibited the highest HMF yield (36%) among all the materials studied. This catalyst combined poorly crystalline or amorphous Al-containing phases identified by XRD (Figure 2b), a moderate apparent Brønsted acidity ($A_{\text{tot}} = 0.8 \text{ mmol H}^+ \cdot \text{g}^{-1}$), and the highest concentration of accessible acid sites together with a broad distribution of weak-, medium-, and strong-acid sites according to the NH₃-TPD results. These findings suggest that the superior catalytic performance resulted from the

combined effects of favourable textural properties and a diverse distribution of accessible acid sites. Furthermore, the catalyst's highly developed porous structure and the highest specific surface area among all the materials studied ($S_{\text{BET}} \approx 422 \text{ m}^2 \cdot \text{g}^{-1}$) likely enhanced the accessibility of the acid sites and facilitated the transport of reactants and products.

Our findings are consistent with the literature, which reports that poorly crystalline or amorphous Al-containing species are active catalysts for glucose isomerisation to fructose [17,53,56]. For example, Liu et al. [57] investigated alumina-supported hydrochar catalysts for glucose isomerisation and concluded that amorphous Al species provided the catalytically active sites, whereas the formation of more crystalline Al phases negatively affected fructose yields.

In contrast, although C-Al-HTC-N₂-600 also exhibited considerable total acidity according to the NH₃-TPD results, the lower contribution of medium- and strong-acid sites, resulting from the absence of NaOH during hydrothermal carbonisation and the different thermal post-treatment, was accompanied by inferior catalytic performance. These observations suggest that catalytic performance depends not only on the amount of acidity but also on the accessibility and strength distribution of the acid sites. Collectively, these results indicate that the beneficial effect of NaOH addition became apparent only when combined with CO₂ activation, highlighting the strong interplay between catalyst composition, acidity, and textural properties in determining catalytic performance.

In comparison, the metal-free carbon treated at 750 °C under a CO₂ atmosphere (C-HTC-CO₂-750) exhibited a relatively high HMF yield of approximately 32% (Figure 8), indicating that the carbon support itself is catalytically active under the applied reaction conditions. Although C-HTC-CO₂-750 exhibited substantially lower total acidity than the Al-containing catalysts according to the NH₃-TPD results (Figure 4), it still produced a relatively high HMF yield. This observation suggests that the oxygen-containing surface functionalities remaining after CO₂ activation provide sufficient acidic sites to catalyse sucrose hydrolysis and fructose dehydration. However, in the absence of Al-containing phases, which are reported to provide Lewis acid sites [17], glucose isomerisation was less efficient, as reflected by the higher residual glucose yield (35.8%), only slightly lower than that obtained in the blank experiment (49.2%). These results indicate that although the porous carbon effectively promotes fructose dehydration, it is considerably less effective at catalysing the isomerisation of glucose to fructose. In contrast, the incorporation of Al-containing phases markedly reduced glucose accumulation while maintaining or increasing the HMF yield, with C-Al-NaOH-HTC-CO₂-750 achieving the highest HMF yield (36%).

Although the presented results demonstrate the importance of the synergistic interplay between Brønsted and Lewis acid sites, the quantitative determination of an optimal Brønsted/Lewis acid site ratio is beyond the scope of this study. Such an investigation would require a dedicated series of catalysts with systematically varied acid-site distributions, together with complementary characterisation techniques capable of quantitatively distinguishing Brønsted and Lewis acidity.

The HMF yields obtained in the present work are compared with representative literature reports describing the conversion of glucose and sucrose to HMF over heterogeneous catalysts in water, as shown in Table 6. Studies on sucrose conversion in aqueous media are relatively scarce; therefore, selected reports on glucose conversion were also included to provide a broader benchmark for catalyst performance. Despite the challenges associated with HMF production in water, including rehydration and humin formation, aqueous systems remain attractive because water is an inexpensive, environmentally benign solvent that enables high sugar loadings. Under microwave-assisted reaction conditions (190 °C, 30 min), the Al-carbon hybrid catalyst afforded an HMF yield of 36%, which favourably compares with results reported in the literature for HMF production from glucose and su-

crose. The catalyst outperformed conventional niobium-based catalysts, including Nb₂O₅ and HNb₃O₈, and exhibited catalytic performance comparable to that of the previously reported S, N-doped hydrochar [8].

Table 6. Comparison of HMF yields obtained from glucose and sucrose over various catalysts in water.

Substrate	Catalyst	HMF Yield (%)	Temperature (°C)	Time (min)	Reference
sucrose	Al–carbon hybrid	36	190	30	This work
sucrose	S, N-doped hydrochar	37	180	30	[8]
glucose	Phosphorylated 60%Nb ₂ O ₅ /carbon xerogel	31	180	30	[13]
glucose	Niobic acid	37	180	90	[58]
glucose	NbPO	45	140	60	[59]
glucose	Amberlyst-15	16	140	60	[59]
glucose	Co ₃ (PO ₄) ₂	28	160	90	[60]
glucose	Fe/zeolite	15	190	240	[61]
sucrose	HNb ₃ O ₈	27	180	180	[62]
sucrose	Nb ₂ O ₅	17	180	180	[62]
sucrose	SO ₄ ^{2−} /B ₂ O ₃ /ZrO ₂	9–35	190	60	[63]

4. Conclusions

Sugarcane molasses was successfully utilised as a renewable carbon precursor for the one-pot synthesis of bifunctional metal oxide–carbon hybrid catalysts for the catalytic production of 5-hydroxymethylfurfural (HMF). The incorporation of Sn and Al precursors, together with thermal post-treatment under N₂ or CO₂, produced materials with distinct physicochemical properties, including differences in crystallinity, acidity, morphology, textural characteristics, and acid strength distribution.

The introduction of aluminium and tin species significantly influenced both the hydrothermal carbonisation process and the properties of the resulting catalysts. NaOH-assisted synthesis promoted the formation of spherical particles and poorly crystalline or amorphous aluminium-containing phases, while CO₂ activation substantially enhanced the surface area and pore volume of the hybrid materials compared with N₂ treatment.

Among the investigated materials, the CO₂-treated, NaOH-derived aluminium-containing catalyst (C-Al-NaOH-HTC-CO₂-750) exhibited the highest HMF yield (36%). The results suggest that its superior catalytic performance in the cascade conversion of sucrose to HMF was associated with the synergistic combination of a highly developed porous structure, moderate apparent Brønsted acidity, the highest concentration of accessible acid sites with a broad acid-strength distribution, and the presence of poorly crystalline or amorphous Al-containing phases identified by XRD.

Although the present results establish clear correlations between catalyst synthesis, total acidity, textural properties, and catalytic performance, further surface-sensitive characterisation is required to directly distinguish Brønsted and Lewis acid sites and to elucidate their respective roles in the catalytic reaction. Future work will therefore focus on complementary characterisation using techniques such as pyridine-adsorbed FTIR and X-ray photoelectron spectroscopy (XPS), together with catalyst regeneration, recyclability, and metal leaching studies.

Overall, this work demonstrates a simple and sustainable strategy for transforming an abundant agro-industrial by-product into functional metal oxide–carbon catalysts

with tailored acidity and pore structure. The findings improve our understanding of the relationships between catalyst synthesis, physicochemical properties, and catalytic performance, and further support the valorisation of sugarcane molasses within sustainable biorefinery concepts.

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