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Preparation and Characterization of Enhanced Hierarchical Zn-Ni/HZSM-5 Catalysts for Potential use in Catalytic reactions to Upgrade Bio-Oil and Hydrogen from Biomass Pyrolysis

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Abstract

This study investigates the synthesis and characterization of hierarchical ZSM-5 and metal-doped hierarchical Zn-Ni/ZSM-5 catalysts to potentially improve the bio-oil and hydrogen production from biomass (rice husk) pyrolysis. Traditional zeolites, due to their microporous structure, often pose limitations in reactant accessibility, adversely affecting catalytic performance. To address these challenges, hierarchical zeolites incorporating mesoporosity were developed. The hierarchical ZSM-5 was synthesized via an alkaline desilication process, enhancing its mesoporous characteristics, with surface area increasing from 111 m^2/g to 141 m^2/g and average pore size expanding from 2 nm to 5 nm. Characterization techniques, including X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR), confirmed the retention of the MFI-type zeolite framework post-modification. The findings indicate that the hierarchical structure has the potential to enhance mass transfer and reactant accessibility, making these catalysts promising candidates for the reforming of biomass pyrolysis products, which can lead to sustainable bio-oil and hydrogen production. This research provides a foundation for future optimization of catalyst performance and exploration of diverse biomass feedstocks, contributing to advancements in cleaner energy technologies.

Keywords: *Hierarchical ZSM-5, biomass pyrolysis, bio-oil upgrading, metal-doped catalysts, desilication.*

1.0 Introduction

Porous solids, particularly zeolites, have garnered significant attention in various applications due to their unique pore structures, which can be classified according to the International Union of Pure and Applied Chemistry (IUPAC) into three categories: microporous (pores less than 2 nm), mesoporous (pores from 2 to 50 nm), and macroporous (pores between 50 and 1000 nm). These pore characteristics, size, shape, and inter-connectivity play a crucial role in determining the capabilities of zeolites, such as molecular sieving and selective adsorption. However, the limitations posed by the pore structure can hinder the accessibility of large reactants to active sites within the micropores, leading to diffusional constraints and potential coking, which can deactivate catalysts and diminish their lifespan [1], [2], [3], [4].

To overcome these challenges, hierarchical zeolites have been developed, incorporating secondary porosity into traditional zeolites. These materials exhibit a combination of micropores and larger meso- or macropores, facilitating improved mass transfer and diffusion of reactants and products within the catalytic system. Hierarchical ZSM-5, a variant of the zeolite, has shown promise in enhancing the yield of aromatic products from catalytic fast pyrolysis of biomass [5], [6].

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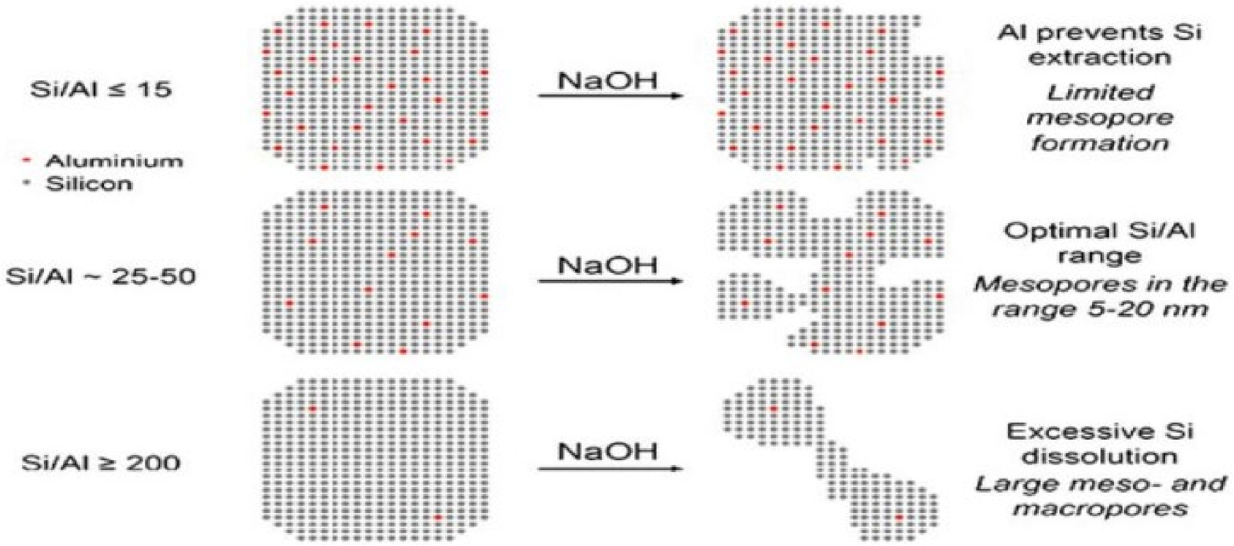

Figure 1: Effect of NaOH on Si/Al ratio during desilication of ZSM-5 (Source: American Chemical Society)

The synthesis of hierarchical zeolite catalysts can be categorized into two main approaches: 'bottom-up' and 'top-down'. Bottom-up methods involve the introduction of secondary porosity during the synthesis of zeolites through techniques such as hard templating, soft templating, and non-templating. In contrast, top-down methods involve post-synthetic modifications of existing zeolite materials, such as desilication, dealumination, and recrystallization [7]. Among these, desilication through alkaline treatment has proven effective, particularly for high-silica zeolites, where Si species are leached from the zeolite framework, as seen in Figure 1, to create interconnected mesopores accessible from the external surface [8], [9].

The use of hierarchical ZSM-5 in catalytic cracking processes, combined with a sorbent like calcined dolomite, which effectively captures CO_2, is essential for advancing sustainable energy technologies focused on minimizing greenhouse gas emissions.

In this study, the preparation and characterization of hierarchical ZSM-5 catalysts are explored. The synthesis processes, including calcination, desilication and metal oxide impregnation, are detailed to highlight the effectiveness of the hierarchical structure in catalytic applications. The characterization techniques employed, including X-ray diffraction (XRD), Fourier transform infrared (FTIR) spectroscopy, and Brunauer-Emmett-Teller (BET) analysis, provide insights into the structural and textural properties of the catalysts, laying the groundwork for understanding their performance in catalytic reactions.

2.0 Materials and Methods/Methodology

2.1. Materials

ZSM-5 zeolite (Si/Al = 50) was procured from Zeolyst International, while Zinc nitrate hexahydrate and Nickel (II) nitrate hexahydrate were acquired from Sigma-Aldrich.

2.2. Catalyst and Sorbent Preparation

Hierarchical ZSM-5 was synthesized through the alkali treatment of commercial ZSM-5 ($SiO_2/Al_2O_3 = 50$, Zeolyst). The commercial ZSM-5 was initially calcined at 550°C for 5 hours. Following this calcination, the ZSM-5, now referred to as HZSM-5, underwent desilication using a 0.2 M sodium hydroxide (NaOH) solution, adhering to established protocols in the literature [10].

The synthesis process commenced with the addition of calcined HZSM-5 to a preheated (to 65°C) 0.2 M NaOH solution. This mixture was stirred continuously for 90 minutes, after which it was cooled in an ice bath and filtered. The resulting filter cake was rinsed with distilled water until a neutral pH was achieved, followed by drying in an oven at 70°C for one hour as illustrated in Figure 2.

Subsequently, ion-exchange was conducted using a 0.5 M ammonium chloride (NH_4Cl) solution at 70°C for 3 hours. Post-treatment, the catalyst was allowed to cool before being filtered and washed. The final drying step was performed at 95°C, followed by a second calcination at 550°C for 5 hours to yield the hierarchical HZSM-5 (denoted as HZ).

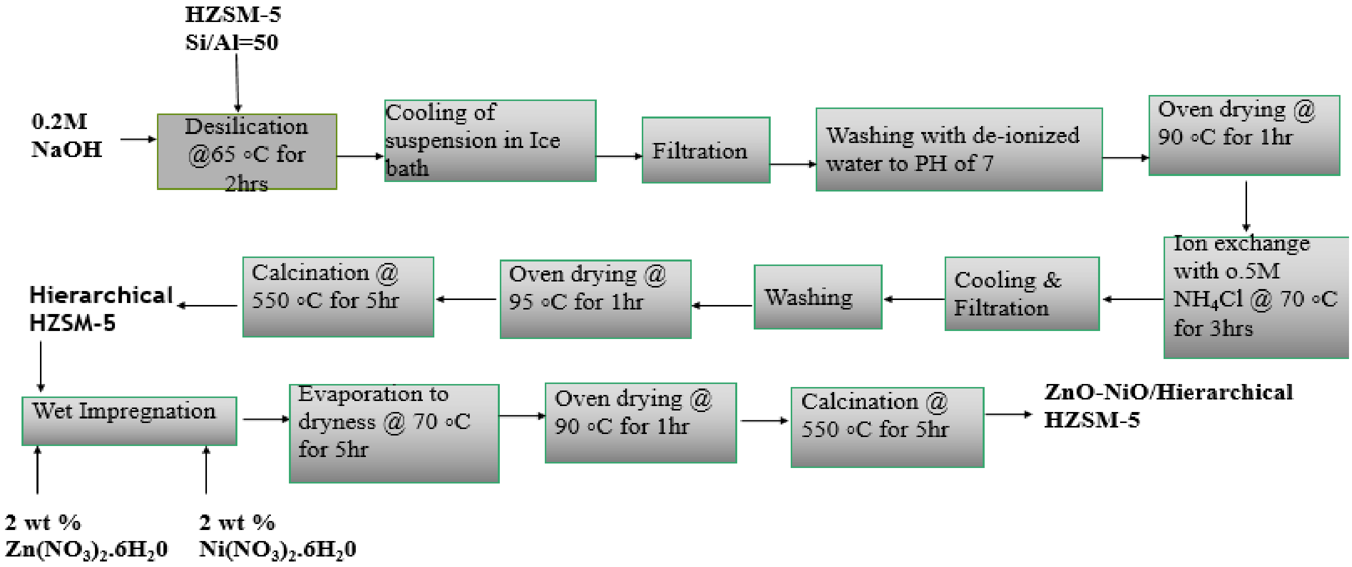

Figure 2: Flow Chart for Catalyst Preparation

For the preparation of the metal-doped catalyst, Zinc nitrate hexahydrate ($Zn(NO_3)_2 \cdot 6H_2O$) and Nickel nitrate hexahydrate ($Ni(NO_3)_2 \cdot 6H_2O$), both containing 2 wt.% ZnO and 2 wt.% NiO were dissolved in 100 ml of deionized water. This solution was introduced drop-wise into a beaker containing a calculated amount of the dispersed hierarchical HZSM-5. The resultant mixture was evaporated at a constant temperature of 70°C and then dried in an oven at 95°C for 1 hour. A final calcination at 550°C for 5 hours produced the hierarchical 2 wt.% Zn - 2 wt.% Ni HZSM-5, referred to as ZN-HZ [11] as shown in Figure 2.

2.3. Catalysts Characterization

The characterization of the catalysts in this study was conducted using several techniques, namely X-ray Diffraction (XRD), Fourier Transform Infrared Spectroscopy (FTIR), Nitrogen adsorption-desorption studies (BET), and Thermogravimetric Analysis (TGA).

The prepared catalysts were characterized using multiple analytical techniques for comprehensive evaluation. X-ray diffraction (XRD) patterns were recorded using a Rigaku MiniFlex 600 with Cu Kα radiation, employing a scan speed of 10° per minute, step size of 0.02°, and 2θ scanning range of 5° to 80°. Fourier Transform Infrared (FTIR) analysis was conducted using a Shimadzu FTIR-8400S spectrometer with potassium bromide (KBr) pellets as the medium, recording infrared spectra in transmission mode within the wavenumber range of 500 to 4000 cm^{-1}. The textural properties of the catalysts, including specific surface area, pore volume, and pore size distribution, were analyzed using the Brunauer–Emmett–Teller (BET) method through nitrogen (N_2) adsorption-desorption isotherms at -195.85°C using an Accelerated Surface Area and Porosimetry System (ASAP 2000 Micromeritics). The analysis was conducted with an equilibrium interval of 10 seconds and sample density of 1.000 g/cm^3. Micropore area and volume were calculated using Langmuir surface area and t-plot methods, while pore size distribution was determined through the Barrett-Joyner-Halenda (BJH) method applied to the adsorption branch of the isotherm.

3.0 Results and Discussion

3.1. X-ray Diffraction (XRD) analysis

The XRD patterns for the parent HZSM-5 catalyst, the alkali-treated HZSM-5 catalyst, and the alkali-treated Zn/Ni HZSM-5 catalyst are shown in Figure 3. All the catalysts demonstrate distinct diffraction peaks characteristic of MFI-type zeolite at 2θ values of 8.10°, 8.51°, 23.25°, 24.5°, and 45.2° [12]. This observation indicates that the characteristic diffraction peaks of the MFI zeolite remained intact even post-desilication, suggesting that the structural integrity was preserved. However, upon closer analysis, a decrease in the intensities of the peaks at 8.10°, 8.51°, and 23.25° was noted after desilication. This reduction infers fractional dissolution of the HZSM-5 framework and a slight decrement in crystallinity, consistent with findings reported in the literature [13], [14]. Additionally, the absence of peaks confirming the presence of Zn and Ni in the hierarchical HZSM-5 impregnated with these metals suggests that the concentrations of 2 wt. % Zn and 2 wt. % Ni employed for impregnation fell below the detection limit, as corroborated by previous studies [13].

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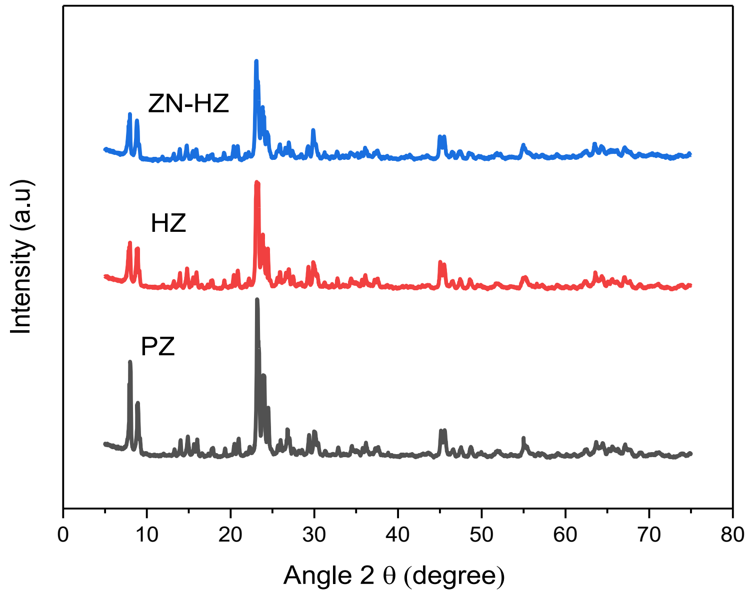

Figure 3: XRD Patterns of the Parent HZSM-5, Hierarchical HZSM-5, and Zn-Ni Hierarchical ZSM-5

3.2. Fourier transformed infrared (FTIR) analysis

The FTIR spectra of the parent HZSM-5 (PZ), hierarchical HZSM-5 catalysts (HZ) and the Zn/Ni hierarchical HZSM-5 catalyst (ZN-HZ), particularly within the lattice vibration region of 400 to 4000 cm⁻¹, are illustrated in Figure 4. Notable wave bands at 450 cm⁻¹, corresponding to the T-O-T bending vibrations (where T represents Si or Al), and at 550 cm⁻¹, indicative of the five-membered ring pentasil unit of HZSM-5, corroborate the findings from the X-ray diffraction (XRD) analysis. This suggests that the HZSM-5 catalyst retains its fundamental crystalline structure despite undergoing alkaline treatment. A detailed examination of the band at 1100 cm⁻¹, which signifies internal tetrahedral bridged Si-OH-Al vibrations in the asymmetric region, reveals a noticeable broadening of the peak following the alkaline treatment with 0.2 M NaOH. This broadening contrasts with the sharper peak observed in the parent HZSM-5, aligning with the observations presented in literature [14], regarding the performance of hierarchical HZSM-5 zeolites prepared through NaOH treatments in the context of glycerol aromatization.

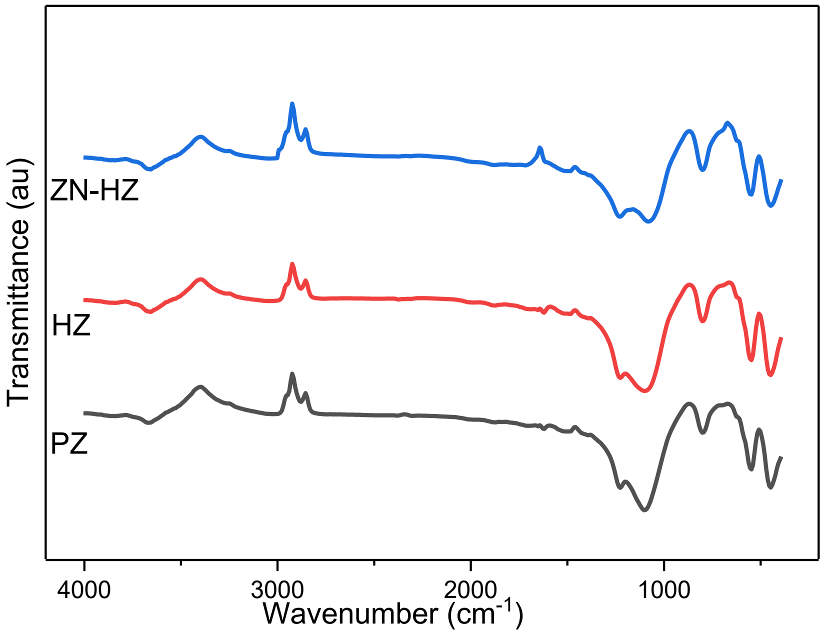

Figure 4: FTIR Spectra of Parent HZSM-5 (PZ), Hierarchical HZSM-5(HZ) Zn-Ni- Hierarchical HZSM-5 (ZN-HZ)

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Additionally, the bands observed at 790 cm^{-1} and 1225 cm^{-1}, in Figure 4, correspond to the external symmetric and asymmetric stretching of the Si-O-Si bond, respectively. The band at 3400 cm^{-1} suggests the presence of hydroxyl groups (OH^-) associated with absorbed water on the ZSM-5 surface. These findings are consistent with similar FTIR analyses in the literature [12], [15].

3.3. Nitrogen sorption studies (BET)

The nitrogen adsorption and desorption isotherms for the parent ZSM-5, hierarchical ZSM-5, and Zn-Ni hierarchical ZSM-5 are depicted in Figure 5. The nitrogen adsorption-desorption isotherms reveal that the parent HZSM-5 catalyst exhibited a typical Type I isotherm, consistent with the International Union of Pure and Applied Chemistry (IUPAC) classification, confirming its microporous nature. In contrast, the alkali-treated HZSM-5 displayed a Type IV isotherm with an underlying H3 hysteresis loop, indicative of a transition from a microporous to a hierarchical porous system that integrates both microporosity and mesoporosity. This finding is in agreement with the observations made in literature [16] regarding desilication.

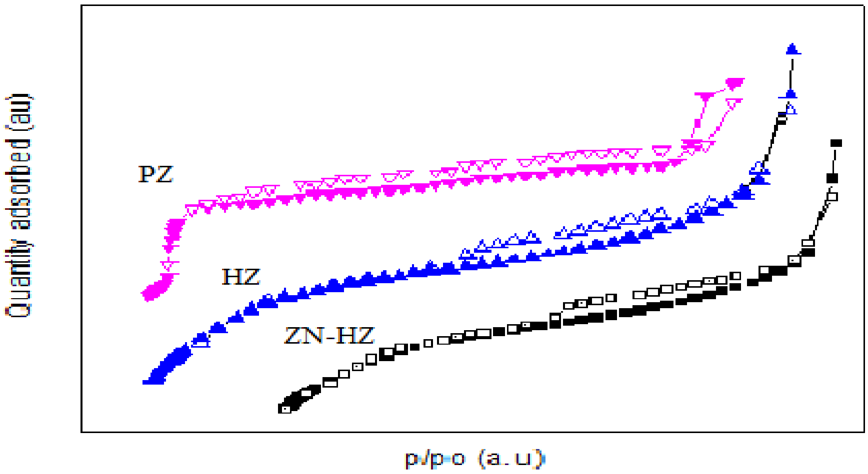

Figure 5: Nitrogen Adsorption and Desorption Isotherms of Parent ZSM-5(PZ), Hierarchical ZSM-5(HZ), and Zn-Ni Hierarchical ZSM-5(ZN-HZ)

Following alkaline treatment with 0.2 M NaOH at 650°C, an increase in the surface mesopores was noted for the HZSM-5 catalyst (Si/Al 50), as shown in Table 1. The hierarchical HZSM-5 (HZ) exhibited an external surface area of 141 m^2/g, in comparison to 111 m^2/g for the parent HZSM-5 (PZ). This enhancement in mesoporosity can be attributed to the desilication process induced by the alkaline treatment.

Table 1: Structural and textural properties of catalysts and calcined dolomite

SAMPLES	S_{BET}^{1}	S_{micro}^{2}	S_{meso}^{3}	S_{meso}^{4}	V_{total}^{5}	V_{micro}^{6}	V_{meso}^{7}	V_{meso}^{8}	**Average Pore Width⁹**
	(m^2/g)	(m^2/g)	(m^2/g)	(%)	(cm^3/g)	(cm^3/g)	(cm^3/g)	(%)	(nm)
(PZ)	386	275	111	28.8	0.202	0.110	0.092	41.8	2.03
(HZ)	416	275	141	33.9	0.221	0.086	0.119	53.8	5.10
(ZN-HZ)	387	251	136	35.1	0.225	0.106	0.119	52.9	5.04

1 From N_2 adsorption measurement (BET method)
2 From N_2 adsorption measurement (t–plot)
3 $S_{MESO} = (S_{BET} - S_{MICRO})$
4 % Surface Mesopores
5 From N_2 adsorption measurement at P/P0 = 0.9882
6 From N2 adsorption measurement (t–plot)
7 Vmeso = (Vtotal - Vmicro)
8 % Volume Mesopores
9 BJH adsorption average pore diameter

Furthermore, the results in Table 1, indicate a notable increase in the volume of mesopores following alkaline treatment, with both the hierarchical HZSM-5 and Zn-Ni hierarchical HZSM-5 samples exhibiting a mesopore volume of 0.119 cm^3/g, compared to 0.092 cm^3/g for the parent HZSM-5. Importantly, the development of mesoporosity on the surface of ZSM-5 did not lead to significant reductions in microporous surface areas and volumes, suggesting that the micropores were predominantly retained within the samples. This observation aligns with findings as reported by [5], [17] concerning desilication using NaOH concentrations of ≤ 0.2 M.

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The average pore size, as determined by the Barrett-Joyner-Halenda (BJH) method, was recorded as 2.03 nm for the parent HZSM-5, which increased significantly post-alkaline treatment to 5.10 nm for the hierarchical HZSM-5 and 5.04 nm for the metal-treated hierarchical HZSM-5.

The low surface area of dolomite was confirmed by the BET analysis, which yielded a surface area of 8.77 m²/g, consistent with the range reported in literature [18], which spans from 7.3 m²/g to 11.14 m²/g.

3.4. Thermo gravimetric analysis

Thermo gravimetric analysis of the catalyst was carried out between the temperatures of 20 - 9000°C to determine the thermal stability of the catalyst and sorbent, this is illustrated in Figure 6. Parent and alkaline treated catalyst had three regions of weight loss at 20-150°C, 150 - 400°C, and a sharp thermal step at 400°C. Weight loss between three thermal regions can be assigned to the desorption of water molecules [19]. All the catalysts have been shown to have a thermal effect at 400°C, but are ultimately thermally stable, which reflects crystalline stability. This is affirmed by the XRD and the presence of basic functional groups, after desilication and metal impregnation, using the FTIR technique.

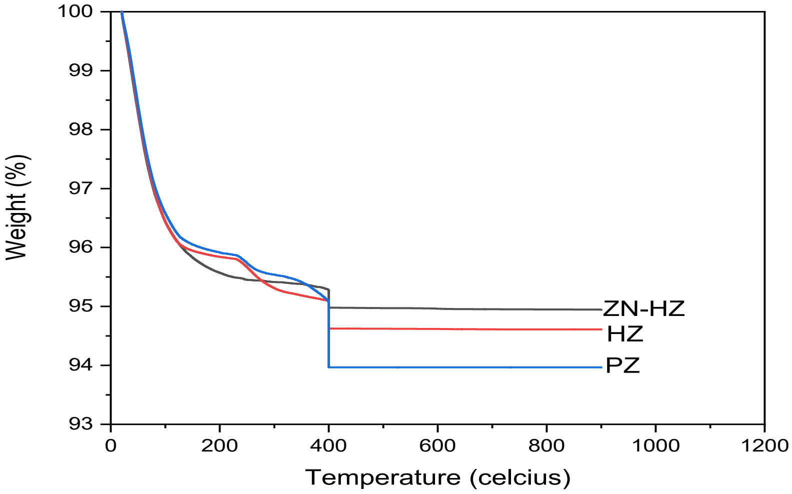

Figure 6: TGA of Parent ZSM-5(PZ), Hierarchical ZSM-5 (HZ), and Zn-Ni Hierarchical ZSM-5 (ZN-HZ)

4.0 Conclusion

This study successfully demonstrates the preparation and characterization of selective sorption-enhanced hierarchical HZSM-5 and hierarchical Zn-Ni/HZSM-5 catalysts. The innovative approach of incorporating mesoporosity into the conventional HZSM-5 structure through alkaline treatment resulted in significant improvements in the catalysts' textural properties, as evidenced by BET analysis. The hierarchical HZSM-5 exhibited enhanced mesoporosity and pore volumes with an increase from 111 to 141 m²/g and 2 to 5 nm, respectively. This is theoretically expected to facilitate better mass transfer and accessibility for larger reactants, which are critical for catalytic efficiency. Characterization techniques, including XRD and FTIR, confirmed the structural integrity of the hierarchical HZSM-5 even post-desilication and metal impregnation, ensuring that the essential MFI-type zeolite characteristics were retained.

Overall, this research lays a foundation for future investigations into optimizing these catalysts, exploring different metal loadings, and assessing their performance for use in the reforming of the products of biomass pyrolysis, which has the capacity to enhance the efficiency and sustainability of bio-oil and hydrogen production technologies and cleaner energy solutions.

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