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Research Article

Oxidation of Styrene to Benzaldehyde Using Environmentally Friendly Calcium Sulfate Hemihydrate-Supported Titania Catalysts

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Abstract

This paper presents the synthesis and characterization of calcium sulfate hemihydrate (CSH)-supported titania (TiO_2) catalysts and their application in the environmentally friendly oxidation of styrene to benzaldehyde using hydrogen peroxide (H_2O_2) as the oxidant. The study explores the catalyst's structure-activity relationship, emphasizing the importance of mesoporous materials for enhanced catalytic performance. The CSH-Titania catalysts were synthesized using fish bone-derived CSH as a support, which aligns with green chemistry principles. Characterization techniques such as Fourier Transform Infra Red (FTIR), X-ray Diffraction (XRD), Scanning Electron Microscope (SEM), and Brunauer-Emmett-Teller (BET) surface area analysis confirmed the successful impregnation of titania and its catalytic efficiency. The catalysts exhibited high selectivity for benzaldehyde, achieving up to 49.45% conversion of styrene, with benzaldehyde as being the main product. The research highlights that the catalyst's performance decreased after calcination due to a reduced surface area and pore volume, yet it maintained recyclability across three cycles with minimal lose in selectivity loss. Overall, this study introduces a cost-effective and sustainable approach to styrene oxidation, demonstrating the potential for industrial application in producing high-value chemicals with minimal environmental impact.

Keywords: CSH-Titania; styrene oxidation; benzaldehyde; green chemistry; hydrogen peroxide; mesoporous materials

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1. Introduction

Benzaldehyde is a versatile synthetic intermediate widely used in the chemical industry, with applications in the manufacture of perfumery, anthelmintics, epoxy resins, plasticizers, drugs, sweeteners, epoxy paints, pharmaceuticals, dyestuffs, and agrochemicals. [1-4]. Currently, benzaldehyde is produced industrially by two processes: the catalytic

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oxidation of toluene with oxygen and the hydrolysis of benzyl chloride. However, both synthetic routes present significant drawbacks, such as high temperatures, long reaction times, and the production of chloride wastes, leading to low catalytic conversion, poor benzaldehyde yields (up to 20%), and low selectivity. The oxidation of styrene to benzaldehyde is particularly challenging because styrene is a terminal olefin. Many researchers have made considerable efforts to identify catalysts that could increase the conversion of styrene to benzaldehyde, including various homogeneous and heterogeneous catalytic processes [5-8]. The use of homogeneous catalysts presents major challenges, such as high cost, difficulty in separating the catalyst from the reaction mixture, low recycling performance, and, in some cases, poor catalytic activities. In addition, most of these homogeneous catalysts become inactive after the reaction, which is undesirable in industrial applications.

To overcome the problems associated with homogeneous catalysts, heterogeneous catalysts have been considered and successfully developed for styrene oxidation due to their efficiency and environmental friendliness in line with green chemistry principles. The common strategy for creating heterogeneous catalysts is to embed active sites on various supports, such as molecular sieves, graphene oxide, zeolites, carbon, and clay. Noble metals that have been reported as active sites for catalysts in the oxidation of styrene include gold, silver, palladium, platinum, etc. However, these metals are often expensive and environmentally unfriendly. Furthermore, to obtain a heterogeneous catalyst that is practical for industrial applications—easy to manufacture, environmentally friendly, cheap, and easy to recycle–further exploration is necessary.

The use of calcium sulfate hemihydrate (CSH) derived from fish bone waste as a catalyst supports a significant environmental advantage by recycling biological waste into a high-value material. This approach aligns with the principles of green chemistry, promoting the use of renewable feedstocks and minimizing waste. By utilizing a waste-derived material, the overall environmental footprint of the catalytic process is reduced, making it more sustainable compared to traditional synthetic supports

The synthesis of CSH from fish bones represents an innovative approach to valorize waste materials, promoting sustainability and reducing reliance on synthetic alternatives. This process not only aligns with circular economy principles but also minimizes environmental impacts by transforming biological waste into high-value catalytic supports, a key goal in green chemistry.

Currently, many researchers have tried to develop styrene oxidation catalysts using H_2O_2 as an oxidant, such as Ag-WO_3 [9], $NiCo_2O_4$ and Co(Ni)PW_{12} [10], Ag-ferrite [11], V_2O_5/g-C_3N_4 [12], Spherical V-MCM-48 [13], ZnPc–MWCNTs [14], Ni–Gd ferrites [15], Fe- and Ti-SBA-1 [16], Mg–Co–Al hydrotalcite [17], Mg–Cu ferrite [18], Ag-Co-MCM-41 [19], and $H_3PW_{12}O_{40}$ on SBA-15 [20]. Although these catalysts have high styrene conversion and good selectivity for benzaldehyde, they are not cheap due to the expensive catalyst supports and active sites used, and they are not environmentally friendly.

This study addresses critical gaps in green oxidation by developing a novel catalyst based on mesoporous CSH derived from fish bones. Current supports like zeolites and silica, while effective, are associated with high production costs, limited recyclability, and significant environmental impact. In contrast, the use of fish bone-derived CSH not only reduces reliance on non-renewable resources but also promotes waste valorization, transforming biological waste into valuable catalytic materials. This approach aligns with circular economy principles and the goals of green chemistry by minimizing environmental impact, enhancing resource efficiency, and utilizing renewable feedstocks.

In this work, cheap heterogeneous catalysts were proposed as alternative catalysts for the oxidation of styrene. The catalysts were created using CSH as the support, which was produced from fish bone waste following previous research [21]. Titania was chosen as the active site in this work due to its structural stability, biocompatibility, and optical and electrical properties. Titania has been reported to give good activity and selectivity in the oxidation of styrene when used with a catalyst support [5,16,22-33]. It has four kinds of species—Ti^{+}, Ti^{2+}, Ti^{3+}, and Ti^{4+}. Ti^{+} and Ti^{2+} ions are quite unstable and easily oxidized into Ti^{3+} and Ti^{4+}[34]. The anatase and rutile forms of TiO_2 are commonly used in oxidation reactions due to their commercial availability and the generation of large amounts of reactive oxygen species (ROS), such as hydroxyl ($\cdot$OH) radicals, hydroperoxy radicals ($\cdot$OOH), and superoxide ($\cdot O_2^-$) radical anions on the TiO_2 surface [33]. Therefore, in the oxidation of styrene, H_2O_2 was used as an oxidant, which decomposes to produce H_2O and O_2, making it an environmentally benign approach.

2. Materials and methods

2.1 Fabrication of CSH

Fabrication of CSH procedure was carried out following the previous research [21]. The carbon from fishbone was immersed in 6 mL of concentrated sulfuric acid (H_2SO_4; JT Beker) for every 1 gram. The mixture was stirred at room temperature for 3 h and washed with distillate water to remove any loosely bound acid until pH of filtrate 2. Then, the carbon solution was saved at room temperature for few days until the crystal growth. Furthermore, decantation and filtration were conducted to separate carbon and crystal. The crystal was washed with distilled water until the filtrate reached neutral pH. The crystal then dried at 110 °C for overnight.

2.2 Titania Impregnation

The impregnation process follows the previous research [5]. Firstly, the CSH crystal was crushed until the size 200 mesh. 1 gram CSH was impregnated by titanium(IV) isopropoxide (500 μmol, Sigma Aldrich) that was immersed in 10 mL acetone (Merck) and stirred until all of the toluene solvents completely evaporated. The residual acetone was removed from the CSH sample by washing with ethanol (Merck) and subsequently dried at 110 °C overnight. The CSH sample was impregnated and labeled as CSHTix, x = concentration of Ti. For example, CSHTi500 was the CHS that was impregnated by titanium(IV) isopropoxide (500 μmol) and CSHTi500Cal was CSH impregnated titania with calcinations at 500 °C for 2h.

Calcination at 1000 °C was optimized to maintain anatase phase stability, as corroborated by studies demonstrating anatase retention at this temperature through strong titania lattice interactions. This high temperature prevents phase transition to rutile by stabilizing the anatase crystal structure, ensuring enhanced catalytic performance linked to the increased ROS production capacity of anatase.

2.4 Samples Characterizations

A series of catalysts were characterized, including CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal, to investigate the structure-activity relationships between the catalysts and the styrene oxidation. The catalysts were characterized by Wavelength Dispersive X-ray Fluorescence (WDXRF), FTIR, XRD, SEM, N_2 adsorption-desorption and TEM. The chemical composition from the catalyst was investigated by using WDXRF (PANalytical, Minipal 4). FTIR spectrometer (IR−Prestige−21 Shimadzu) was used to identify the functional groups in the catalyst. The crystallinity and phase content of the catalyst was analyzed using Powder XRD instrument (Philips PANalytical X'Pert PRO) in which Profex 5.4 and OriginPro software were used for crystal data analysis. The SEM-EDX (FEI Inspect S50) instrument was used to determine the surface morphology and element containing the catalyst. The nitrogen adsorption-desorption instrument (Quantachrome NovaWIn instrument version 11.0) was used to investigate surface area, pore volume and pore size of the catalyst. TEM images were recorded on a JEM-2100F high resolution transmission electron microscope at an accelerating voltage of 200 kV.

2.5 Catalytic Activity Test

The performance of catalysts was investigated in a styrene oxidation reaction with aqueous H_2O_2 as an oxidant. The reactions procedure was carried out following the previous research [5,35]. All reactions were conducted for 24 h at room temperature with reacting 5 mmol styrene (Merck), 5 mmol aqueous H_2O_2 (Merck), 4.5 mL acetonitrile (Merck), and 100 mg catalyst under stirring. The reaction products were withdrawn and analyzed by GC-2010 Shimadzu-gas chromatograph equipped with a SH-Rxi-5ms column (30 m × 0.25 mmID × 0.25 μm df), serial 1652111, a flame ionization detector (FID) and nitrogen as the carrier gas. The GC method: the temperatures of the injector and detector were programmed at 250 and 260 °C, respectively; the temperature of the column oven was programmed at 80 °C; pressure 100kPa; flow 28 mL/min; collumb flow 1.19 mL/min; linear velocity 31.1 cm/sec; purge flow 3.0 mL/min; spit ration 20. All reactions were conducted in 10 mL of deionized water to maintain consistency and ensure reproducibility. This standardized volume also minimizes diffusion limitations, enhancing the interaction between hydrogen peroxide and the active catalytic sites.

To assess the reuseablelity and stability, all catalysts were recovered and recycled for further reaction. Post-reaction, the catalyst was recovered via centrifugation at 5000 rpm, washed with ethanol to remove residual reactants, and dried at 110 °C overnight to ensure complete removal of moisture. These steps maintain the structural integrity of the catalyst and prevent contamination during reuse.

3. Results and Discussion

3.1 Physical Properties

The elements present in CSH, CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal were determined using wavelength dispersive X-ray fluorescence (WDXRF). The complete results of the elemental analysis are shown in Table 1. CSH consists primarily of calcium (Ca) and sulfur (S) as major elements. Various metal elements were also found within the CSH, such as iron (Fe), copper (Cu), and ytterbium (Yb). The impregnation of titania is evidenced by the percentage of titanium present: 9.93% in CSHTi500; 8.34% in CSHTi500Cal; 14.10% in CSHTi1000; and 12.8% in CSHTi1000Cal. The calcination process caused a slight decrease in the amount of titanium.

The FTIR spectra of (a) TiO_2, (b) CSH, (c) CSHTi500, (d) CSHTi500Cal, (e) CSHTi1000, and (f) CSHTi1000Cal were measured over the range of 400–4000 cm^{-1} and are shown in Figure 1. All spectra display absorption peaks around 3200–3600 cm^{-1}, which are assigned to O–H stretching and might be attributed to adsorbed water molecules. The FTIR spectra of CSH show absorption bands at 3613, 3559, and 1687 cm^{-1}, associated with crystal water molecules combined in $CaSO_4$ [36-38]. The characteristic bands of $CaSO_4$ can be identified by the band at 1272 cm^{-1}, assigned to Ca^{2+}, and bands at 1108, 1007, 673, and 618 cm^{-1}, assigned to SO_4^{2-} stretching. The absorption peaks due to titania impregnation can be observed in Figure 1 (c–f). The presence of titania in the catalyst samples is evidenced by absorption peaks around 900–1000 cm^{-1}, which indicate the local stretching modes of [TiO_4] and/or [O_3TiOH], and the titanyl [Ti=O] vibration [25,39-40]. However, the absorption band of Ti–O in these FTIR spectra is indistinct, which is attributed to the small amount of titania impregnated onto CSH.

Figure 2 shows the XRD patterns illustrating the crystallinity of (a) TiO_2, (b) CSH, (c) CSHTi500, (d) CSHTi500Cal, (e) CSHTi1000, and (f) CSHTi1000Cal catalysts. The crystal phase and structure of the sample were analyzed by using Profex 5.4 software and the particle size was

Table 1. Elements analysis of CSH, CSHTi500, CSHTi500Cal, CSHTi1000 and CSHTi1000Cal obtained using WDXRF.

Element (wt%)	CSH	CSH-Ti500	CSH-Ti500Cal	CSH-Ti1000	CSH-Ti1000Cal
S	26.5	24.4	26.9	24.2	24.4
Ti	-	9.93	8.34	14.1	12.8
Ca	71.2	57.9	59.6	59.6	59.9
Fe	0.065	0.19	0.06	0.054	0.065
Cu	0.052	0.095	0.055	0.067	0.061
Yb	0.27	0.20	0.15	0.21	0.21

Table 2. Particle size and phase of the sample by using Profex 5.4 and OriginPro2021 software

Samples	Calcium Sulfate Hemihydrate (CSH; nm)	Calcium Sulfate Dihydrate (CSD; nm)	Calcium Sulfate Anhydrate (CSA; nm)	Anatase (TiO_2; nm)
TiO_2	-	-	-	41.9
CSH	48.4	72.6	-	-
CSHTi500	39.6	73.6	-	0.101
CSHTi500Cal	-	-	27.7	0.866
CSHTi1000	31.4	74.8	-	0.169
CSHTi1000Cal	-	-	26.5	0.730

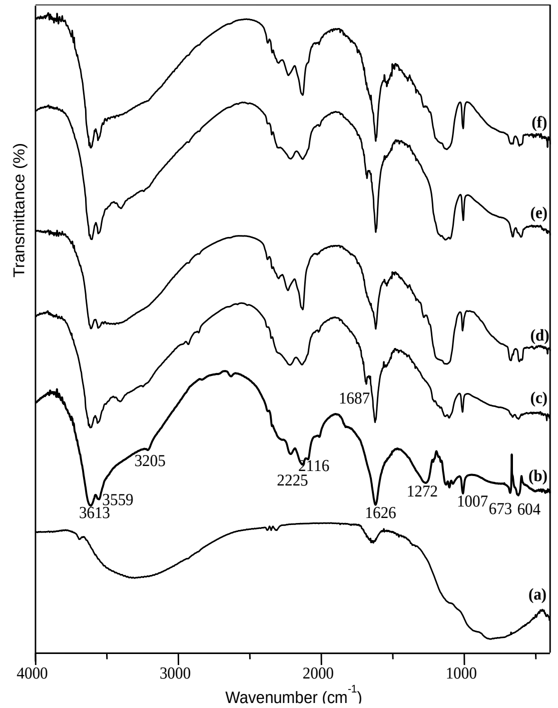

Figure 1. FTIR spectra of (a) TiO_2, (b) CSH, (c) CSHTi500, (d) CSHTi500Cal, (e) CSHTi1000, and (f) CSHTi1000Cal

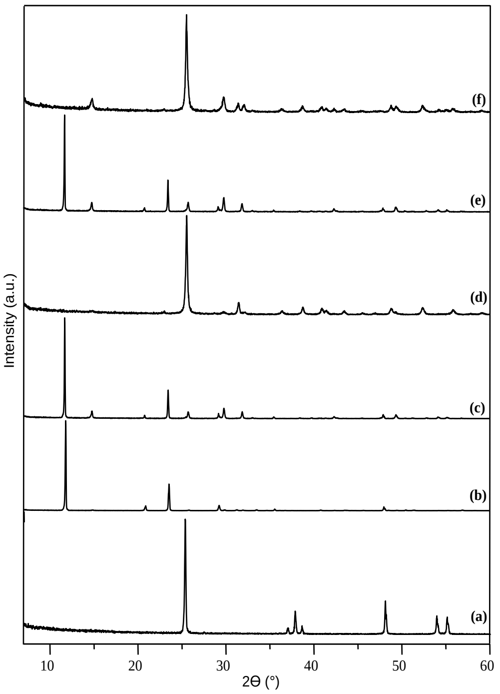

Figure 2 XRD pattern of (a) TiO_2, (b) CSH, (c) CSHTi500, (d) CSHTi500Cal, (e) CSHTi1000, and (f) CSHTi1000Cal

determined by using OriginPro 2021b software. The detail of phase and particle sizes were listed in Table 2. Figure 2(a) displays the anatase form of TiO_2 (JSPDF number 04-007-0701) catalyst, as evidenced by diffraction peaks at 2θ angles of 25.2°, 37.7°, 47.9°, 53.7°, and 55.1°. Figure 2(b) shows the diffraction peaks at 2θ angles of 14.7°, 25.7°, 29.7°, 31.9°, 42.2°, and 49.4° in which based on the the Profex 5.4 analysis, it was identified as Calcium Sulfate Dihydrate (CSD; $CaSO_4$. $2H_2O$ (JSPDF number 00-033-0311); 72.6 nm) and Calcium Sulfate Hemihydrate (CSH; $CaSO_4$. 0.5 H_2O (JSPDF number 00-041-0224); 48.4 nm). Figures 2(c) and 2(e) after were analyzed by using Profex 5.4 and OriginPro software obtained CSH ($CaSO_4$. 0.5 H_2O (JSPDF number 00-041-0224); 39.6 and 31.4 nm), CSD ($CaSO_4$. $2H_2O$ (JSPDF number 00-033-0311); 73.6 and 74.8 nm) and anatase TiO_2 (JSPDF number 04-007-0701; 0.101 and 0.169 nm). Figures 2(d) and 2(f) show CSH impregnated with titania after the calcination process. After analysing by using Profex 5.4 and OriginPro software, the samples were confirmed as Calcium Sulfate Anhydrate ($CaSO_4$ (JSPDF number 00-037-1496); 27.7 and 26.5 nm) and TiO_2 anatase (JSPDF number 04-007-0701; 0.866 and 0.730 nm). The calcination process caused the release of H_2O that bonded with $CaSO_4$ as CSH and CSD, thus converted into anhydrous $CaSO_4$. This is evidenced by the dominant peaks at 2θ angles of 25.5°, 31.3°, 38.6°, 48.8°, 52.3°, and 55.8°. The calcinations process also cause the agglomeration and clustering of anatase TiO_2 which indicated by increasement the particle size from ~ 0.135 to 0.798 nm.

The identification of the anatase phase in the CSH-Titania catalysts is particularly significant for their catalytic performance. Anatase is known to generate more reactive oxygen species (ROS), such as hydroxyl and superoxide radicals, compared to rutile. This increased ROS generation plays a critical role in facilitating the oxidation of styrene, leading to higher conversion rates and improved selectivity for benzaldehyde.

Figure 3 exhibits the SEM images of catalysts (a) CSHTi500, (b) CSHTi500Cal, (c) CSHTi1000, and (d) CSHTi1000Cal. All catalysts show roughened surfaces due to titania deposition. The

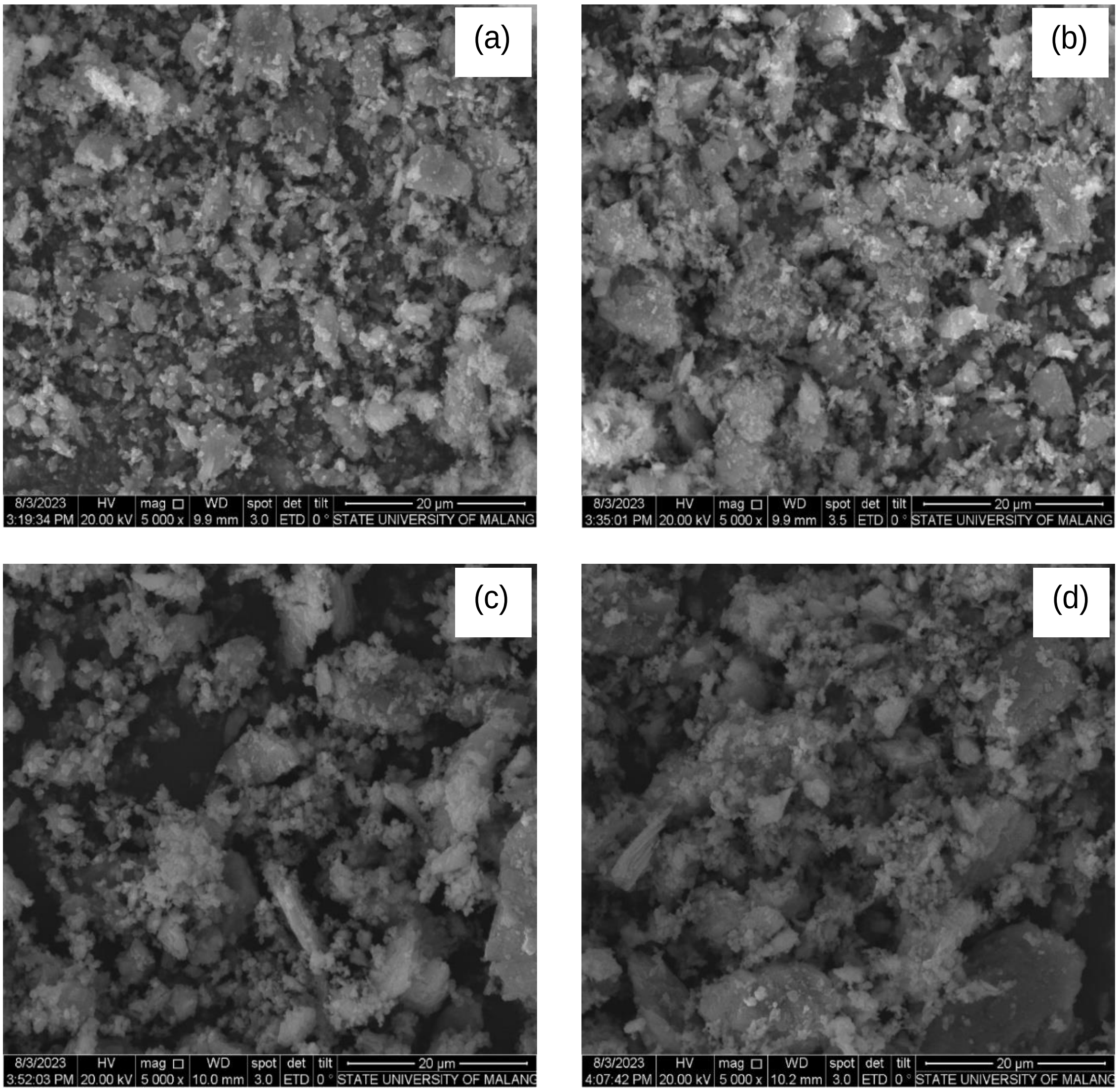

Figure 3. SEM Image of (a) CSHTi500, (b) CSHTi500Cal, (c) CSHTi1000, and (d) CSHTi1000Cal

calcination process did not significantly change the surface morphology of the catalysts. The rough surface morphology observed in the SEM images suggests an increase in the active surface area, facilitating more efficient contact between the catalyst and the styrene molecules. This enhanced surface area allows for a higher conversion rate as more reactant molecules interact with the catalyst's active sites. However, after calcination, the surface area is reduced due to particle agglomeration and sintering, leading to a decrease in catalytic performance, as evidenced by the drop in styrene conversion post-calcination.

Nitrogen adsorption-desorption analysis was used to determine the BET surface area, pore volume, and mean pore size of CSH, CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal. Figure 4 shows the isotherms for (a) CSHTi500, (b) CSHTi500Cal, (c) CSHTi1000, and (d) CSHTi1000Cal, which exhibit type IV isotherms according to IUPAC classification, with narrow hysteresis loops. This indicates the mesoporous character of the pore materials. The isotherms display narrow hysteresis loops in the relative pressure range of approximately 0.6–1.0 for CSHTi500, and 0.45–1.0 for CSHTi500Cal, CSHTi1000, and CSHTi1000Cal. The pore size distribution of all samples is between 2 nm and 50 nm, indicating the presence of uniform mesopores. The BET surface area and pore volume showed the following values: CSH (11.33 m^2/g, 0.043 cm^3/g), CSHTi500 (21.99 m^2/g, 0.0304 cm^3/g), CSHTi500Cal (1.76 m^2/g, 0.0411 cm^3/g), CSHTi1000 (32.12 m^2/g, 0.0381 cm^3/g), and CSHTi1000Cal (23.85 m^2/g, 0.0419 cm^3/g). The complete data are listed in Table 3. In this phenomenon, the calcination process can cause a decrease in the BET surface area and pore volume. Calcination can lead to clustering or sintering, which results in larger metallic particles and poorer dispersion, ultimately reducing the catalytic activity of the catalyst.

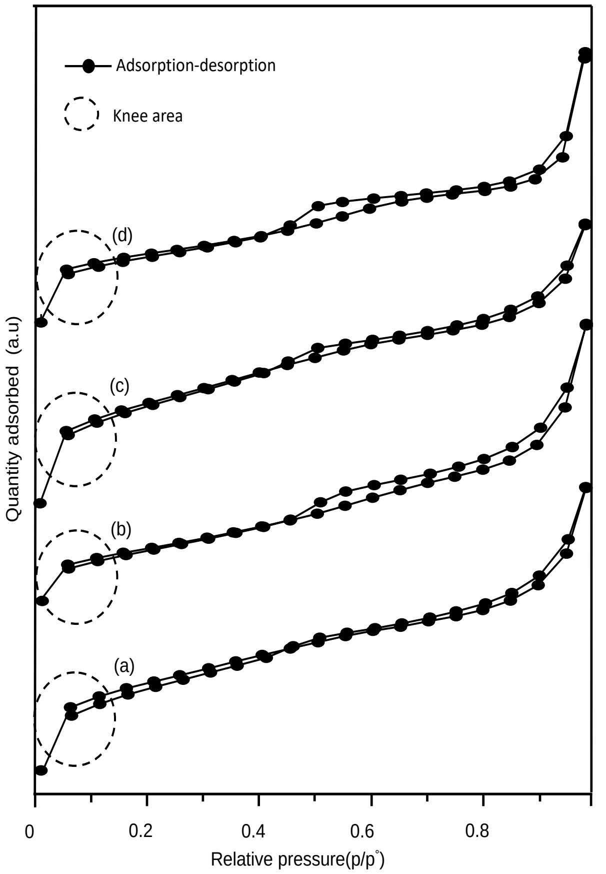

Figure 4. The physisorption isotherms of (a) CSHTi500, (b) CSHTi500Cal, (c) CSHTi1000, and (d) CSHTi1000Cal

Figure 5 shows the TEM images of catalysts (a) CSHTi500, (b) CSHTi500Cal, (c) CSHTi1000, and (d) CSHTi1000Cal. TEM imaging was used to investigate the influence of impregnation conditions on the morphology and titania particle distribution within the CSH matrix. In Figure 5, TEM images (a)–(d) capture TiO_2/CSH at different magnifications, each with a 50 nm scale. Figure 5(a) shows that TiO_2 particles are unevenly distributed, with a tendency to form agglomerations measuring tens of nanometers. This indicates a strong interaction between TiO_2

Table 3. Physical properties of the samples

Samples	BET surface area (m^2/g)	Pore Volume (cm^3/g)	Mean pore size (nm)
CSH	11.336	0.0428	7.5
CSHTi500	21.986	0.0304	2.7
CSHTi500Cal	1.761	0.0411	46.7
CSHTi1000	32.125	0.0381	2.4
CSHTi1000Cal	23.855	0.0419	3.5

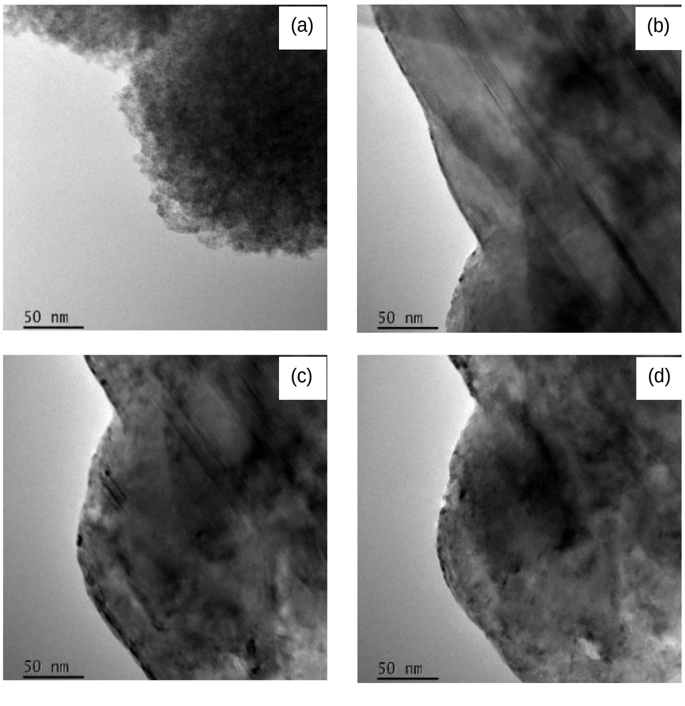

Figure 5. The TEM image of (a) CSHTi500, (b) CSHTi500Cal, (c) CSHTi1000, and (d) CSHTi1000Ca

particles and the possibility of preferential interaction with the surface or defects in CSH. Figure 5(b) shows that the distribution of TiO_2 particles is more homogeneous compared to Figure 5(a), but agglomeration is still visible, indicating that interactions between TiO_2 particles remain dominant. Figures 5(c) and 5(d) reveal that the distribution of TiO_2 particles is more even with less agglomeration, indicating that the different impregnation conditions in these two samples resulted in better dispersion of TiO_2 particles in the CSH matrix. Overall, these TEM images indicate that the impregnation conditions can affect the morphology and distribution of TiO_2 particles on CSH.

The uniform distribution of titania particles observed in the TEM images, particularly in the CSHTi1000 and CSHTi1000Cal samples, enhances the exposure of active sites, allowing more styrene molecules to access the catalyst surface. This increased accessibility correlates with improved catalytic performance, as shown by the higher conversion rates in these samples. Conversely, the agglomeration of particles in other samples reduces the number of accessible active sites, leading to lower conversion rates.

3.2 Catalytic Activity

3.2.1 Catalysis testing

After the successful incorporation of titanium into the CSH, the material was employed as a catalyst for the classical oxidation of styrene, as depicted in Scheme in Figure 6. Catalysts, such as TiO_2, CSH, CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal, were tested in the oxidation of styrene using H_2O_2 as the oxidant. The products of styrene oxidation using H_2O_2 were benzaldehyde, phenylacetaldehyde, styrene oxide, and others, with benzaldehyde being the dominant product. The formation of benzaldehyde results from the nucleophilic attack of H_2O_2 on styrene oxide, followed by cleavage of the intermediate hydroxy–hydroperoxystyrene, oxygen transfer from metallic oxides to styrene, and finally cleavage of the metalloepoxy intermediate and the C=C bond [41-42]. In this study, benzaldehyde was the main product when using TiO_2, CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal catalysts, with selectivity around 60–88%. When CSH was used as the catalyst, styrene oxide was the main product, with a selectivity of approximately 65%. The complete yields and product selectivities for the oxidation of styrene with H_2O_2 as the oxidant are shown in Table 4.

Hydrogen peroxide (H_2O_2) was chosen as the oxidant in this process due to its environmentally benign nature. Upon decomposition, H_2O_2 produces only water and oxygen, avoiding the generation of harmful by-products typically associated with other oxidants. This makes H_2O_2 an ideal oxidant for green chemistry applications, ensuring that the oxidation of styrene proceeds with minimal environmental impact while maintaining high selectivity for the desired product, benzaldehyde.

H_2O_2 serves as an effective oxidant in this reaction due to its ability to decompose into reactive oxygen species (ROS) on the surface of the titania catalyst. The interaction between H_2O_2 and Ti^{3+}/Ti^{4+} species on the catalyst surface facilitates the homolytic cleavage of the O–O bond, producing hydroxyl radicals (•OH) and hydroperoxy radicals (•OOH), which drive the oxidation of styrene. This interaction allows the oxidation to occur under mild conditions, making H_2O_2 a highly efficient and environmentally friendly oxidant for this process.

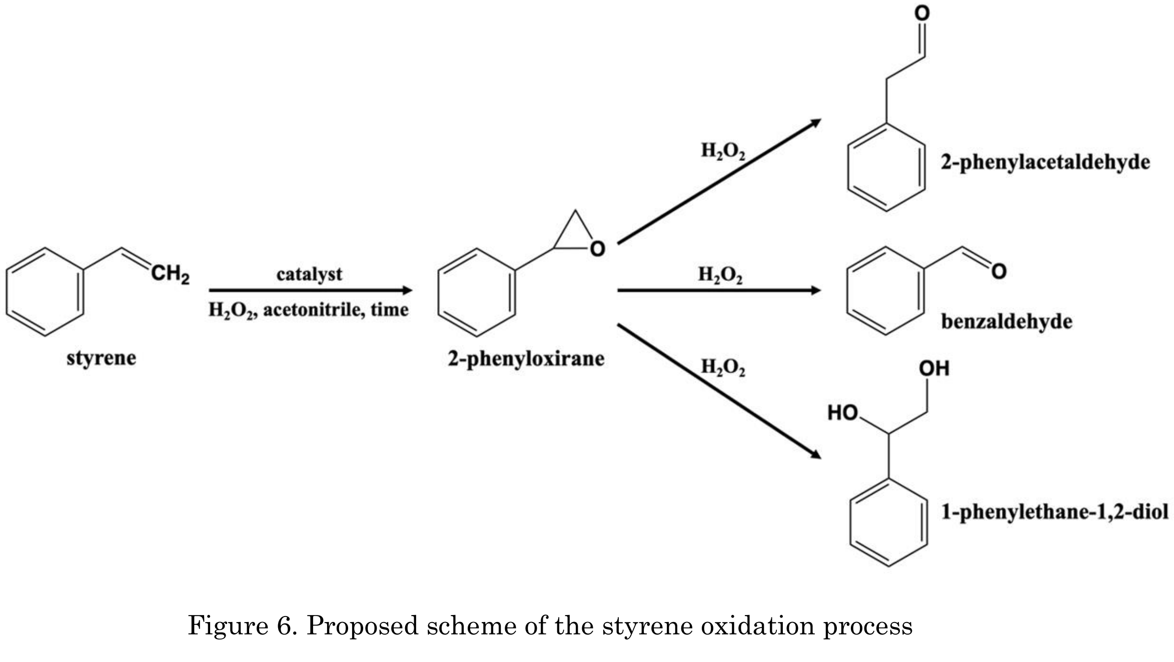

Figure 6. Proposed scheme of the styrene oxidation process

The high selectivity for benzaldehyde observed in the oxidation of styrene can be attributed to the surface properties of the CSH-Titania catalyst. The presence of acidic sites on the titania promotes the cleavage of the C=C bond and the epoxide ring, favoring the formation of benzaldehyde over styrene oxide or phenylacetaldehyde. Additionally, the dispersion of titania particles on the CSH support enhances the accessibility of active sites, ensuring that the oxidation process proceeds efficiently with minimal by-product formation.

The styrene conversions over no catalyst, TiO_2, CSH, CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal catalysts were 1.43%, 3.16%, 5.86%, 49.45%, 7.95%, 30.40%, and 20.04%, respectively. Reactions using only titania or CSH as catalysts occurred at a very low rate. The role of the catalyst support is demonstrated by comparing the styrene conversions using TiO_2, CSH, and CSHTi500 as catalysts. The styrene oxidation using the metal catalyst (TiO_2) and the support catalyst (CSH) showed lower activity than titania supported on fish bone-derived CSH (CSHTi500). The effect of the calcination process on the catalyst support can be observed when CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal were used as catalysts. The calcination process decreased the styrene conversion, as shown by the styrene conversion over CSHTi500 being 49.45%, while CSHTi500Cal gave only 7.95%. The decrease in styrene conversion correlates with the decrease in surface area from CSHTi500 (21.99 m^2/g) before calcination to CSHTi500Cal (1.76 m^2/g) after calcination. During the calcination process, clustering or sintering leads to larger metallic particles that block the pores. This result is in agreement with previous research where styrene oxidation with H_2O_2 as an oxidant was catalyzed with CSH-loaded TiO_2. Increasing the amount of titania impregnated in CSH does not necessarily increase the styrene conversion, as shown by the styrene conversion over CSHTi500 being 49.45%, while CSHTi1000 gave only 30.40%. This is because increasing the amount of metal impregnated onto the support can cause clustering and agglomeration, leading to larger metallic particles.

The superior activity of CSHTi500 can be attributed to its optimal pore size distribution and homogenous titania dispersion, which enhance reactant accessibility and ROS generation. Despite its lower surface area compared to CSHTi1000, these properties facilitate efficient oxidation by providing readily available active sites and maintaining high catalytic selectivity.

The high catalytic activity of CSHTi500 (49.45% conversion) can be attributed to its large surface area (21.99 m^2/g) and pore volume (0.0304 cm^3/g), which allow for greater interaction between styrene and the active titania sites. In contrast, the calcination process reduces the surface area of CSHTi500Cal to 1.76 m^2/g, leading to a dramatic decrease in conversion (7.95%). The reduction in surface area and pore accessibility after calcination limits the availability of active sites, directly impacting the overall catalytic performance.

The distribution of titania particles on the CSH support plays a crucial role in determining catalytic efficiency. In catalysts like CSHTi1000, where titania particles are more evenly dispersed, a higher number of active sites are available for the oxidation of styrene, leading to a higher conversion rate (30.40%). In contrast, catalysts with less uniform distribution of titania, such as CSHTi500Cal, exhibit lower catalytic performance due to the limited accessibility of active sites, as indicated by the lower conversion rate (7.95%).

The decrease in BET surface area from 21.99 m^2/g for CSHTi500 to 1.76 m^2/g for CSHTi500Cal is directly reflected in the catalytic performance, where the styrene conversion drops from 49.45% to 7.95%. The reduced surface area limits the adsorption of both H_2O_2 and styrene onto the catalyst surface, thereby decreasing the efficiency

Table 4. Catalytic performance of the catalysts in the oxidation of styrene[a]

Catalyst	Conversion (%)	Selectivity (%)				TON[c]
		BzA[b]	PhA[c]	SO[d]	Other	
No catalyst	1.43	25.19	0	41.05	33.75	-
TiO_2	3.16	88.27	4.60	0	7.13	0.232
CSH	5.80	18.07	1.59	65.21	15.13	-
CSHTi500	49.45	60.21	0.71	0.69	38.39	4.945
CSHTi500Cal	7.95	73.28	1.26	6.67	18.78	0.795
CSHTi1000	30.40	82.53	0.73	1.18	15.56	3.040
CSHTi1000Cal	20.04	83.90	0.99	1.81	13.28	2.004

[a] Reaction conditions: The reactions were carried out at room temperature for 24 h with styrene (5 mmol), 30% H_2O_2 (5 mmol), and catalyst (100 mg). BzA[b] = benzaldehyde, PhA[c] = phenylacetaldehyde, and SO[d] = styrene oxide

of the oxidation reaction. This strong correlation between surface area and catalytic performance highlights the importance of maintaining a high surface area to ensure optimal reactivity.

The calcination process induces sintering and agglomeration of titania particles, which significantly reduces the available surface area and pore volume, leading to fewer accessible active sites for styrene oxidation and, consequently, decreased catalytic efficiency. For example, the surface area reduction from 21.99 m^2/g in CSHTi500 to 1.76 m^2/g in CSHTi500Cal correlates directly with the sharp drop in styrene conversion from 49.45% to 7.95%, as the decreased surface area limits the interaction between reactant molecules and the catalyst's active sites. In addition, calcination can alter the structure of titania, diminishing its ability to generate the reactive oxygen species (ROS) essential for styrene oxidation. As a result, calcined catalysts, such as CSHTi500Cal, show significantly lower conversion rates compared to their non-calcined counterparts like CSHTi500, clearly demonstrating the adverse impact of calcination on catalytic performance.

The process of sintering during calcination results in the coalescence of smaller titania particles into larger clusters, which blocks the mesopores and reduces the overall active surface area. This agglomeration of particles diminishes the number of available active sites on the catalyst, contributing to the sharp decline in catalytic activity. For instance, the styrene conversion rate drops significantly from 49.45% for CSHTi500 to 7.95% for CSHTi500Cal, as larger particles are less effective in catalyzing the reaction due to limited surface accessibility.

Despite promising results, limitations such as CSH hydration in aqueous conditions and performance drop post-calcination need addressing. The hydration of CSH in aqueous environments compromises its structural integrity, impacting the catalyst's durability. Similarly, calcination at high temperatures reduces surface area and pore volume, limiting active site accessibility. To overcome these challenges, future work will explore stabilizing CSH with protective coatings like silica or alumina, which have been shown to enhance resistance to hydration. Additionally, optimizing calcination parameters could preserve structural integrity while maintaining catalytic activity, aligning with principles of green chemistry by improving material efficiency and recyclability.

The findings demonstrate a scalable method to integrate waste-derived materials in industrial catalysis, addressing the dual challenges of reducing environmental impact and enhancing sustainability in chemical production. By converting fish bone waste into mesoporous CSH supports, this approach aligns with green chemistry principles by reducing reliance on non-renewable feedstocks, minimizing waste generation, and lowering the environmental footprint of catalytic processes. Such advancements hold significant potential for scaling up to industrial applications in fine chemical production and environmental remediation, contributing to circular economy objectives.

3.2.2 Recyclability of catalyst

The recyclability of the catalyst is an important parameter for evaluating the performance of a catalytic system. Therefore, a series of experiments were performed for the selective oxidation of styrene using CSHTi500, CSHTi500Cal, CSHTi1000, and CSHTi1000Cal as catalysts to assess their recyclability. All catalysts were recovered and recycled for further reactions. The spent catalysts were washed with ethanol, centrifuged three times, and dried at 110 °C in a vacuum oven overnight. The styrene conversion was used as a basis to compare each reaction cycle. As shown in Figure 7, all catalysts exhibited a decrease in styrene conversion over the first, second, and third reaction cycles: CSHTi500 (49.5%, 17.2%, and 14.8%), CSHTi500Cal (7.9%, 7.3%, and 3.4%), CSHTi1000 (30.4%, 21.4%, and 15.1%), and CSHTi1000Cal (20.0%, 11.3%, and 9.1%).

The decrease in styrene conversion might be due to the physical detachment of some catalyst powder during mechanical stirring. Moreover, another possible explanation for the decrease in activity is the leaching out of titania active sites from the pores during the washing process with

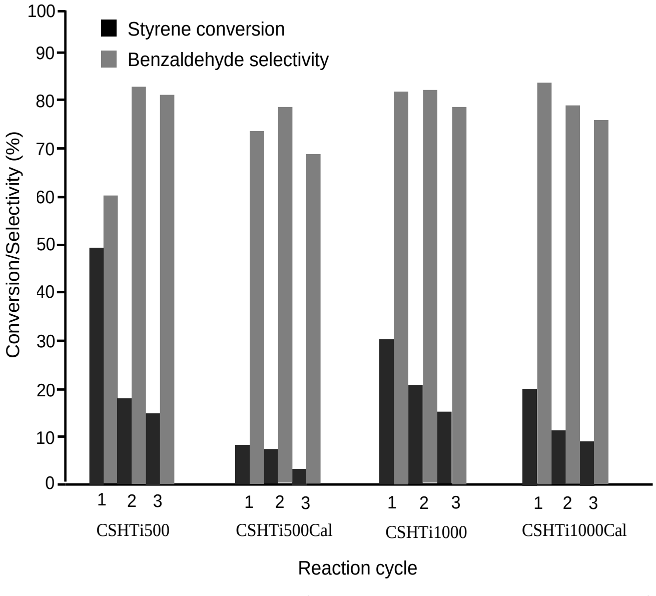

Figure 7. The reuse of Catalyst in the oxidation of styrene (5 mmol), 30% H_2O_2 (5 mmol) and catalyst (50 mg). The conversion of styrene at room temperature for 24 h

ethanol solvent [28,43]. The selectivity for benzaldehyde over the first, second, and third cycles remained almost similar: CSHTi500 (60.2%, 82.6%, and 81.3%), CSHTi500Cal (73.3%, 78.5%, and 68.5%), CSHTi1000 (82.5%, 82.5%, and 78.7%), and CSHTi1000Cal (83.9%, 78.9%, and 75.81%).

Calcination improves the structural stability of the catalyst, which is beneficial for its mechanical properties. However, this thermal treatment also reduces the number of accessible active sites due to sintering, leading to lower catalytic activity and diminished recyclability. This effect is particularly evident in the CSHTi500Cal sample, where the styrene conversion decreases significantly after calcination and continues to drop over subsequent cycles. Thus, while calcination enhances stability, it compromises the catalyst's overall performance and reusability.

The decline in catalytic performance over multiple cycles is primarily due to the leaching of titania active sites during the washing and mechanical stirring process. Additionally, the physical detachment of catalyst powder and potential fouling of the active sites by reaction by-products contribute to the reduction in catalytic efficiency. By improving the stability of the titania particles on the CSH support and preventing active site leaching, the reusability and overall performance of the catalyst could be enhanced for industrial applications.

The presence of titania in the catalyst, confirmed by absorption bands around 900–1000 cm^{-1} (see FTIR spectra in Figure 1), is associated with the formation of reactive oxygen species (ROS), such as hydroxyl radicals (•OH) and hydroperoxy radicals (•OOH). These species are crucial in enhancing the catalytic activity of CSH-Titania by promoting the oxidation of styrene, thereby increasing the conversion and selectivity toward benzaldehyde.

The catalytic oxidation of styrene over CSH-Titania is driven by the generation of reactive oxygen species (ROS) on the titania surface. When H_2O_2 is introduced, it decomposes into hydroxyl radicals (•OH) and hydroperoxy radicals (•OOH), which are highly reactive and capable of initiating the oxidation of styrene. These ROS facilitate the nucleophilic attack on the C=C bond of styrene, leading to the formation of styrene oxide, which subsequently undergoes cleavage to produce benzaldehyde. The presence of these ROS on the catalyst surface enhances the overall catalytic efficiency and selectivity for benzaldehyde.

The oxidation of styrene begins with the formation of styrene oxide, acting as an intermediate. The nucleophilic attack of reactive oxygen species (•OH and •OOH) on the epoxide ring leads to the cleavage of the C=C bond, ultimately resulting in the formation of benzaldehyde. The selective formation of benzaldehyde can be attributed to the ability of the titania catalyst to stabilize the intermediate and direct the reaction toward the cleavage of the metalloepoxy intermediate, which favors the production of benzaldehyde over other side products such as phenylacetaldehyde or styrene oxide.

Activity reduction over cycles is primarily due to titania leaching and pore fouling, which block active sites. Recycling methods like acid regeneration or surface reactivation could restore catalytic efficiency. These methods align with green chemistry principles by reducing waste and enhancing material reuse, contributing to the development of sustainable catalytic systems.

4. Conclusions

This research successfully demonstrated the oxidation of styrene using hydrogen peroxide (H_2O_2) as an oxidant over titania-impregnated calcium sulfate hemihydrate (CSHTix, where x denotes the number of moles of titania). The catalyst achieved a maximum styrene conversion of 49.45% with a benzaldehyde selectivity of 82.6%. Importantly, these catalysts were recyclable up to three cycles, maintaining selectivity above 60%. Compared to conventional catalysts—such as noble metal-based systems or those requiring harsh reaction conditions—the CSH-Titania catalyst offers significant environmental advantages. Utilizing renewable CSH derived from fish bone waste as a support, in conjunction with H_2O_2 as an environmentally friendly oxidant, reduces both material costs and environmental impact. This catalyst system represents a greener, more sustainable alternative for the selective oxidation of styrene, featuring lower energy requirements and minimal waste production.

This study presents a green and scalable catalyst for styrene oxidation, achieving high benzaldehyde selectivity. Future work will address carrier stability and recyclability through material improvements, ensuring sustainable applications in fine chemical production. The findings demonstrate a scalable method to integrate waste-derived materials in industrial catalysis, addressing the dual challenges of reducing environmental impact and enhancing sustainability in chemical production. By converting fish bone waste into mesoporous CSH supports, this approach aligns with green chemistry principles by reducing reliance on non-renewable feedstocks, minimizing waste generation, and lowering the environmental footprint of catalytic processes. Such advancements hold significant potential for scaling up to industrial applications in fine chemical production and environmental remediation, contributing to circular economy objectives.

Future research will focus on stabilizing CSH using protective coatings like silica or alumina, which are known to enhance resistance to hydration and improve structural stability. Additionally, exploring alternative biowaste-derived carriers such as shell-derived calcium carbonate or plant-based ashes could expand the range of sustainable supports. Efforts to optimize recycling protocols, such as acid washing or surface reactivation, are critical for enhancing catalyst reusability. These directions align with green chemistry principles by reducing waste, improving material efficiency, and advancing scalable, environmentally friendly catalytic processes.

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CRediT Authors Statement

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