Assessment of Modified Zeolite Catalysts Using FTIR, XRD, and TGA for Sustainable Biodiesel Synthesis

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Abstract: The growing need for sustainable energy sources has intensified interest in biodiesel as an alternative to fossil fuels. Efficient production of biodiesel through transesterification requires catalysts with high surface activity, structural stability, and thermal resistance. In this study, two modified zeolite-based catalysts Sn-RH-Zeolite, synthesized from rice husk-derived silica doped with tin, and K_2CO_3-CaO-Zeolite, prepared by alkali modification of natural zeolite were evaluated for their suitability in biodiesel synthesis. Characterization was performed using Fourier-transform infrared spectroscopy (FTIR), X-ray diffraction (XRD), and thermogravimetric analysis (TGA). FTIR analysis confirmed the presence of functional groups associated with Brønsted and Lewis acidic sites, vital for catalytic activity. XRD patterns revealed that both catalysts retained crystalline integrity, with identifiable phases corresponding to zeolite frameworks and incorporated active components. TGA indicated thermal stability up to 500°C, with Sn-RH-Zeolite retaining 83.2% weight at 800°C. Sn-RH-Zeolite exhibited superior thermal resistance, while K_2CO_3-CaO-Zeolite provided enhanced basicity. These catalysts show potential for sustainable biodiesel synthesis. This study underscores the potential of low-cost, eco-friendly zeolite modifications in advancing green fuel technologies.

Keywords: Zeolite catalyst, FTIR, XRD, TGA, transesterification, surface properties, acidity, thermal stability

1.Introduction: The urgent need to reduce dependence on fossil fuels has driven global research toward alternative and renewable energy sources. Biodiesel, a renewable biofuel produced from the transesterification of triglycerides with alcohol, has emerged as a promising substitute for conventional diesel due to its biodegradability, low toxicity, and favourable emission profile. However, achieving efficient and cost-effective biodiesel production depends heavily on the selection of suitable catalysts that can operate under mild conditions while offering high conversion rates and reusability. Heterogeneous catalysts, particularly zeolite-based materials, have attracted considerable attention due to their high surface area, tunable acidity, well-defined porous structures, and thermal stability. Natural zeolites can be further enhanced by metal or alkaline modifications to introduce or improve catalytic sites, making them more active for reactions such as transesterification. Among various modifications, tin (Sn) incorporation and alkali metal impregnation (such as K_2CO_3 and CaO) have been shown to boost catalytic activity by introducing additional acidic or basic functionalities. Despite extensive research on zeolite catalysts, a comprehensive understanding of how their surface properties, acidity, and thermal stability influence their catalytic performance in biodiesel synthesis is still evolving. Detailed physicochemical characterization is essential to evaluate their suitability and to optimize their catalytic potential.

In this study, we explore the physicochemical characterization of two modified zeolite catalysts: Sn-RH-Zeolite and K_2CO_3-CaO-Zeolite. The Sn-RH-Zeolite catalyst was synthesized using silica extracted from rice husk a renewable agricultural waste and doped with Sn to create Lewis acidic sites. The K_2CO_3-CaO-Zeolite was prepared by co-impregnating natural zeolite with potassium carbonate and calcium oxide, introducing basic sites to promote transesterification.

This study not only evaluates these catalysts using FTIR, XRD, and TGA but also provides a comparative understanding of how metal incorporation and basic modifications affect thermal behaviour and crystalline integrity—critical parameters for biodiesel synthesis. The catalysts' development aligns with the goals of waste valorization, green chemistry, and sustainable energy solutions.

2.Materials and Methods

2.1 Materials: Rice husk ash (RHA) was used as the silica source for synthesizing the Sn-RH-Zeolite catalyst. Silica was extracted from 100 g of pre-washed and dried rice husk, yielding approximately 32g of calcined silica. The extraction involved refluxing with 1 M NaOH to dissolve silica, followed by acid neutralization, gel aging, and calcination, resulting in high-purity silica suitable for tin (Sn)-based doping. Natural zeolite, obtained from a local supplier which can be activated, served as the support material for the preparation of the K_2CO_3-CaO-Zeolite catalyst. Analytical-grade reagents, including tin chloride ($SnCl_2$), potassium carbonate (K_2CO_3), and calcium oxide (CaO), were sourced from commercial suppliers and used without further purification. All synthesis steps were carried out using deionized water.

2.2 Catalyst Preparation

2.2.1 Synthesis of Sn-RH-Zeolite: Silica was extracted from rice husk ash (RHA) by treating it with 1 M sodium hydroxide (NaOH) solution under reflux at 70°C for 2 hours, forming a sodium silicate solution. The solution was filtered and neutralized with 1 M hydrochloric acid (HCl) until a silica gel precipitated. The silica gel was aged for 24 hours, then washed thoroughly with deionized water and dried at 100°C. For tin doping, an aqueous $SnCl_2$ solution was slowly added to the dried silica under continuous stirring. The mixture was aged again, followed by drying at 110°C overnight and calcination at 600°C for 4 hours to obtain the Sn-RH-Zeolite catalyst.

2.2.2 Synthesis of K_2CO_3-CaO-Zeolite: Natural zeolite was first cleaned by washing with distilled water to remove impurities, then dried at 110°C and ground into fine powder. The zeolite powder was impregnated using the wet impregnation method: a mixed aqueous solution containing potassium carbonate (K_2CO_3) and calcium oxide (CaO) was added dropwise to the zeolite powder while stirring vigorously to ensure uniform distribution. The resulting paste was dried at 120°C for 12 hours, followed by calcination at 600°C for 3 hours to activate the K_2CO_3-CaO-Zeolite catalyst.

2.3 Catalyst Characterization

2.3.1 Fourier-Transform Infrared Spectroscopy (FTIR): FTIR spectra were recorded using a spectrometer in the range of 4000–400 cm^{-1}. Catalyst powders were mixed with KBr and pressed into pellets before analysis. The main absorption bands were identified to determine the functional groups and surface acidity of the catalysts.

2.3.2 X-ray Diffraction (XRD): XRD patterns were collected using a diffractometer equipped with Cu Kα radiation ($\lambda = 1.5406$ Å) operated at 40 kV and 30 mA. Data were recorded over a 2θ range of 10°–80° at a scanning rate of 2°/min. The crystalline phases and structural integrity of the catalysts were identified by matching diffraction peaks with standard reference patterns.

2.3.3 Thermogravimetric Analysis (TGA): TGA was performed using a thermogravimetric analyzer under a nitrogen atmosphere. Approximately 10 mg of catalyst sample was heated from room temperature to 800°C at a heating rate of 10°C/min. Weight loss profiles were analyzed to assess thermal stability and decomposition behaviour.

3.1 FTIR Analysis

Fourier-transform infrared (FTIR) spectroscopy was used to investigate the surface functional groups and structural features of the synthesized catalysts. The spectra were collected over the range 4000–400 cm⁻¹.

Sn-RH-Zeolite (Batch SR2):

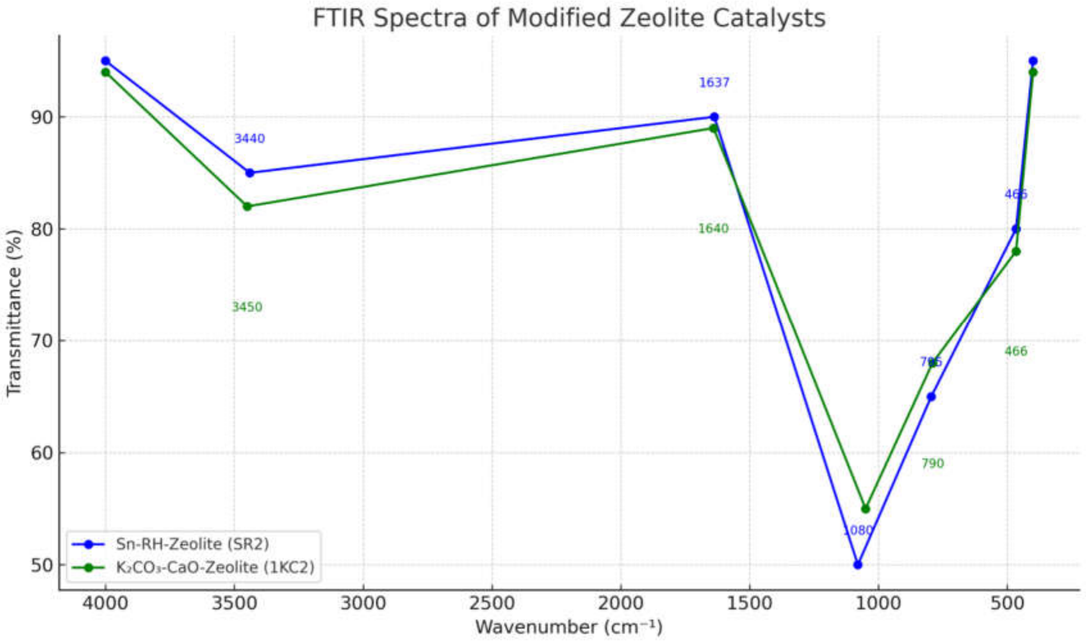
The FTIR spectrum (see Figure 1a) shows a strong and broad absorption band near 1080 cm⁻¹, corresponding to Si–O–Si asymmetric stretching vibrations, confirming the zeolitic framework. A band near 795 cm⁻¹ is attributed to Si–O symmetric stretching, while the peak at 466 cm⁻¹ arises from Si–O bending vibrations. A broad band at around 3440 cm⁻¹ is assigned to O–H stretching vibrations of surface hydroxyl groups and adsorbed water, indicating surface acidity. The small band near 1637 cm⁻¹ corresponds to O–H bending vibrations of molecular water. These features confirm successful incorporation of tin into the silica-based zeolite framework, maintaining structural integrity.

K_2CO_3-CaO-Zeolite (Batch 1KC2):

The FTIR spectrum (see Figure 1b) displays similar characteristic bands of the zeolite framework, including a prominent Si–O–Si asymmetric stretch at 1050 cm⁻¹ and Si–O symmetric stretch at 790 cm⁻¹. The peak at 466 cm⁻¹ again indicates Si–O bending vibrations. The broad band around 3450 cm⁻¹ corresponds to surface hydroxyl groups and adsorbed moisture, while the band near 1640 cm⁻¹ is due to H–O–H bending. The appearance of new or slightly shifted bands compared to the pure zeolite suggests successful impregnation with K_2CO_3 and CaO, introducing basic functionalities without compromising the zeolite framework.

Summary Table : FTIR Bands

Catalyst	**Wavenumber (cm⁻¹)**	**Assignment**
Sn-RH-Zeolite (SR2)	1080, 795, 466	Si–O–Si, Si–O stretches; Si–O bends
	3440, 1637	O–H stretch and bend (hydroxyl, water)
K_2CO_3-CaO-Zeolite (1KC2)	1050, 790, 466	Si–O–Si, Si–O stretches; Si–O bends
	3450, 1640	O–H stretch and bend (hydroxyl, water)



3.2 TGA Analysis:

Thermogravimetric analysis (TGA) was performed to evaluate the thermal stability and decomposition behavior of the synthesized catalysts up to 800°C under a nitrogen atmosphere.

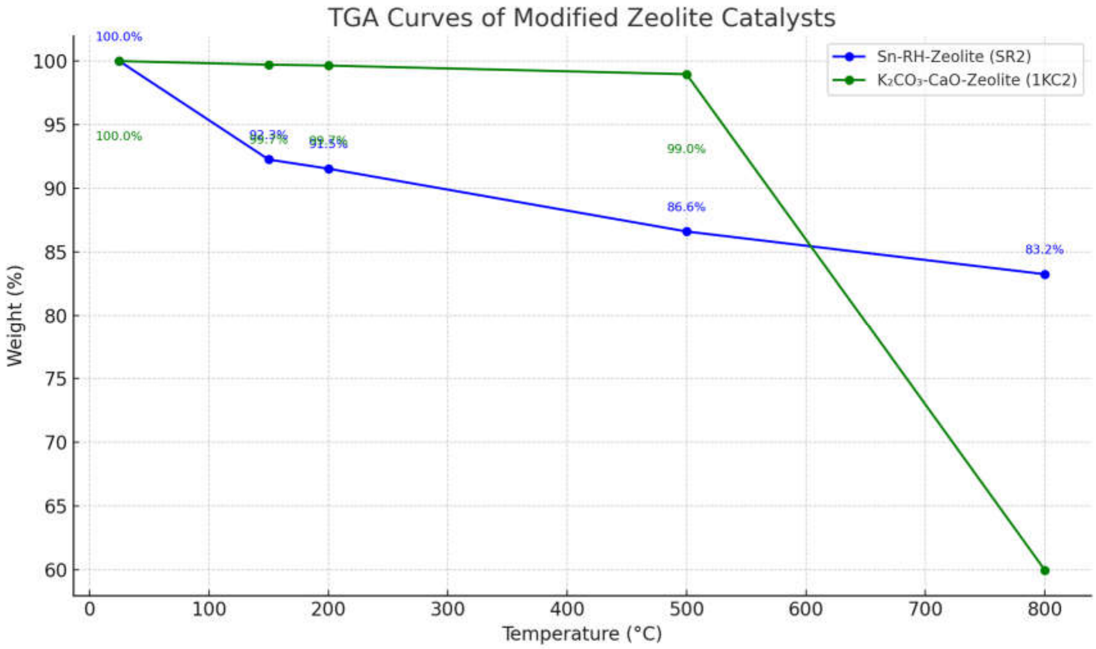
Sn-RH-Zeolite (SR2):

The TGA curve for Sn-RH-Zeolite (Figure 2a) shows an initial weight loss of ~7.7% up to 150°C, attributed to the removal of physically adsorbed moisture and surface hydroxyl groups. A further minor weight loss of ~4.9% between 150–200°C is likely due to desorption of weakly bound water and organic residues from synthesis. Beyond this, gradual weight loss occurs, with ~13.4% total weight loss up to 500°C, and a final residue of ~83.2% at 800°C, indicating high thermal stability and structural integrity of the zeolite framework even at elevated temperatures.

K_2CO_3-CaO-Zeolite (1KC2):

The TGA profile for K_2CO_3-CaO-Zeolite (Figure 2b) indicates lower thermal stability compared to Sn-RH-Zeolite. An initial weight loss of ~0.3% at 150°C corresponds to moisture removal, followed by minor loss (~0.7% at 200°C) likely from surface-adsorbed species. A significant decomposition step occurs between 200–500°C, with ~39% weight loss at 500°C, attributed to decomposition of carbonate species (K_2CO_3) and release of CO_2. By 800°C, the catalyst retains only ~60% of its original weight, showing partial degradation of the impregnated basic components.

Catalyst	Major Weight Loss (%)	Temperature Range (°C)	Final Residue at 800°C (%)
Sn-RH-Zeolite (SR2)	13.4	up to 500	83.2
K_2CO_3-CaO-Zeolite (1KC2)	39.0	up to 500	60.0



3.3 XRD Analysis

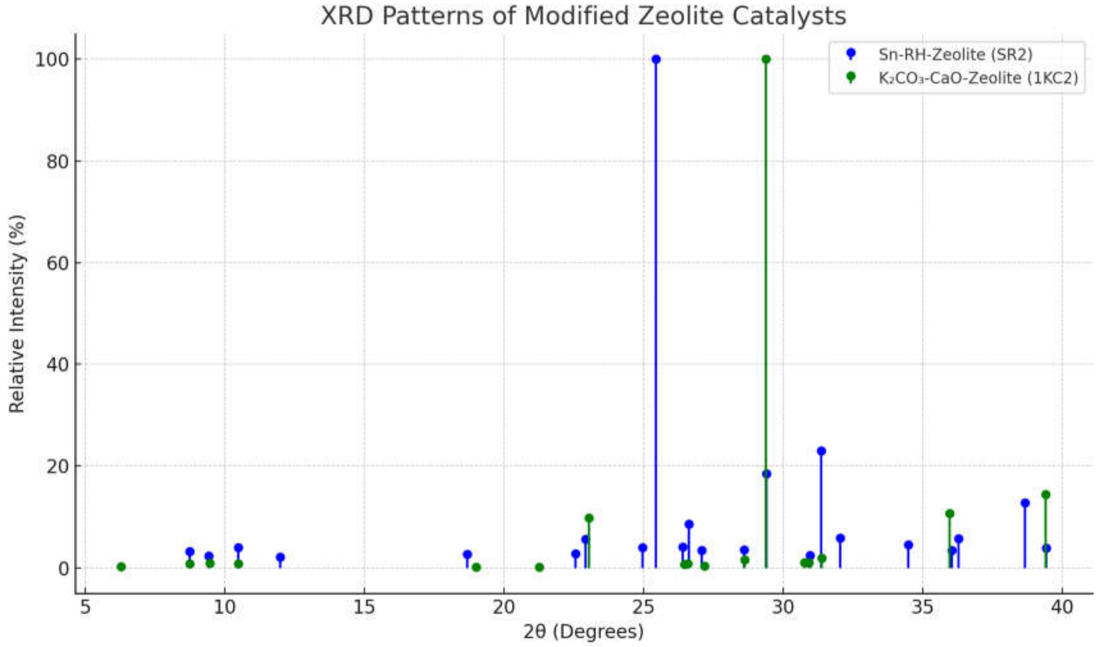
X-ray diffraction (XRD) analysis was conducted to investigate the crystallinity and phase composition of the synthesized catalysts. The diffraction patterns were recorded over a 2θ range of approximately 3°–40° at room temperature using Cu Kα radiation (λ = 1.5406 Å).

The XRD pattern of **Sn-RH-Zeolite (SR2)** (Figure 1a) exhibits prominent peaks at 8.7°, 9.4°, 10.5°, 22.6°, 23.0°, 24.9°, 25.4°, 26.4°, 27.1°, 28.6°, 29.4°, 31.4°, 32.0°, 34.5°, 36.0°, 38.7°, and 39.4° (2θ), corresponding to d-spacings from 10.1 Å to 2.3 Å. The intense diffraction at 25.4° confirms the preservation of a well-crystallized clinoptilolite-type zeolite framework. The presence of minor peaks around 26.6° and 29.4° suggests the successful incorporation of Sn species into the zeolite lattice without significant structural distortion. These reflections, along with weak signals likely related to SnO_2, indicate partial substitution or surface dispersion of Sn, further verifying successful doping while maintaining the crystalline integrity of the zeolite.

In contrast, the **K_2CO_3-CaO-Zeolite (1KC2)** XRD pattern (Figure 1b) shows peaks at 6.3°, 8.7°, 9.5°, 10.5°, 23.1°, 26.5°, 26.6°, 27.2°, 28.6°, 29.4°, 30.8°, 31.4°, 35.9°, and 39.4° (2θ). The strong reflection at 29.4° confirms that the zeolite framework is largely retained after modification. However, additional peaks at 35.9° and 39.4° are attributed to crystalline CaO and K_2CO_3 phases, indicating their successful loading onto the zeolite. The broader and less intense diffraction features suggest partial amorphization or formation of basic metal oxide clusters during high-temperature calcination.

Summary Table of Major XRD Peaks

Catalyst	**2θ Peaks (°)**	**Main Phases Identified**
Sn-RH-Zeolite (SR2)	8.7, 9.4, 10.5, 22.6, 25.4, 26.6, 29.4	Zeolite (clinoptilolite), Sn species
K_2CO_3-CaO-Zeolite (1KC2)	6.3, 8.7, 9.5, 23.1, 26.5, 29.4, 35.9, 39.4	Zeolite, CaO, K_2CO_3



4. Conclusion

The physicochemical analysis of Sn-RH-Zeolite and K_2CO_3-CaO-Zeolite catalysts using FTIR, XRD, and TGA confirms their suitability for biodiesel production. FTIR verified the presence of key functional groups and active acidic/basic sites essential for catalysis, while XRD confirmed the structural integrity of the zeolitic frameworks and successful incorporation of active components. TGA results established the thermal stability of both catalysts, with Sn-RH-Zeolite demonstrating superior resistance to high temperatures and better crystallinity retention. This makes it particularly well-suited for high-temperature transesterification processes. The successful synthesis of Sn-RH-Zeolite using rice husk-derived silica not only enhances catalytic efficiency but also promotes agricultural waste valorization, aligning with the principles of green chemistry. In parallel, the K_2CO_3-CaO-Zeolite catalyst, rich in basic sites, shows promise for biodiesel synthesis under milder thermal conditions. Together, these findings underscore the potential of both catalysts as cost-effective, environmentally friendly alternatives for sustainable biodiesel production. Future work should assess catalytic performance in actual transesterification reactions, regeneration cycles, and scalability.

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