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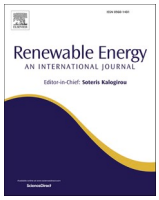

Accelerated 5-hydroxymethylfurfural synthesis: Microwave-driven carbohydrate dehydration with mixed metal spinel catalysts

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ABSTRACT

In this study, a series of spinel mixed metal oxide catalysts, namely $ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2 were synthesized using the sol-gel method followed by sulfate impregnation. The characterization results confirmed the spinel structure of $ZnAl_2O_4$ and anatase phase of TiO_2. Ternary metal oxides Ti-Zn-Al exhibit enhanced Lewis (L) acidity, while Brönsted (B) acidic sites were incorporated due to ammonium sulfate treatment and calcination. Total acidity and B/L ratio increased after the impregnation of sulfate groups; however, a higher sulfate loading (>1M) did not enhance acidity but instead caused agglomeration on the catalyst surface. The selective glucose dehydration to 5-hydroxymethylfurfural was performed in a microwave reactor, and the reaction parameters were optimized for a higher 5-HMF yield. Experimental results demonstrated very high glucose conversion (~90 %) with ~58 % of 5-HMF at 150 °C in 25 min in the presence of 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst in a biphasic NaCl-H_2O/THF medium. The B/L ratio and the solvent used played an important role in the yield of 5-HMF. After several cycles, the regenerated 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst demonstrated its consistent activity and 5-HMF yield. This study provides detailed insights into mixed metal spinel catalysts for biomass valorization and reveals a fast, efficient microwave-assisted route for sustainable 5-HMF production.

1. Introduction

The increasing demand for energy and chemicals, driven by population growth and urbanization, underscores the need for alternative renewable sources. This challenge is further intensified by the depletion of non-renewable fossil resources and their associated environmental impacts [1,2]. Biomass-derived cellulose, a polymer of D-glucose, presents a promising avenue for energy, fuel, and chemical production. In this context, 5-hydroxymethylfurfural (5-HMF) is identified as a valuable compound derived from sugars and listed among the top ten bio-based building block chemicals [2,3]. Converting fructose into 5-HMF is comparatively more straightforward; however, its limited availability and higher cost are the major hurdles for large-scale production. In contrast, with its abundance and lower cost, glucose appears to be a favorable substrate despite its pyranose structure stability, which hinders its transformation into 5-HMF.

The catalytic dehydration of glucose to 5-HMF involves a two-step process, namely the isomerization of glucose to fructose, followed by the dehydration of fructose to 5-HMF by eliminating three water molecules. This process requires suitable catalysts and a reaction medium for obtaining high glucose conversion and 5-HMF yield. For the isomerization step, the presence of Lewis (L) acidic sites and in the dehydration step, Brönsted (B) acidic sites are necessary on the catalyst surface [4,5]. Moreover, the selective conversion of glucose to 5-HMF requires a specific B/L ratio to drive the reaction predominantly towards 5-HMF formation rather than other byproducts. Consequently, various Brönsted-Lewis acid catalysts have been explored, including zeolites such as ZSM-5 [6], Hf/ZSM-5 [7], chromium catalysts Cr_2O_3 [8], $CrCl_3$ [9], transition metal oxides-based catalysts [10,11], metal-organic frameworks (MOFs) [2,12,13], ionic liquids (ILs) based acidic catalysts [14] and more recently carbon-based materials [4,15]. Each type of catalyst has its unique advantages and challenges that influence the reaction kinetics and product selectivity. For instance, recently developed MOFs such as MIL-53(Al)-NH_2 [12], UiO-66-SO_3H-Cl [13], and

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MIL-53(Al)-NO_2 [2] have demonstrated robust catalytic activity with an excellent 5-HMF yield of ~42–73 % with very high glucose conversion of >90 %. However, poor stability of MOFs at high temperatures and expertise in synthesizing unique materials with desired properties are essential. On the other hand, phosphate and sulfated metal oxides such as TiO_2, ZrO_2, SnO_2, and ZnO offer tunable acidity, particularly in the B/L ratio, to enhance 5-HMF yield (35–80 %) [16]. Composite mixed metal oxides such as silica-tin oxide composites [17], WO_3-TiO_2 [18], Al_2O_3-TiO_2 modified sulfonated carbon [19], ZrO_2-SnO_2 [10], $NbOPO_4$ [11], MCM-41/NH-SO_3H [20] have also been explored due to their acid-base properties and excellent performance in producing 5-HMF from various substrates. Zhang et al. [17] synthesized H_3PO_4-treated SiSnO catalysts and obtained ~76 % yield of 5-HMF with 97 % glucose conversion in DMSO/1 % HCl-water at 160 °C after 60 min. It was reported that the catalytic performance was more selective towards 5-HMF formation due to the P-OH bond, which increased the B acidity in the catalyst by H_3PO_4 treatment. A WO_3-TiO_2 catalyst was synthesized by Ganji et al. [18], and 90 % glucose conversion with 58 % of 5-HMF yield was achieved at 170 °C after 2 h in water/MIBK solvent under microwave irradiation. However, the reaction time was relatively long considering microwave irradiation. Zhang et al. [19] developed the Al_2O_3-TiO_2 modified sulfonated carbon (Al-Ti@SCHOP) for glucose dehydration reaction and obtained 57 % yield of 5-HMF at 130 °C after 5 h of reaction. Significantly high acidity of sulfonated carbon and Al_2O_3/TiO_2 doping increased the Lewis acidity of the catalyst, which improved the 5-HMF yield. Niakan et al. [20] synthesized an MCM-41 mesoporous silica-based acid-base bifunctional catalyst (MCM-41/NH-SO_3H) and achieved an HMF yield of 89 % at 100 °C after 2 h of reaction in aqueous medium in a 25 mL pressure reactor. It was reported that the basic sites (-NH_2) facilitate the isomerization of glucose to fructose, while the dehydration of fructose to HMF is promoted by the acidic sites (-SO_3H). Moreover, the choice of reaction medium also significantly affected the 5-HMF yield and selectivity. The organic solvents such as DMF, MIBK, and DMSO prevented the rehydration of 5-HMF and increased the 5-HMF yield. However, organic solvents have several drawbacks, including their toxicity and environmental impact, and, most importantly, the separation of 5-HMF from organic solvents is a challenging and energy-intensive process. As an alternative, biphasic media like water-NaCl/THF enhanced glucose conversion and 5-HMF selectivity. THF stands out due to its lower cost, high extraction affinity, and low boiling point [21,22]. Various previous studies demonstrated higher 5-HMF yields (48–62 %) from cellulose and glucose in water-NaCl/THF biphasic medium at 170–210 °C after 3–8 h [21,23,24]. However, the reaction temperature and duration are very high.

This study aimed to synthesize a mixed metal composite, i.e., spinel xM-SO_4/$ZnAl_2O_4$-TiO_2 catalyst, for the selective conversion of glucose to 5-HMF. The advantage of ternary metal oxides such as Ti-Zn-Al lies in their ability to synergistically enhance Lewis acidity by incorporating multiple electron-deficient sites depending on their oxidation states. The order of oxidation states among these metals is $Ti^{4+} > Al^{3+} > Zn^{2+}$. Among them, Ti^{4+} is the strongest Lewis acid due to the highly charged Ti^{4+} cations, which readily accept electron pairs. Further, Brönsted acidity was incorporated by modifying it with sulfate groups. The acidity is required to catalyze the glucose dehydration to 5-HMF. The spinel catalyst was synthesized by sol-gel and impregnation methods. The physicochemical properties of the catalyst were characterized and correlated with the catalytic activity data. The best reaction conditions were achieved by optimizing the reaction parameters, including temperature, time, glucose/catalyst ratio, and reaction solvents, in a microwave irradiation reactor. The synthesized materials demonstrated good catalytic activity, which correlated well with the catalysts' acidity. Furthermore, the reusability of the catalyst was evaluated at the optimized reaction conditions. After each cycle, the catalyst was separated and evaluated for further cycles at the optimum condition. The catalyst regenerated even after cycle 3 demonstrated consistent activity with the fresh run. To the best of our knowledge, no studies have been reported using sulfated $ZnAl_2O_4$-TiO_2 catalysts for 5-HMF production from sugars. This work introduces a novel application of mixed metal spinel catalysts in a new reaction and expands the potential of mixed metal oxide catalysts to develop more efficient reaction pathways. Additionally, this study also provides insights into the rapid and efficient microwave-assisted glucose dehydration to 5-HMF in the presence of an acid catalyst.

2. Experimental

2.1. Catalyst synthesis

The spinel catalyst was prepared in three consecutive steps [25,26]. In the first step, 1 g of zinc nitrate hexahydrate [98.5 %, Thomas Baker, India] and 2.5 g of aluminum nitrate nonahydrate [98 %, Thomas Baker, India] were dissolved to obtain the Zn: Al mol ratio of 1:2 in 40 mL of isopropanol under vigorous stirring. Then, Pluronic P-123 [Sigma Aldrich, Germany] (5 wt% of total nitrate salts) was added to the above solution and stirred for 4 h to make a slurry. The obtained slurry was heated in a vacuum oven at 80 °C to obtain a gel, which was then dried overnight at 100 °C. The obtained powder was calcined at 600 °C for 5 h to obtain the spinel structure. The resulting powder was named spinel $ZnAl_2O_4$.

In the next step, a mixture of 3.8 mL of distilled water, 5 mL of titanium isopropoxide [Sigma Aldrich], 5 mL of ethanol [99.9 %, Jiangsu Huaxi International, China], 5 mL of acetic acid [99.5 %, Thomas Baker, India] was prepared in a volume ratio of 0.76:1:1:1 and stirred for a few minutes for homogenous mixing. Further, the required amount (1 g) of spinel $ZnAl_2O_4$ ($ZnAl_2O_4$: TiO_2 = 1:1 (wt.%)) was added to the above mixture, followed by stirring for another 4 h at room temperature. The prepared suspension was aged for 1 h at 65 °C in a water bath and dried overnight at 100 °C in a conventional oven. The white dried powder was named spinel $ZnAl_2O_4$-TiO_2.

In the last step, $ZnAl_2O_4$-TiO_2 was modified by treating it with ammonium sulfate [99 %, Thomas Baker, India] to enhance the acidity of the material. In this step, a 10 mL solution of different molar concentrations (1M, 1.5M, and 2M) of $(NH_4)_2SO_4$ was prepared and stirred for 4 h after adding 1 g $ZnAl_2O_4$-TiO_2 powder. The obtained slurry was aged for a day, followed by overnight drying at 80 °C in a conventional oven. The resulting powder was calcined at 500 °C for 3 h in the air to obtain xM-SO_4/$ZnAl_2O_4$-TiO_2 catalyst, where x is the molar concentration of sulfate added (1M, 1.5M, and 2M). The prepared calcined catalysts were therefore named 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2, respectively.

2.2. Catalysts characterization

The BET surface area of the prepared spinel catalysts was determined by the N_2 adsorption-desorption technique using a Micromeritics Instruments, USA [Model no: ASAP 2020]. Before the analysis, the samples were degassed at 200 °C for 10 h under vacuum. The Brunauer-Emmett-Teller (BET) method was used to calculate the specific surface area. In contrast, the Barret-Joyner-Halenda (BJH) method was employed to analyze the pore size distributions of the catalysts.

The XRD diffractograms of all the samples were obtained using a D8-Advance diffractometer (Bruker, Germany) using the Cu-Kα radiation, λ = 1.5406 Å in the 2θ range of 5–90° at the scan speed of 4°/min. The Scherrer formula was used to calculate the crystallite size of spinel catalysts using the line width of the diffraction peaks corresponding to different crystal planes.

The thermal stability of the prepared materials was recorded using a Mettler Toledo TGA/DSC 3+ STAR^e instrument from 25 to 850 °C at a heating rate of 10 °C/min under 100 mL/min of N_2 flow.

The total acidity was measured by temperature-programmed desorption technique using ammonia as a probe molecule in a Hiden

Catlab gas analyzer coupled with QGA Hiden quadrupole mass spectrometer. Before the analysis, the samples were degassed at 200 °C for 1 h under Ar at a flow rate of 30 mL/min, followed by NH_3 adsorption at 60 °C for an hour under the gas mixture of Argon and 5 % NH_3-He at a flow rate of 15 mL/min each. Next, NH_3 desorption was recorded under an Ar flow of 30 mL/min in the temperature range of 60–550 °C at a heating rate of 10 °C/min.

The Brönsted and Lewis acidity ratio of pyridine adsorbed onto the catalyst was determined using an FTIR spectrophotometer (Model no Bruker Tensor II, Germany) as reported earlier [27].

SEM images were obtained on a JEOL 7600F Field-Emission Scanning Electron Microscope operating at 15.0 kV. The samples were prepared by placing the powders on a double-faced copper tape supported on a thin aluminum lamina. The applied probe current was set at 12 A for direct imaging on powders, and at 16 A in case of Energy Dispersive X-ray Spectroscopy (EDX) probing (that was used for semi-quantitative elemental analyses for C, O, Zn, Ti, Al, S, qualification as average of three different points). The analytical accuracy of the performed EDX probing is ±2 %. (The detailed morphology analysis is reported in the supplementary information.)

Elemental analysis of the reaction mixture was performed using an Inductively Coupled Plasma - Optical Emission Spectrometer (ICP-OES), model iCAP 6500 DUO ICP-OES, provided by Thermo Fisher Scientific. The THF solvent from the reaction mixture was removed using a rotary evaporator, and only the aqueous phase was analyzed. The water samples were diluted 10-fold with 2 % nitric acid (HNO_3) to ensure appropriate conditions for the ICP-OES analysis.

2.3. Catalytic tests

The dehydration of glucose over the spinel catalysts, i.e., $ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2, was conducted in a 10 mL pressure tube, sealed tightly with a Teflon cap, in a microwave reactor (CEM Discover, USA). The reaction occurred under autogenous pressure and electromagnetic stirring, employing a biphasic solvent system comprising NaCl-saturated water (NaCl-H_2O) and tetrahydrofuran (THF) in a volume ratio of 1:3. The impact of various reaction parameters, including temperature (130–160 °C), duration (5–70 min), glucose-to-catalyst ratio (0.5–2), organic solvents (THF, MIBK, and DMSO) or biphasic solvent (water-NaCl/organic solvent), and feedstocks (fructose, sucrose, and glucose), was systematically optimized for the higher yield of 5-HMF. The reaction samples were analyzed in a High-Performance Liquid Chromatography (Ultimate 3000 UHPLC, Thermo-Fisher Scientific, USA) equipped with a Refractive Index (RI) detector, pump (Dionex Ultimate 3000), column compartment (Dionex Ultimate 3000) utilizing a Bio-Rad Aminex HPX-87H + column (300 mm × 7.8 mm), and a refractive index detector (RefractoMax 520). A mobile phase of 0.005M sulfuric acid aqueous solution was employed at a flow rate of 0.55 mL/min. The column and RI detector temperatures were maintained at 50 °C and 55 °C, respectively. Before analysis, the reaction samples were diluted with the mobile phase and filtered through a 0.22 μm nylon filter (25 mm diameter). Injection volumes and analysis durations were set at 20 μL and 45 min, respectively. Glucose conversion and product yield were determined using appropriate standard calibration curves for the respective compounds with the following formula:

$$Conversion\ (\%) = \frac{(Moles\ of\ substrate\ fed - Moles\ of\ substrate\ remaining)}{Moles\ of\ substrate\ fed} \times 100 \quad (1)$$

$$Yield\ (\%) = \frac{Moles\ of\ product\ formed}{Moles\ of\ substrate\ fed} \times 100 \quad (2)$$

2.3.1. Recycle runs

The recycle study was conducted under the best conditions obtained during the optimization of reaction parameters, i.e., under microwave irradiation with magnetic stirring in the presence of spinel 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst. After each reaction cycle, the catalyst was first centrifuged at 5000 rpm for 10 min to separate it from the reaction mixture, followed by washing with distilled water and acetone to remove the deposited byproducts from the active surface of the catalyst. Further, the washed catalyst was dried at 120 °C overnight in a conventional oven and used for the next cycles.

2.3.2. Hot filtration test

The hot filtration test was conducted under the optimized reaction conditions (150 °C for 25 min with a glucose-to-catalyst ratio of 1, in a NaCl-H_2O/THF solvent system). The reaction was allowed to proceed at 150 °C for the first 15 min using a microwave reactor. Afterward, the microwave reactor was turned off, and the mixture was allowed to cool to 60 °C due to microwave safety constraints. The catalyst was then separated from the reaction mixture by centrifugation at 5000 rpm for 10 min. Minimal amounts of samples were collected from both the aqueous and THF phases. The catalyst-free reaction mixture was subsequently returned to the same reaction conditions and heated for an additional 10 min under microwave irradiation. The resulting samples were analyzed by HPLC.

3. Results and discussion

3.1. N_2-physisorption

The textural properties of the catalysts ($ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2) after calcination are presented in Table 1. The adsorption-desorption isotherms are shown in Fig. 1. The spinel $ZnAl_2O_4$ catalyst displayed type-IV isotherms with the H3 type of hysteresis loop at the $P/P_o = 0.4$ to 1, which demonstrated its mesoporous nature with slit-like pores. Initially, the surface area of the bare support, i.e., pure unmodified $ZnAl_2O_4$ spinel, was measured as 77.8 m^2/g. After TiO_2 addition and ammonium sulfate impregnation, the calcined xM-SO_4/$ZnAl_2O_4$-TiO_2 catalysts retained their mesoporous characteristics, confirmed by type-IV adsorption-desorption isotherms with a H3-type hysteresis loop at the $P/P_o = 0.4$–1 value (Fig. 1(a)). This variation in the shape of the hysteresis loop (Fig. 1 (b)) for the sulfated catalysts compared to the spinel $ZnAl_2O_4$ catalyst indicates the strong interaction of sulfate ions with the surface. The synthesized sulfated spinel-based materials exhibited a surface area ranging from ~79 to 90.4 m^2/g (Table 1). After composite formation with TiO_2 and impregnation with 1M ammonium sulfate during the calcination process, the surface area of the catalyst increased to 90.4 m^2/g. However, the surface area decreased with increasing concentration of ammonium sulfate (>1M) onto $ZnAl_2O_4$-TiO_2 due to surface coverage. Interestingly, the surface was almost unaffected with increasing the sulfate amount (>1M) on the surface of the spinel

Table 1
Physicochemical properties of synthesized spinel-based materials.

Catalyst	BET Surface area (m^2/g)	Pore volume (cc/g)	Pore Diameter (nm)	Average Crystallite size (nm)	Total acidity (mmol/g cat. × 10^{-3})	B/L
$ZnAl_2O_4$	77.8	0.15	7.12	18.05	0.19	0.01
1M-SO_4/$ZnAl_2O_4$-TiO_2	90.4	0.14	5.16	14.10	4.28	1.22
1.5M-SO_4/$ZnAl_2O_4$-TiO_2	79.4	0.13	6.16	14.50	3.44	0.85
2M-SO_4/$ZnAl_2O_4$-TiO_2	83.5	0.17	7.76	14.73	2.29	0.86

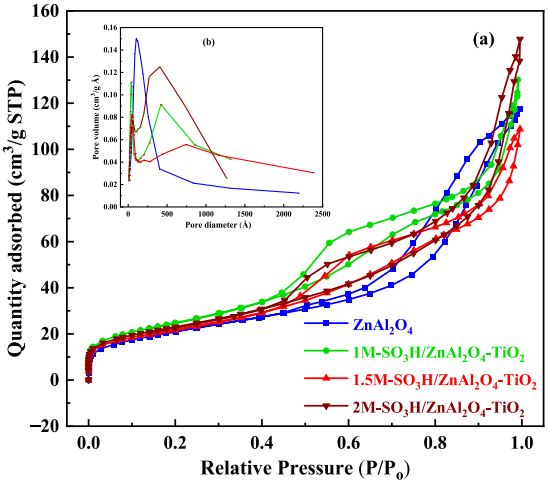

Fig. 1. (a) Nitrogen physisorption isotherms (b) Pore size distribution of synthesized catalysts.

support. The pore volume (0.13–0.17 cc.g^{-1}) and pore diameter (5.16–7.76 nm) of the sulfated catalysts were remarkably close to those of the unmodified $ZnAl_2O_4$ catalyst.

3.2. X-ray diffraction

The diffraction patterns of synthesized spinel catalysts ($ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2) after calcination are presented in Fig. 2. The analysis of diffraction patterns highlighted the presence of distinct phases in the synthesized materials. For $ZnAl_2O_4$, the primary phase was spinel $ZnAl_2O_4$ [JCPDS file no. 01-082-1538] together with the hexagonal ZnO [01-079-0206]. The major diffraction peaks detected for spinel $ZnAl_2O_4$ were at the 2θ value of 31.3°, 36.9°, 44.9°,49.1°, 55.7°, 65.2°, 67.9°,74.2°, 77.4° [01-082-1538] [28,29] with few additional peaks of ZnO phase at 31.8°, 34.5°, 36.3°, 47.6°, 56.7°, 62.9°, respectively [01-079-0206] [28]. The major ZnO peaks at 31.8° and 36.3° were observed as shoulders of prominent spinel peaks at 31.3° and 36.9°. This revealed the minimal formation of ZnO during the synthesis of spinel $ZnAl_2O_4$. After the formation of xM-SO_4/$ZnAl_2O_4$-TiO_2 composite, anatase TiO_2 and monoclinic sulfur together with the spinel phase of $ZnAl_2O_4$ were observed in accordance with the JCPDS file no. 01-083-2243 and 01-076-0183, respectively. After modification with ammonium sulfate, i.e., for xM-SO_4/$ZnAl_2O_4$-TiO_2 catalyst, the intensity of spinel peaks decreased significantly and broadened due to the strong interactions of spinel surface and titania with sulfur. These results are attributed to the transformation of ammonium sulfate to other sulfur-containing species during calcination [30,31]. These results might also indicate the formation of a lower crystallite size after the formation of the composite. The additional peaks at 25.3° corresponded to JCPDS no. 01-083-2243, confirming the presence of anatase phase of titania, which is an active phase for glucose dehydration reaction [32]. Moreover, other observed major peaks at 9.8°, 10.6°, 15.1°, 16.2°, 18.6°, 21.3°, 23.8° were

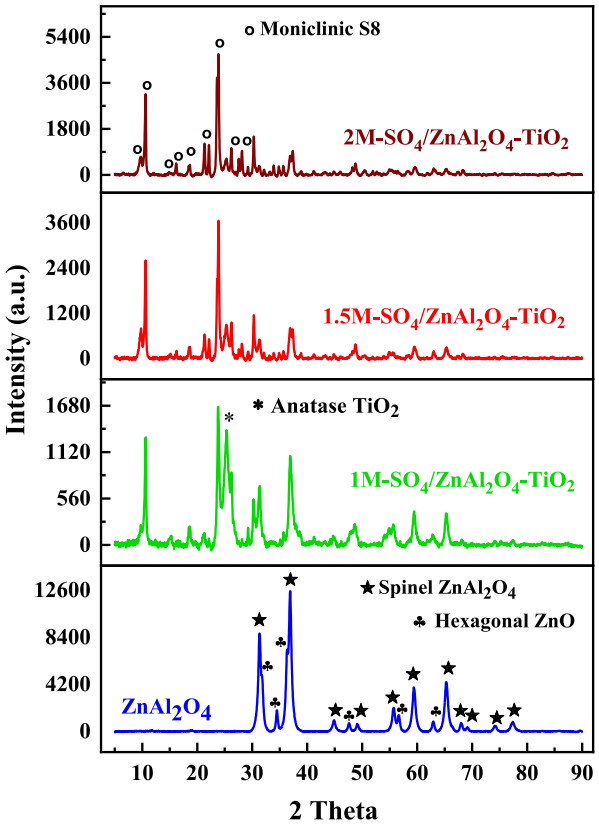

Fig. 2. XRD patterns of the synthesized catalysts.

associated with monoclinic sulfur [01-076-0183]. The intensity of these sulfur peaks increased logically with increasing the concentration from 1M to 2M of sulfate compound loading on $ZnAl_2O_4$-TiO_2. Similarly, the spikes formation of sulfur at higher concentrations of ammonium sulfate can also be seen in the SEM images (See the supplementary information, Fig. S1).

The average crystallite size (Table 1) in all the catalysts was calculated by using the Scherrer formula by considering the most prominent peaks of spinel phase at 31.8°, 36.8°, 59.4°, and 65.2°. The bigger crystallite size of 18.5 nm was observed for unmodified calcined spinel $ZnAl_2O_4$, and it was observed to decrease in the range of 14.1–14.7 nm for 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2 catalysts, respectively. The low average crystallite size of sulfated catalysts was due to the presence of charged sulfate species, which might have hampered the expansion of spinel crystals during calcination, as they bonded to the surface of the spinel [33].

3.3. Thermal stability

TGA of all the spinel catalysts after being calcined at 500 °C was

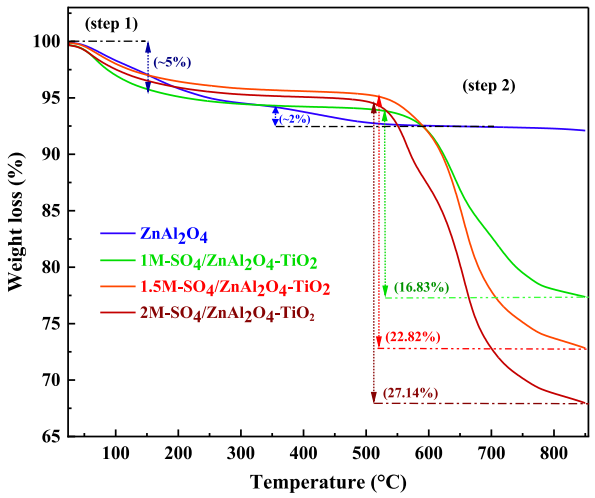

Fig. 3. TGA patterns of catalysts after calcination, recorded in a nitrogen environment.

performed in an N_2 environment. The obtained TGA profiles are presented in Fig. 3. During the thermal analysis, two major weight losses were detected. In stage 1, ~5 % weight loss was observed at < 150 °C, due to evaporation of volatile matter or physically absorbed water, and in stage 2, ~17–27 % weight loss was observed at > 500 °C due to the decomposition of the pyrosulfate group. The stage 2 wt loss was raised from 16.8 % to 27.1 % for the xM-$ZnAl_2O_4$-TiO_2 catalysts series with an increase in the ammonium sulfate concentration (1M–2M) during the synthesis. Previously, Zou et al. [30] studied the thermal decomposition of ammonium sulfate and bisulfate and reported that ammonium sulfate decomposition took place at various temperature ranges and stable sulfate ions were formed at 500 °C due to the complete decomposition of ammonium ions into ammonia. Consequently, the xM-SO_4/$ZnAl_2O_4$--TiO_2 catalysts synthesized were calcined at 500 °C for 3 h in the presence of air to ensure the thermally stable SO_4 groups formation on the $ZnAl_2O_4$-TiO_2 catalysts' surface for glucose dehydration reaction. Additionally, the TGA profiles also showed no major degradation steps before 500 °C, which confirmed the stability of the synthesized catalyst.

3.4. Acidity

The total acidity of the spinel $ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2 catalysts was determined by using the ammonia desorption technique, and the desorption patterns obtained are shown in Fig. 4(a). For spinel $ZnAl_2O_4$, the desorption profiles showed a small peak at < 200 °C associated with weak acidic sites. After sulfate impregnation on $ZnAl_2O_4$-TiO_2 and calcination, a dominant peak at higher temperature >300 °C associated with stronger acidic sites was observed (Fig. 4(a)). For the 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst, a large peak at ~314 °C was observed, which shifted towards a little higher temperature of 355 °C and 370 °C for 1.5M-SO_4/$ZnAl_2O_4$-TiO_2 and 2M-SO_4/$ZnAl_2O_4$-TiO_2 catalysts, respectively. Additionally, a small shoulder peak at around 142–149 °C was also noticed at higher concentrations of sulfate demonstrated the presence of weak acid sites in the materials. The total acidity of the spinel $ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2 catalysts was calculated based on the integral area of molecules of NH_3 desorbed per second recorded via the mass spectrometer. The spinel $ZnAl_2O_4$ showed the lowest total acidity (0.19×10^{-3} mmol/g cat.), which was increased significantly to 4.28×10^{-3} mmol/g cat. After 1M sulfate impregnation (Table 1). On further increasing the concentration of sulfate to 2M, the total acidity reduced to 2.29×10^{-3} mmol/g cat. This result dictated that increasing the sulfate loading beyond an optimum level resulted in agglomeration and transformation of the catalyst surface into the less-acidic species during calcination. For instance, SEM images also revealed agglomeration at higher sulfate concentrations (>1.5M) (Fig S1 (c) and (d)). Similarly, the XRD peak intensity of monoclinic sulfur (that is not providing the acidity to the materials) was found to be increased with higher sulfate ions loading and was the highest for the 2M sample (Fig. 2). The observations from TPD, SEM, and XRD characterizations are consistent with each other, which confirms the consistency of the results.

The Py-FTIR spectra of spinel $ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2 show the presence of Lewis (L) and Brönsted (B) sites, as displayed in Fig. 4(b). In the spectra, three different peaks are attributed to adsorbed pyridine at 1445 cm^{-1}, 1490 cm^{-1}, and 1590 cm^{-1}, which correspond to the L sites, L + B sites, and B sites, respectively [12,34]. The B/L ratio was calculated by using the integral area of the respective peak of L sites (1445 cm^{-1}) and B-sites (1545 cm^{-1}) and reported in Table 1. The spinel $ZnAl_2O_4$ showed the lowest B/L ratio (0.01) due to the absence of Brönsted acidity, while it significantly increased to 1.22 for 1M-SO_4/$ZnAl_2O_4$-TiO_2. On further increasing the concentration of sulfate groups to 1.5M, the B/L ratio drastically reduced to 0.85 for 1.5M-SO_4/$ZnAl_2O_4$-TiO_2. On further increasing the sulfate concentration to 2M, the observed B/L (0.86) ratio was almost constant, which might be attributed to the significant presence of monoclinic sulfur (Fig. 2). These Brönsted-Lewis acidity ratios (B/L) trend are in agreement with the total acidity calculated by NH_3-TPD. At higher sulfate concentration (>1.5M) on the spinel surface, polysulfide compounds might be formed due to the accumulation of sulfur, as a large, aggregated structure can be seen in Fig S1 (c) and (d). In the XRD patterns

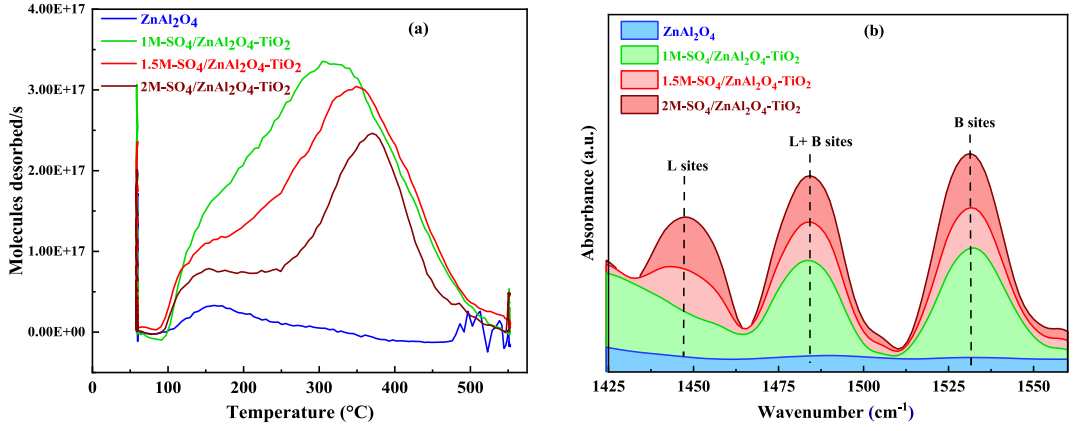

Fig. 4. (a) NH_3-TPD curves **(b)** Py-FTIR spectra of synthesized catalysts.

(Fig. 2) of the catalyst with high sulfate loading, high intensity peaks were detected for monoclinic sulfur. These results also supported the sulfur accumulation.

4. Catalytic performances

The catalytic activity of the synthesized catalysts was evaluated for glucose dehydration to 5-HMF in a biphasic NaCl-H_2O/THF (1/3 vol%) medium. In the biphasic medium, the organic medium helps in the easy and continuous extraction of 5-HMF from the reaction medium by shifting the reaction equilibrium towards 5-HMF, while salt addition in the aqueous phase helps for phase separation by improving the partition coefficient between two phases [23]. In this study, the effect of various reaction parameters such as the nature of the catalyst, temperature, time, glucose to catalyst ratio, solvents, and feedstocks on the yield of 5-HMF was studied in a microwave reactor. The catalyst's stability was also studied. The results obtained are described in the following sections.

4.1. Catalyst screening

The formation of 5-HMF via glucose dehydration was investigated in the presence of various catalysts such as our previously synthesized sulfated TiO_2 [27], sulfated ZnO [35], mesoporous TiO_2 [36], spinel $ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$, 1M-SO_4/$ZnAl_2O_4$-TiO_2, 1.5M-SO_4/$ZnAl_2O_4$-TiO_2, and 2M-SO_4/$ZnAl_2O_4$-TiO_2. The reaction was performed at 150 °C for 15 min under microwave heating, and the obtained results are shown in Fig. 5. Overall, the catalysts, the primary reaction product was 5-HMF. In addition to that, other glucose rehydration products, including formic acid (FA) and levulinic acid (LA), were also detected. The glucose conversion was found in the domain of 44–91 % with up to 44 % yield of 5-HMF, 1–17 % yield of FA and up to 11 % yield of LA, respectively. Sulfated TiO_2, sulfated ZnO and mesoporous TiO_2 catalysts showed a comparatively lower 5-HMF yield (~4–32 %) and glucose conversion (~22–83 %) in the biphasic reaction system under microwave heating. The ammonium sulfate impregnated TiO_2 catalyst favored glucose isomerization reaction over dehydration reaction (Table S2, supplementary information). While the spinel $ZnAl_2O_4$ demonstrated the highest (91.1 %) glucose conversion among all other catalysts assessed, it was not found selective towards the formation of 5-HMF because of its lower acidity (0.19×10^{-3} mmol/g cat.) and lower B/L ratio (0.01), as reported in section 3.3. The 1M-SO_4/$ZnAl_2O_4$ catalyst exhibited complete conversion with only 7.8 % 5-HMF along with ~31 % fructose at 150 °C after 15 min of reaction (Table S2). Further,

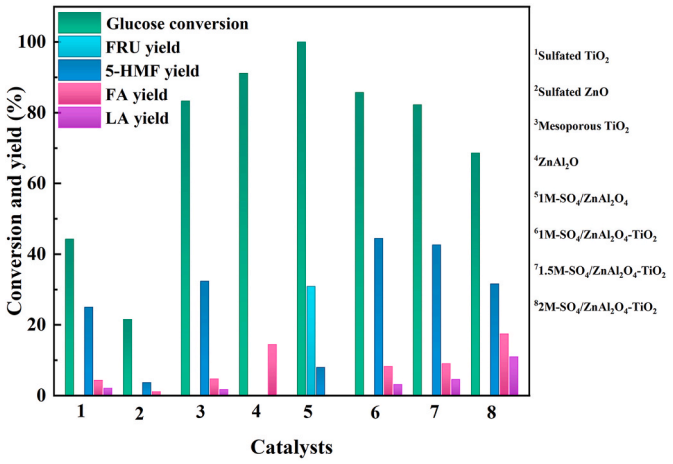

Fig. 5. Performance of various catalysts in glucose dehydration to 5-HMF. (Reaction conditions: 150 °C, 15 min, 50 mg of glucose, NaCl-H_2O/THF (1/3 vol%), 50 mg of catalyst).

over the xM-SO_4/$ZnAl_2O_4$-TiO_2 series of catalysts, acidity was improved, which gave an enhanced formation of 5-HMF. The highest 5-HMF yield of 44.5 % with 85.8 % conversion of glucose, along with 8.3 % yield of FA and 3.2 % yield of LA, was observed in the presence of 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst. This result is attributed to its suitable B/L ratio (1.22) for 5-HMF formation. However, further loading of sulfate to a concentration of 1.5M (1.5M-SO_4/$ZnAl_2O_4$-TiO_2) resulted in a slight decrease in glucose conversion and 5-HMF yield to 82.3 % and 42.6 %, respectively, accompanied by an increase in FA (9 %) and LA (4.6 %) yields. In the presence of the 2M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst, there was a decrease in both glucose conversion (to 68.6 %) and 5-HMF yield (to 31.6 %), but a significant increase in FA (to 17.4 %) and LA (to 11 %) yields were observed. This shift in product distribution could be attributed to the heightened presence of monoclinic sulfur on the catalyst surface, as observed by XRD analysis. It is plausible that the observed B/L ratio and total acidity for 1.5M and 2M samples (Table 1) potentially decreased due to a higher concentration of sulfate or an enlargement in pore diameter (7.76 nm, Table 1) that facilitated the additional side reactions which led to the formation of FA and LA.

4.2. Effect of reaction time and temperature

The next step of our investigation aimed at elucidating the impact of temperature and reaction duration on the product distribution of the glucose dehydration reaction, targeting 5-HMF as the final product. The experimentation spanned temperatures ranging from 130 to 160 °C and reaction durations of 5–70 min, employing the 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst under microwave heating. The resulting data, including glucose conversion, yield of 5-HMF, FA and LA, are illustrated in Fig. 6(a), (b), 6 (c), and 6(d), respectively. Temperature and reaction duration exerted substantial influence on the glucose dehydration reaction, as evidenced by Fig. 6. At the lowest temperature (130 °C), glucose conversion gradually rose from 13.6 % to 52.2 % over the course of 5–70 min, accompanied by a gradual increase in 5-HMF formation from 3.5 % to 31.7 %. Elevating the temperature by 10 °C (to 140 °C) resulted in a rapid increase in glucose conversion to 42 % within 5 min with a 14.2 % yield of 5-HMF. Subsequent reaction progression further augmented conversion (86.6 %) and 5-HMF yield (48.8 %), along with increased production of rehydration products, namely FA (12 %) and LA (~7 %) after 70 min. Hence, the extended reaction duration at lower temperatures notably enhanced 5-HMF yield, alongside increased rehydration product formation as well. At 150 °C, glucose conversion rates were notably accelerated, and approximately 62 % conversion was achieved within 5 min and further increased to approximately 98 % conversion within 45 min. Concurrently, the highest 5-HMF yield reached 55.7 % within 25 min, then slightly declined to ~48 % at 45 min, with an upward trend in FA and LA yields, as illustrated in Fig. 6(c) and (d), respectively. At 160 °C, a higher yield of 53 % 5-HMF was obtained, with nearly complete conversion of glucose within a 15-min reaction duration. Subsequent reaction progression witnessed a decrease in 5-HMF yield, simultaneously with increased formation of FA (18 % yield) and LA (17 % yield) due to the kinetics of consecutive reactions of glucose dehydration. These results highlighted the precise control of temperature and reaction duration needed to optimize 5-HMF yield while managing the formation of undesirable byproducts. Hence, for subsequent evaluation of other reaction parameters, 150 °C and 25 min of reaction were considered the optimal conditions, which yielded ~56 % of 5-HMF over ~90 % of glucose conversion under microwave heating with the chosen catalyst.

4.3. Effect of glucose/catalyst ratio

The effect of the glucose to catalyst ratio on both glucose conversion and 5-HMF yield was investigated at 150 °C for a 25-min reaction period, utilizing the 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst. The glucose to catalyst ratio was varied from 0.5 to 2 (wt./wt.) by keeping the catalyst

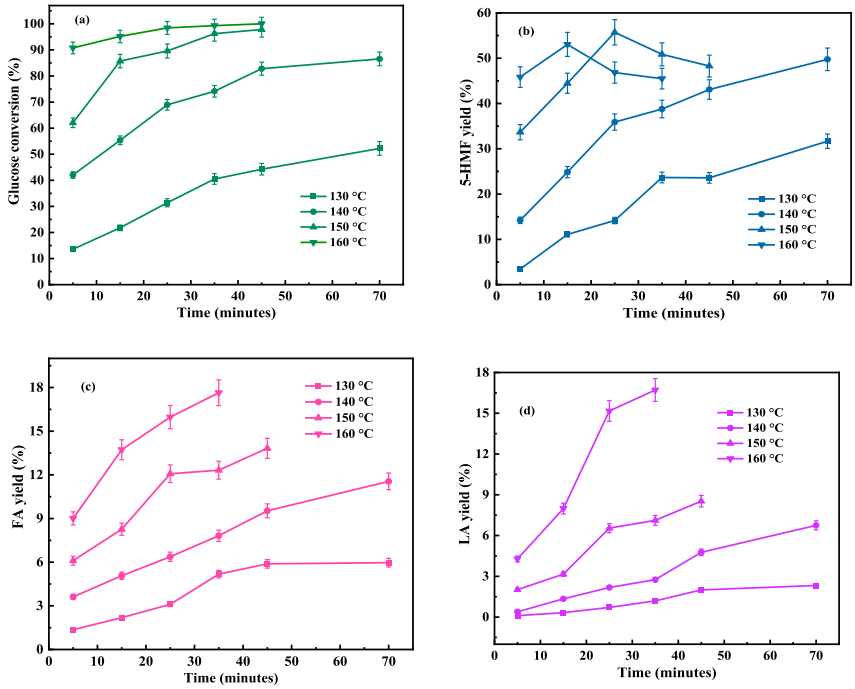

Fig. 6. Effect of reaction time and temperature on glucose dehydration. Reaction conditions: 50 mg of glucose feed, NaCl-H_2O/THF (1/3 vol%), 50 mg of 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst.

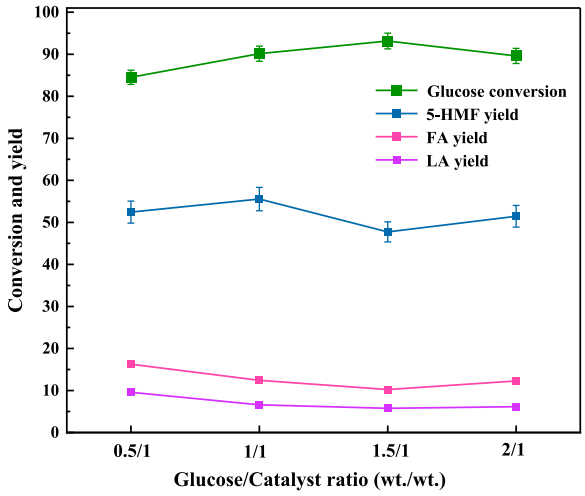

Fig. 7. Effect of glucose to catalyst ratio in glucose dehydration to 5-HMF. Reaction conditions: 150 °C, 25 min, NaCl-H_2O/THF (1/3 vol%), catalyst (50 mg): 1M-SO_4/$ZnAl_2O_4$-TiO_2.

amount at 50 mg and varying the glucose quantity between 25 and 100 mg, as shown in Fig. 7. Notably, the lowest glucose/catalyst ratio (0.5; 25 mg of glucose, 50 mg of catalyst) gave an 84.5 % glucose conversion rate and a 52.4 % 5-HMF yield, accompanied by increased formation of rehydration products such as FA (~16 %) and LA (~10 %). These findings indicated that an increased availability of active centers enhanced side product formation which reduced 5-HMF yield. [37]. At a glucose to catalyst ratio of 1, glucose conversion increased to approximately 90 %, and a 55.5 % yield of 5-HMF with slightly diminished yields of FA (12.4 %) and LA (6.6 %) due to optimal availability of active sites of the catalyst. Subsequently increasing the ratio to 1.5 to 2 resulted in an insignificant decline in both conversion and product yields, attributed to the reduced accessibility of active sites relative to the substrate quantities. Therefore, the study elucidates the crucial role of the glucose to catalyst ratio in dictating both the conversion of glucose and the yield of 5-HMF, with lower ratios favoring the formation of side products and higher ratios exhibiting diminishing yields due to limited active site accessibility. Hence, the glucose/catalyst ratio of 1 was found to be the most optimal ratio to achieve a high yield of 5-HMF and glucose conversion in NaCl-H_2O/THF (1/3 vol%) biphasic reaction medium.

4.4. *Effect of different solvents*

Glucose dehydration to 5-HMF reaction involves a series of two

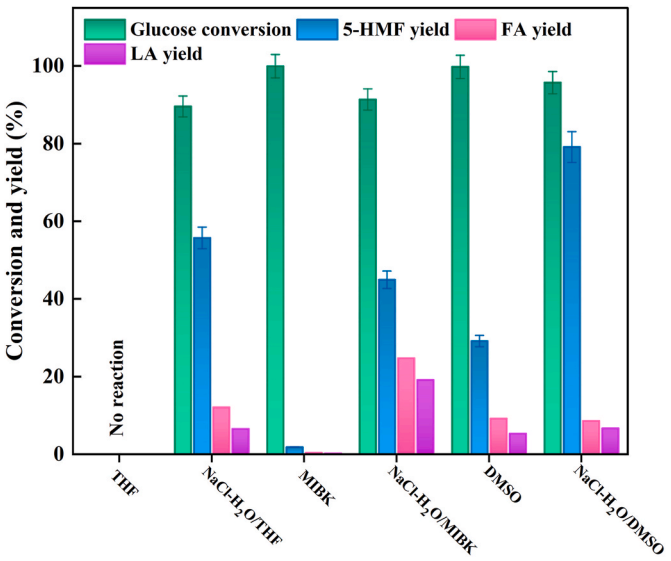

Fig. 8. Effect of various reaction solvents on glucose dehydration to 5-HMF. Reaction conditions: 150 °C, 25 min, glucose/catalyst = 1, catalyst: 1M-SO_4/$ZnAl_2O_4$-TiO_2.

consecutive reactions: isomerization of glucose to fructose followed by dehydration of fructose to 5-HMF, which is also followed by another rehydration reaction, i.e., rehydration of 5-HMF to FA and LA. The product distributions are highly dependent on the reaction conditions, most importantly on the reaction solvents. Reaction solvents such as water, organic solvents, biphasic medium, ionic liquid, etc., play a significant role in achieving the selective formation of 5-HMF. Therefore, to obtain the best reaction solvent at previously optimized reaction conditions such as 150 °C, 25 min, glucose/catalyst ratio of 1, various reaction solvents such as THF, MIBK, DMSO, NaCl-H_2O/THF, NaCl-H_2O/MIBK, and NaCl-H_2O/DMSO were studied in the presence of 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst, as shown in Fig. 8. The pure THF solvent did not show any catalytic activity due to the insolubility of sugars in THF. However, after adding the NaCl-H_2O in THF, it became a two-phase biphasic medium, NaCl-H_2O/THF (NaCl-H_2O represented NaCl saturated water in THF in a volume ratio of 1/3). Thereafter, 5-HMF, FA, and LA were found in the reaction mixture because glucose dehydration happened in the aqueous phase and 5-HMF was extracted in situ and continuously by the THF layer. Therefore, 89.6 % of glucose conversion with 55.7 % of 5-HMF yield, 12 % of FA, and 6.5 % of LA were observed. A very high glucose conversion with traces of 5-HMF yield was obtained in pure MIBK solvent. In contrast, NaCl-H_2O/MIBK solvent changed the product distribution completely with 91 % of glucose conversion and ~45 % of 5-HMF yield with a very high yield of rehydration products such as ~25 % of FA yield and ~19 % of LA due to the drastic shift in the equilibrium concentration in comparison to the pure MIBK solvent [38, 39]. Biphasic MIBK solvent system was found to enhance more rehydrating products, which resulted in a lower yield of 5-HMF than in biphasic THF solvent. Pure DMSO solvent was found to be comparatively more active towards 5-HMF formation than the pure THF and pure MIBK solvent due to its better dehydration capacities and abilities to avoid the side reactions [40]. NaCl-H_2O/DMSO solvent system showed the best activity among all the solvents with 95.7 % of glucose conversion and ~79 % of 5-HMF yield with ~8 % of FA and ~7 % of LA due to its higher affinity towards 5-HMF [41]. Its beneficial effect might also be due to its higher tangent value (tan δ = 0.825) converting more electromagnetic energy into heat energy at the same temperature and frequency [42]. However, the isolation difficulty and thermal degradation of 5-HMF during the separation process from DMSO due to its high boiling point (189 °C, at 1 atm) make it less desirable towards industrial applications. Therefore, NaCl-H_2O/THF biphasic medium was considered the most suitable solvent owing to the easy separation of 5-HMF due to the lower boiling point of THF.

4.5. Comparison of various substrates

The versatility of our best synthesized 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst was investigated by evaluating various feedstocks i.e., fructose, sucrose, and glucose to produce 5-HMF under previously optimized reaction conditions: namely 150 °C, 25 min, glucose/catalyst = 1/1, in NaCl-H_2O/THF solvent under microwave irradiation (Fig. 9). Sucrose is a nonreducing sugar composed of one unit of fructose and one unit of glucose with an acetal oxygen bridge [43] and is therefore more of a raw material than the other two. Sucrose, along with fructose and glucose, demonstrated conversions exceeding 90 %. However, the amount of 5-HMF formation varied between approximately 45 % and 56 % yield across the different sugars. Fructose dehydration resulted in a complete conversion with 48.4 % of 5-HMF yield, along with 14.8 % yield of FA and 9.4 % yield of LA. Sucrose conversion reached around 96 %, with a comparable 5-HMF yield of approximately 45 %, and lower formation of rehydration products, specifically FA and LA (yielding around 12 % and 7.4 %, respectively). On the other hand, glucose exhibited a slightly lower conversion rate (89.6 %) compared to fructose and sucrose but showed a comparatively higher yield of 5-HMF (55.7 %), accompanied by rehydration product yields of 12 % FA and 6.5 % LA. The study highlights the distinct behavior of different sugars as feedstocks for 5-HMF production using the 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst. Fructose demonstrated high conversion and moderate 5-HMF yield, while sucrose showed comparable conversion with slightly lower 5-HMF yield but reduced formation of rehydration products. Glucose exhibited a lower conversion with the highest yield of 5-HMF among all the tested sugars. These findings demonstrated that the high activity of 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst was maintained across diverse substrates. Despite differences in the composition of the substrate evaluated, the catalyst maintained its robust activity, which underscored its broad substrate tolerance. These findings emphasize its viability for sustainable chemical synthesis from renewable resources.

5. Catalyst reusability

The catalyst recycle is an important parameter of heterogeneous catalysts for the pilot-scale production of 5-HMF. The recycle study was conducted under the best conditions obtained during the optimization of

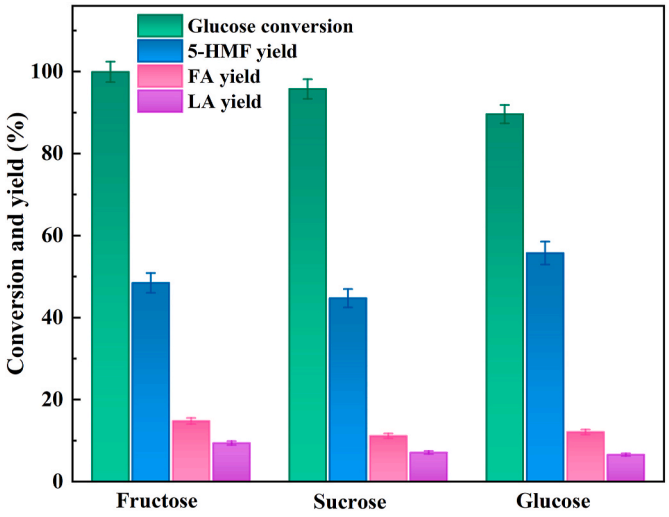

Fig. 9. Effect of various substrates on the yield of 5-HMF. Reaction conditions: 150 °C, 25 min, substrate/catalyst = 1, NaCl-H_2O/THF (1/3 vol%), catalyst: 1M-SO_4/$ZnAl_2O_4$-TiO_2.

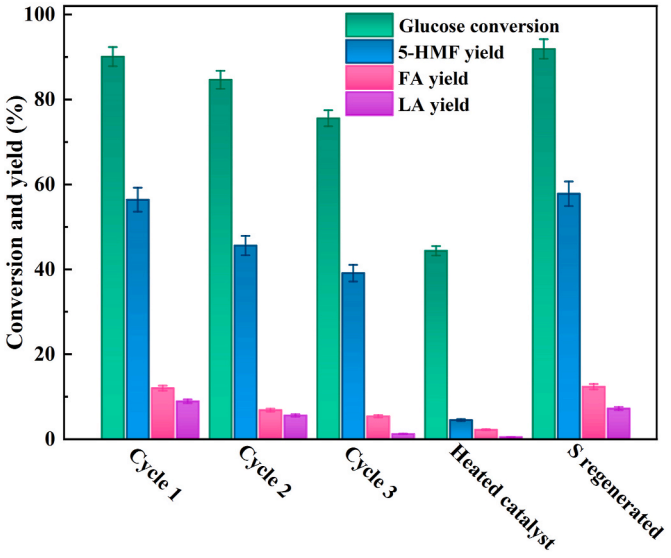

Fig. 10. Recyclability and regeneration of 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst for 5-HMF production. Reaction conditions: 150 °C, 25 min, glucose/catalyst = 1, NaCl-H_2O/THF (1/3 vol%).

reaction parameters, i.e., 150 °C, 25 min, glucose/catalyst = 1, in NaCl-H_2O/THF solvent under microwave irradiation with magnetic stirring in the presence of spinel 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst. After each reaction cycle, the catalyst was first centrifuged at 5000 rpm for 10 min to separate it from the reaction mixture, followed by washing with distilled water and acetone to remove the deposited byproducts from the active surface of the catalyst. Further, the washed catalyst was dried at 120 °C overnight in a conventional oven and used for the next cycles. In cycle 1 (fresh), a glucose conversion of 90.1 % was achieved with a 5-HMF yield of 56.4 %, along with the formation of rehydration products FA (yield of 12 %) and LA (yield of 8.9 %), as reported in Fig. 10. Glucose conversion and 5-HMF yield slightly decreased from 90.1 % to 84.6 % and from 56.4 % to 45.6 %, respectively, in cycle 2. To investigate further, cycle 3 was performed, and it was observed that glucose conversion (75.6 %) and 5-HMF yield (39.1 %) were continuously declining possibly due to the permanent deposition of byproducts, probably polymeric products or humins, on the catalyst's surface, which could lead to further decreases in catalytic activity [44,45]. This was suggested by the physical appearance of the used catalyst after reuse, as the catalyst after the third cycle was observed to be dark brown compared to the fresh catalyst (white), as shown in Fig. S3. Therefore, it was assumed that the catalyst's activity could be regained after regeneration by heating it in a muffle furnace at 400 °C for an hour (developed by us in previous reports [36]. This heated regenerated catalyst after the third cycle is labeled as the Heated catalyst. The activity of the Heated catalyst was tested for further reuse, and it was found that glucose conversion and 5-HMF yield did not improve; instead, they significantly declined further to ~45 % and ~5 %, respectively, due to the loss of Brönsted acidic sites provided by S-containing groups at the catalyst's surface as it was confirmed by XRD and Py-FTIR analysis (Fig S4 and Fig S5), as well as from the EDX data of used catalyst (Table S4). However, indeed, XRD confirmed the absence of several peaks corresponding to monoclinic sulfur at 2θ values of 6.45°, 12.45°, 19.64°, 20.42°, 22.64° and 29.16° (Fig. S5). Notably, the spinel structure remained well-preserved and maintained a stable coexistence with the anatase phase of TiO_2. Leaching of sulfur was also observed by ICP-OES analysis on the reaction filtrate (Table S4). In this context, to improve the B sites on the heated material after use, the sulfate groups were again regenerated on the used material using ammonium sulfate as sulfate ion source by following the same method as reported in the catalyst preparation section 2.1. The sulfate ion-regenerated catalyst was labeled as the S-regenerated catalyst and used for a further cycle of glucose dehydration reaction. It was observed that the S-regenerated catalyst regained its catalytic activity with 92 % of glucose conversion as well as a 5-HMF yield of 57.8 %, along with similar yields of byproducts, i.e., 12.4 % of FA and 7.2 % of LA yield, as reported in the presence of the fresh catalyst. The catalytic activity was improved due to the addition of sulfate groups (source of B sites), as the presence of B sites was confirmed by Py-FTIR spectra, as shown in Fig. S4. Therefore, this demonstrated that with the reimpregnation of sulfate groups even after the fourth use of recycled catalyst, the catalytic activity could be regained and used multiple times with comparable catalytic activity and selectivity to the fresh catalyst.

The carbon balance was also calculated based on the known reaction products obtained at the optimized reaction conditions. A ~75 % portion was accounted for by known products while the remaining carbon was attributed to unknown products, potentially including humins, as indicated by the brown color of the recovered catalyst (Fig. S3(b)), and an unidentified peak observed around ~22 min in the HPLC chromatogram (Fig. S6). The detailed calculation of carbon balance is provided in the supplementary information.

The structure of the 1M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst consists of metal centers (Ti^{4+}/Al^{3+}/Zn^{2+}) supported by a sulfated metal oxide framework. The sulfate groups (SO_4^{2-}) possibly enhanced both Lewis and Brönsted acidity on the catalyst surface. The possible structure of the catalyst is proposed based on literature data and characterization results, particularly XRD and EDX, as shown in Fig. S7 (Supplementary information). To understand the relationship between catalyst properties and catalytic activity, a possible reaction mechanism is proposed in Fig. S8 (Supplementary information), based on available data from the literature. The detailed mechanism is provided in the supplementary information.

6. Comparison of the catalytic performance of a sulfated spinel mixed metal catalyst with previously published results

A comparative study of the performance of previously reported catalytic systems for glucose dehydration under microwave irradiation is presented in Table S5, highlighting the results obtained in our study. Our investigation achieved a 5-HMF yield of ~58 % using a 1.5M-SO_4/$ZnAl_2O_4$-TiO_2 catalyst in a NaCl-H_2O/THF biphasic system. This yield is competitive with various previously reported homogeneous catalysts ($AlCl_3$, formic acid, betaine) and heterogeneous catalysts such as TiO_2, Al_2O_3, ion exchange resins, and $CrCl_3$, which have given yields of 26 %–70 % 5-HMF from glucose. Due to the poor recyclability of homogeneous catalysts, we prefer solid acid catalysts over them. Our reported yield (58 %) is notable in comparison to the lower yield of ~26 % reported by Dutta et al. [42] Utilizing mesoporous TiO_2 nanoparticles in a water/-MIBK system at 130 °C. In contrast, Mittal et al. [46] Reported a higher yield of 70 % using an acidic ion-exchange resin with amorphous silica alumina catalyst under more extreme conditions of 195 °C. Similarly, Guo et al. [47] Achieved a yield of 68 % with a lignin-derived solid acid catalyst at 160 °C for 50 min in the presence of ionic liquid. However, ionic liquids are significantly more expensive and therefore less suited for industrial applications.

7. Conclusions

This study presents the synthesis and characterization of spinel $ZnAl_2O_4$-based catalysts, xM-SO_4/$ZnAl_2O_4$-TiO_2, prepared via sol-gel followed by sulfate impregnation. X-ray diffraction patterns confirmed the formation of the spinel structure and anatase TiO_2, a required active phase for the glucose dehydration reaction. Nitrogen physisorption isotherms revealed mesoporous characteristics with slit type pores in the synthesized xM-SO_4/$ZnAl_2O_4$-TiO_2 materials, with a thermal stability up to 500 °C. An insignificant change in the surface area was observed (~77–90 m^2/g) with sulfate modification. The highest total acidity and B/L ratio were obtained at 1M concentration, with a subsequent decline at higher loadings (>1.5M). Among the catalysts synthesized, 1M-SO_4/$ZnAl_2O_4$-TiO_2 exhibited superior catalytic performance, achieving a remarkable 90 % glucose conversion and ~58 % of 5-HMF yield at 150 °C after 25 min of reaction under microwave irradiation in a H_2O-saturated NaCl/THF medium. Enhanced activity was attributed to the high acidity, optimal B/L ratio, and the presence of ternary metal oxides (Ti-Zn-Al), which synergistically enhance Lewis acidity through multiple electron-deficient sites. Moreover, the selection of solvents employed had a profound influence on product distribution, particularly in biphasic media, where 5-HMF formation was favored. In addition, pure THF exhibited no catalytic activity, contrasting sharply with pure MIBK, which propelled the reaction towards nonselective glucose dehydration. Remarkably, the catalyst displayed consistent activity across various sugars. Moreover, despite a decline in catalytic activity observed in the third cycle due to the leaching of sulfur species, the regeneration of the catalyst with sulfate groups restored performance to levels comparable to the fresh catalyst, highlighting its potential for efficient and sustainable catalytic processes. The successful regeneration of catalytic activity underscores the feasibility of employing this catalyst in sustainable chemical processes. The catalyst's compatibility with various sugars and adaptable solvent systems enhances its applicability across diverse reaction environments. Moreover, the research can be further continued to explore various strategies to improve the stability of acidic functional groups on spinel mixed metal oxide catalysts.

CRediT authorship contribution statement

Richa Tomer: Writing – review & editing, Writing – original draft, Visualization, Validation, Methodology, Investigation, Formal analysis, Data curation, Conceptualization. **Sophie Hermans:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Funding acquisition, Formal analysis. **Prakash Biswas:** Writing – review & editing, Visualization, Validation, Supervision, Resources, Funding acquisition.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.renene.2025.123268.

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