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Structural and Catalytic Characterization of HCl-Modified Molecular Sieves for Enhanced Esterification of Free Fatty Acids

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Abstract
In this study, the catalytic performance of commercial molecular sieves (MS) was enhanced through a systematic acid modification process using hydrochloric acid (HCl) at varying molar concentrations (0.25, 0.5, and 1.0 M). The influence of acid strength on the structural, morphological, and elemental properties of the catalysts was rigorously evaluated using X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), and energy-dispersive X-ray spectroscopy (EDX). Analytical results revealed that acid treatment facilitated the selective removal of extra-framework cations and induced framework dealumination, effectively modulating the Si/Al ratio and increasing surface acidity. The EDX analysis suggested an optimal Si/Al ratio of 4.5 for the 0.5 M HCl-treated sample, which maintained framework integrity while maximizing active site accessibility. The catalytic efficiency was assessed through the esterification of oleic acid for biodiesel production. The MS-0.5 M catalyst exhibited superior performance, achieving a free fatty acid (FFA) conversion of 87.57% under optimized reaction conditions (methanol-to-oil ratio of 20:1, 3 wt% catalyst, and 95 °C). In contrast, higher acid concentrations (1.0 M) resulted in structural degradation and a subsequent decline in catalytic activity. This study demonstrates that precisely controlled acid modification is a robust analytical approach for developing high-performance, stable, and cost-effective heterogeneous catalysts for sustainable biofuel synthesis.

Keywords
(Molecular sieve; Acid modification; Heterogeneous catalysis; Biodiesel; Esterification; Structural characterization.

1. Introduction

The worldwide adoption of biodiesel as a renewable energy source plays a crucial role in reducing greenhouse gas emissions and overcoming the challenges associated with the scarcity of fossil fuels [1]. Given the finite nature of fossil fuel reserves and the urgent need to mitigate greenhouse gas emissions, the search for sustainable energy alternatives has become essential. In this context, biofuels, particularly biodiesel, have attracted significant interest as promising substitutes for conventional fuel [2]. The fuel exhibits enhanced performance characteristics relative to fossil fuels and can be utilized in existing diesel engines in its current form[3]. A commonly adopted approach for biodiesel production is the esterification of feedstocks rich in free fatty acids, a process that necessitates the use of acid catalysts[4]. In the presence of alcohol and an appropriate catalyst, triglycerides are transformed into biodiesel through transesterification, while free fatty acids undergo esterification. The transesterification pathway may employ either acidic or basic catalysts, whereas esterification exclusively requires acidic catalysts. Consequently, acid-based catalysts have the advantage of being applicable to both reaction routes [5]. Biodiesel can be utilized in diesel engines either as a pure fuel or blended with conventional diesel. The characteristics of the fuel introduced into the engine significantly influence its performance, and in some cases, the addition of specific additives is required to enhance engine efficiency. Production of biodiesel generally involves the conversion of free fatty acids (FFAs) and triglycerides (TGs) through esterification and transesterification reactions [6]. Among the various synthesis

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routes, esterification of free fatty acids (FFAs) represents an effective method for biodiesel production [7]. Biodiesel, which belongs to the group of alkyl fatty acid esters, is generally synthesized through esterification or transesterification reactions in the presence of catalysts. Although homogeneous base catalysts such as sodium methoxide, sodium hydroxide, and potassium hydroxide provide high catalytic activity, their application is limited because excessive water or free fatty acids in the feedstock can lead to unwanted saponification [8]. The esterification process is generally carried out in the presence of acidic catalysts, since the use of basic catalysts promotes the conversion of free fatty acids into soap, which in turn reduces the efficiency by consuming part of the catalyst. In contrast, the transesterification reaction can be catalyzed by both acids and bases, offering greater flexibility compared to esterification [6]. Homogeneous catalysts, including strong bases like NaOH and KOH as well as strong acids such as H_2SO_4 and HCl, are commonly utilized in biodiesel synthesis because they enable rapid reaction rates [9]. In the field of biodiesel production, growing interest has been directed toward heterogeneous catalysts, especially solid acids and bases. Among these, alkaline earth metal oxides represent a significant class of solid bases, valued for their relatively high catalytic efficiency and suitability for operation at lower temperatures. However, their use is largely limited to refined feedstocks with very low levels of free fatty acids (FFAs). In contrast, solid acid catalysts can overcome these limitations by effectively promoting FFA esterification and maintaining activity even in the presence of water within the feed oil. Therefore, selecting a catalyst that combines economic feasibility with long-term catalytic stability is essential for sustainable biodiesel manufacture. Key considerations in this selection process include the pore structure, the distribution and type of acid sites, the crystalline phase, and the inherent strength of the acidic functionalities [10]. One of the major advantages of heterogeneous catalysts is their straightforward separation from the reaction medium, which eliminates catalyst loss. This feature allows the production of methyl esters and glycerol with high levels of purity. Furthermore, since soap formation from free fatty acids does not occur, even low-quality feedstocks such as waste cooking oils can be effectively utilized [11] Zeolites are a class of crystalline microporous solids that play a crucial role as catalysts in various branches of the chemical industry, including oil refining, petrochemical production, and fine chemical synthesis. Their exceptional catalytic behavior arises from their ability to provide both high activity and remarkable selectivity [12] . In recent years, zeolites and molecular sieves have received considerable attention due to their unique structural characteristics, high surface area, and tunable acidity, which make them effective catalysts in a wide range of chemical processes [13] .The base material employed in this study was a commercial zeolite, commonly known as Molecular sieve. Owing to its high surface area, well-defined pore structure, and ion-exchange capacity, Molecular sieve has been widely explored as a heterogeneous catalyst in various chemical processes. However, its catalytic performance strongly depends on surface acidity and structural properties, which can be tailored through chemical modification. In order to enhance its suitability for biodiesel production, the Molecular sieve was subjected to acid treatment using hydrochloric acid solutions of different concentrations. Acid modification is known to remove extra-framework cations, increase surface area, and generate additional active sites, thereby improving the catalytic efficiency of the material. For example, wan et al. confirmed that by using acid modification by an organic one, 4A type zeolite's crystal feature was altered and its surface was enhance [14]. In other work, Li et al. HY zeolite with 0.1 M tartaric acid and concluded that the modification by this moderate acid had led to the remove of both extra-framework and a portion of the framework aluminum species, generating secondary mesopores and exposing more accessible Brønsted acid sites on the external surface and within mesopores [15].

By investigating the influence of acid strength on the properties of the treated Molecular sieve, this work aims to establish an optimized preparation route for an effective catalyst in biodiesel synthesis. For the modification process, the powdered Molecular sieve was treated with hydrochloric acid solutions of different molarities under reflux conditions. After the acid treatment, the material was thoroughly washed with deionized water until neutrality and then dried at elevated temperature. This procedure ensured the removal of impurities and facilitated the development of desired acidic sites on the catalyst surface.

2. Experimental

2.1 Materials

The base material employed in this study was a commercial zeolite (molecular sieve 3A, granular), supplied by Daejung Chemicals & Metals Co., Ltd. (South Korea; Cat. No. 8595-1405). Hydro-chloric acid (HCl) of analytical grade was employed for the acid modification process. Deionized water was used throughout the experiments for washing and neutralization.

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2.2 Catalyst preparation

For the modification procedure, 10 g of Molecular sieve powder was placed in a 250 mL round-bottom flask, and 100 mL of hydrochloric acid solution was added. Three different acid concentrations were prepared: 0.25 M, 0.5 M, and 1 M. The mixture was heated under reflux at 80 °C for 8 hours using a magnetic stirrer to ensure uniform contact between the acid and the Molecular sieve. Reflux was applied to prevent solvent loss during the treat-ment. After completion of the acid treatment, the mixture was allowed to cool to room temperature. The solid product was separated by vacuum filtration and thoroughly washed with deionized water until the filtrate reached neutral pH. Finally, the washed powder was placed in an oven at 100 °C for 24 hours to obtain the acid-modified Molecular sieve (Figure 1).

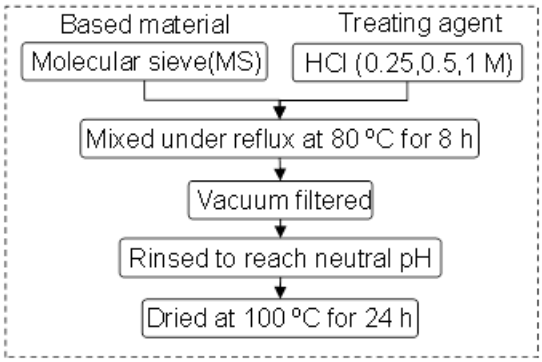

Figure 1. Schematic representation of the synthesis procedure for modified molecular sieve (MS) catalysts.

2.3 Catalysts Characterization Approaches

The crystalline structure and phase purity of the modified molecular sieve samples were analyzed by x-ray diffraction (XRD). the diffraction patterns were used to identify characteristic peaks and to evaluate possible structural changes after modification. in addition, field emission scanning electron microscopy (FESEM) was employed to investigate the surface morphology, particle size distribution, and microstructural features of the samples, providing complementary information on their textural properties. furthermore, energy-dispersive x-ray spectroscopy (EDX) was utilized to determine the elemental composition and distribution within the samples. The EDX spectra and elemental mapping helped confirm the presence of the expected elements, assess compositional uniformity, and identify any potential impurities or changes in chemical composition resulting from the modification process.

2.4 Evaluation of Catalytic Performance through Experimental Configuration

In this study, biodiesel was produced from oleic acid oil containing free fatty acids (FFAs) using a 50 mL batch autoclave reactor. The reaction was performed with a methanol-to-oil molar ratio of 20, and the catalyst concentration was adjusted to 3 wt% relative to the oil. The mixture was maintained at 110 °C for 120 min. After the designated reaction time, the operation was terminated, and the reactor was left to cool naturally before further treatment.

Once cooled, the reaction output separated into two phases. The solid fraction, representing the catalyst, was extracted through washing with a binary mixture of n-hexane and methanol. This was followed by filtration with filter paper, after which the catalyst was dried in an oven at 95-110 °C to prepare it for reuse. The liquid fraction consisted of biodiesel, unreacted fatty acids, and some residual methanol. Excess methanol was eliminated by heating the liquid at 60 °C for 30 min. To purify the product, 3 mL of deionized water was introduced, stirred for 10 min, and then centrifuged at 4000 rpm for 10 min; the washing process was repeated twice.

Following purification, two layers were formed: the upper layer mainly contained biodiesel with minor amounts of FFAs and methanol, whereas the lower layer comprised deionized water mixed with un-evaporated methanol. The upper fraction was carefully removed using a syringe and subjected to an additional heating step at 60 °C to ensure methanol removal. The efficiency of biodiesel production was finally assessed by determining the FFA conversion, using titration with 0.1 M KOH according to the EN 14104 standard[16]. synthesis was using equations 1 and 2, where Ac1 and Ac2 represent the initial and final acid values, respectively

Acid value,

$$mg_{KOH}/g_{oil} = \frac{(56.1056\,gKOH/mole)\times 0.1(moleKOH/L)\times V_{KOH}}{g_{oil}} \quad (1)$$

Conversion,

$$x\% = \frac{Ac_2 - Ac_1}{Ac_1}\times 100 \quad (2)$$

3. Results and Discussions

3.1 Characterization

3.1.1 XRD Analysis

The XRD patterns confirm the multiphasic nature of the MS catalyst, identifying key crys-talline aluminosilicate phases (Na-Al-Si-O-H_2O and $Ca_{0.40}Al_{0.92}Si_{5.03}O_{12}(H_2O)_{1.895}$). The most insightful observation relates to the MS-0.5 M HCl sample: the intensity of the main diffraction peaks is substantially retained, or even slightly enhanced, compared to the pris-tine MS. This suggests that the 0.5 M HCl concentration achieves the required cation-exchange (activation) while maintaining the structural integrity and crystallinity of the framework. The relative enhancement in peak intensity is attributed to the selective removal of

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non-crystalline (amorphous) components by the acid, increasing the relative fraction of the crystalline material in the final solid. Conversely, the MS-1.0 M HCl sample displays severe peak intensity reduction and noticeable peak broadening. This is the definitive fin-gerprint of structural degradation, framework dealumination, and a loss of long-range order (Figure 2).

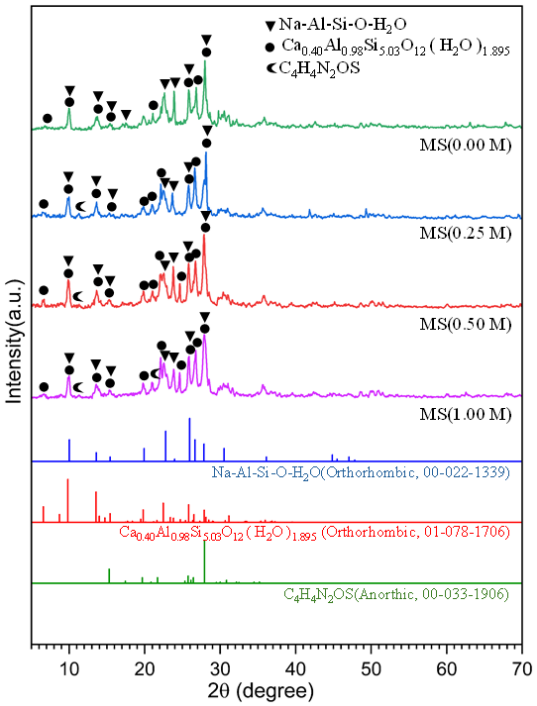

Figure 2. XRD of: (a) MS(0.00), (b) MS(0.25), (c) MS(0.50), and MS(1.00), demonstrating the structural phases of the modified molecular sieves.

3.1.2 FESEM

As shown in Figure 3 the FESEM images suggest that the pristine MS (0.00 M) catalyst exhibits a polycrystal-line and highly aggregated morphology, characterized by irregular particles spanning the micro- and nano-scales. The acid activation process across all concentrations (0.25 M to1.0 M) generally preserved the overall macroscopic structure of the agglomerates. Specifically, the optimal MS-0.50 M HCl sample maintained its integrity, indicating high structural stability under the chosen treatment conditions (80 ºC). The mild acid treatment is hypothesized to induce selective dissolution of non-framework species and amorphous material from the particle surfaces, a "cleaning" process that enhances the pore accessibility without causing bulk framework damage. This structural integrity and enhanced surface quality are essential for ensuring efficient diffusion of the bulky FFA molecules to the internal active sites, which directly supports the observed maximal catalytic conversion. The absence of severe morphological collapse further reinforces the stability evidenced by the XRD results.

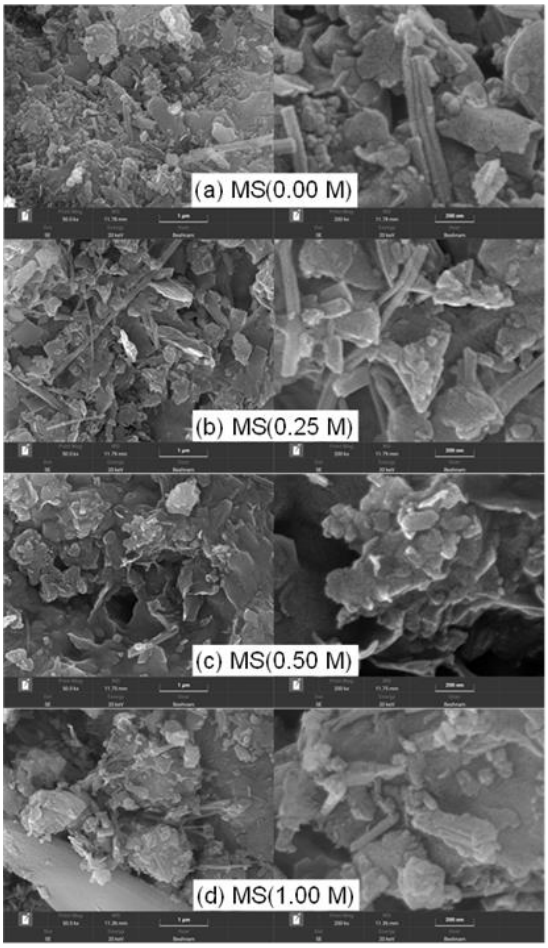

Figure 3. FESEM micrographs showing the surface morphology and particle distribution of: (a) MS(0.00), (b) MS(0.25), (c) MS(0.50), and MS(1.00).

3.1.3 FTIR Analysis

The FTIR spectra of the pristine and HCl-modified molecular sieves (Figure 4) provided critical insights into the evolution of framework bonds and structural integrity as a function of acid concentration. The characteristic vibrational bands in the 500–600 cm^{-1} region, assigned to the stretching modes of framework Al-O and Si-O bonds, exhibited a progressive decline in intensity upon increasing HCl concentration from 0.00 to 1.00 M, indicating a gradual dealumination of the aluminosilicate framework. For the optimally modified MS-0.50 M sample, the reduction in band intensity was moderate and well-controlled, suggesting a selective removal of extra-framework aluminum and amorphous species while preserving the primary crystalline network. In contrast, the MS-1.00 M sample showed a pronounced attenuation of the same bands, particularly at 500 cm^{-1} (intensity dropping from 0.95 in the pristine MS to 0.70), which is a clear fingerprint of excessive framework dealumination and partial structural collapse. Complementary bands in the 650–750 cm^{-1} range, arising from asymmetric T-O-T (T = Si, Al) vibrations, remained largely intact for

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MS-0.50 M but were significantly weakened at the highest acid concentration, further corroborating the preservation of the zeolitic framework under moderate treatment and its degradation under harsh conditions. These FTIR observations are in excellent agreement with the XRD and FESEM results, confirming that the 0.50 M HCl treatment strikes an optimal balance between enhancing surface acidity via controlled dealumination and maintaining the structural robustness required for efficient catalytic esterification of free fatty acids.

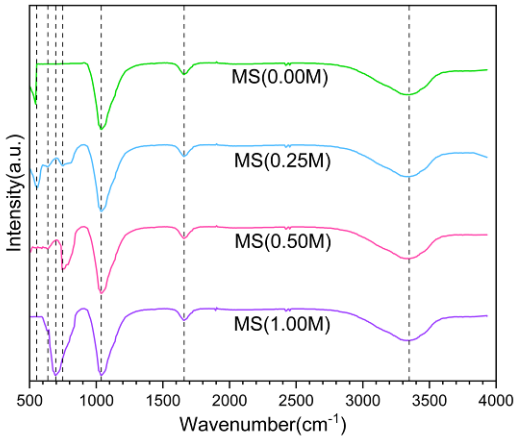

Figure 4. FTIR of: (a) MS(0.00), (b) MS(0.25), (c) MS(0.50), and MS(1.00).

3.1.4 EDX and Dot-Mapping Analysis

Energy-dispersive X-ray spectroscopy (EDX) was employed to examine the surface elemental composition and assess the modifications of the synthesized MS samples following treatment with different HCl concentrations (Figure 5). It is important to note that EDX is a surface-sensitive and semi-quantitative technique; therefore, the reported values are intended to provide surface-representative estimates and highlight relative compositional trends rather than definitive bulk quantification. To ensure the representativeness of the data, EDX spectra were acquired from several scanned regions across the sample surfaces.

The spectra indicated the presence of O, Si, Al, Ca, Na, and S as the primary detected elements in all samples. The relative intensities of these elements shifted with increasing acid concentration. In particular, the Si/Al atomic ratio was utilized as a qualitative indicator of compositional variation and potential dealumination induced by the acid treatment.

For the untreated sample, MS(0.00 M), the silicon and aluminum contents were 24.75 at.% and 6.68 at.%, respectively, corresponding to an estimated Si/Al ratio of 3.7. After treatment with 0.25 M HCl, the silicon content increased to 31.23 at.% while the aluminum content decreased to 5.00 at.%, resulting in a higher Si/Al ratio of 6.2. This observation suggests a modification in the surface elemental composition, which is consistent with the partial removal of aluminum species from the near-surface region of the material.

For MS(0.50 M), the Si/Al ratio was found to be 4.5, which remains higher than that of the untreated sample but lower than the value observed for the 0.25 M-treated sample. This variation may reflect a dynamic balance between dealumination and surface structural rearrangement at intermediate acid concentrations. At the highest acid concentration, MS(1.00 M), the Si/Al ratio was 4.9, indicating further compositional changes under stronger acidic conditions.

To supplement the point analysis and evaluate the homogeneity of the samples, EDX elemental mapping (dot-mapping) was performed (Figure 6). The mapping results demonstrated that O, Si, Al, Ca, Na, and S were distributed across the analyzed particles in a uniform manner, suggesting that the observed elemental composition is representative of the analyzed surfaces rather than being restricted to isolated local inhomogeneities.

Overall, the EDX and mapping results suggest that acid treatment leads to noticeable modifications in the surface elemental composition of MS, primarily characterized by a relative increase in the Si/Al ratio. While these results are semi-quantitative, they provide supportive evidence of compositional trends that complement the structural observations obtained from other characterization techniques.

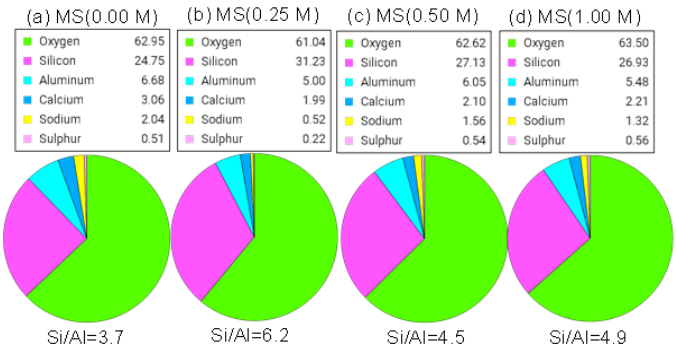

Figure 5. EDX spectra and elemental atomic ratios for: (a) MS(0.00), (b) MS(0.25), (c) MS(0.50), and (d) MS(1.00) based on atomic ratio.

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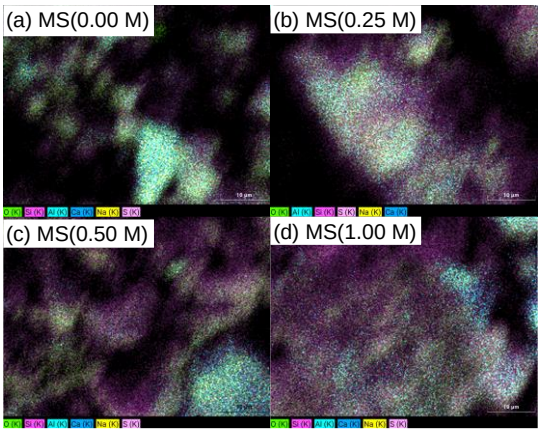

Figure 6. Dot-maps of MS samples before and after HCl treatment: (a) MS(0.00), (b) MS(0.25), (c) MS(0.50), and (d) MS(1.00) based on atomic ratio. The maps show the surface distribution of O, Si, Al, Ca, Na, and S within the analyzed regions. (Scale bar: 10 μm.)

3.1.5 BET-BJH Analysis

The textural characteristics of the optimally acid-modified molecular sieve MS(0.50 M) were quantitatively assessed through nitrogen adsorption-desorption analysis, revealing a hierarchical pore architecture that results from the controlled dealumination process (Figure 7). The catalyst exhibits a specific surface area of 85.70 m^2/g, which, while moderate, signifies the preservation of a substantial fraction of the original microporous framework following HCl treatment. A detailed evaluation of the pore volume distribution indicates that microporosity accounts for 0.0306 cm^3/g, meso-porosity for 0.0346 cm^3/g, and macro-porosity for 0.0269 cm^3/g, leading to a total pore volume of 0.0916 cm^3/g(Table 1). Notably, the coexistence of all three pore regimes confirms the successful generation of a hierarchical structure. The average pore width is determined to be 4.3 nm, placing the material predominantly within the mesoporous range. This textural configuration, particularly the developed meso- and macro-porosity alongside retained microporosity, is critical for facilitating molecular diffusion and ensuring that the internal active sites remain accessible for bulky molecules. The data collectively demonstrate that the 0.50 M HCl treatment achieved an optimal balance: it effectively removed extra-framework species and induced sufficient meso-porosity without causing excessive structural collapse that would otherwise reduce surface area and porosity.

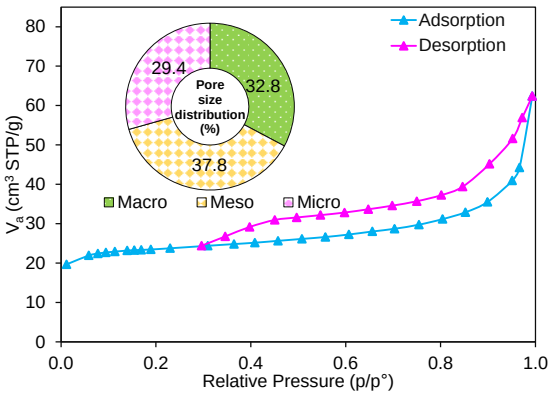

Figure 7. N_2 adsorption-desorption isotherm of MS(0.5) catalyst.

Table 1. BET-BJH characteristic of MS(0.5) catalysts.

Surface area (m^2/g)	Micropore (cm^3/g)	Mesopore (cm^3/g)	Macropore (cm^3/g)	Total pore volume (cm^3/g)	Pore width (nm)
85.70	0.3006	0.0346	0.0269	0.0916	4.3

3.2 Assessing the Efficiency of Catalysts in Biodiesel Generation

3.2.1 Catalytic Performance and Optimization

Figure 8 illustrates the performance of the prepared molecular sieve catalysts and compares the effect of different HCl concentrations during acid treatment on biodiesel production. The conversion of the reaction for MS(0.00), MS(0.25), MS(0.50), and MS(1.00) was 50.17%, 83.26%, 87.57%, and 79.92%, respectively. The experiments were conducted at 115°C for 2 hours with a methanol-to-oil molar ratio of 20:1 and using 3 wt% catalyst. For comparison, the untreated sample was also evaluated, exhibiting the lowest conversion.

The conversion increased with HCl concentration up to 0.50 M, where the acid treatment significantly enhanced the surface activity of the catalyst, resulting in the highest conversion of 87.57% for MS(0.50). However, further increasing the acid concentration to 1.00 M caused a decrease in conversion. This reduction can be attributed to severe acid treatment leading to partial structural degradation, decreased surface area, and excessive leaching of essential cations from the molecular sieve framework, which limits reactant access to active acidic sites. Moreover, maintaining an optimal balance in the molecular sieve framework after moderate acid treatment played a significant role in the superior performance of MS(0.50), whereas excessive acid treatment resulted in partial loss of desirable catalytic properties.

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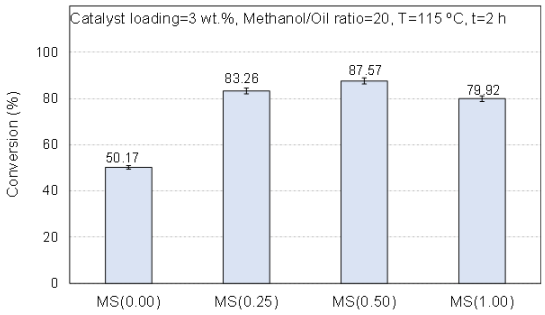

Figure 8. Comparison of the catalytic performance of MS catalysts in the conversion of Free Fatty Acids (FFAs) as a function of HCl activation concentration.

3.2.2 Comparative catalytic performance

To evaluate the efficiency of the synthesized MS(0.5) catalyst, its performance was compared with several previously reported heterogeneous catalysts used for biodiesel production under similar reaction conditions (Table 2). As shown in the table, the MS(0.5) catalyst exhibits a comparable or superior performance regarding reaction time, temperature, and conversion efficiency. Specifically, the high catalytic activity of our catalyst, even with a relatively lower reaction temperature and time compared to some literature values, demonstrates the effectiveness of the acid-modification method employed in this study. This comparative analysis highlights the potential of the MS(0.5) catalyst as a promising heterogeneous candidate for sustainable biodiesel production.

Table 2. Comparison of the catalytic performance of MS(0.5) with other reported heterogeneous catalysts for biodiesel production.

Catalyst	Feedstock	Temperature (°C)	Time (h)	Catalyst (wt.%)	m.r	Conv. %	Ref.
SO_4^{2-}/ZnO-β-zeolite	Waste cooking Oil	200	8h	3	15	96.9	[17]
FAU zeolite	Sun flower oil	65	4h	5	9	91.6	[18]
CaO-zeolite/Fe_3O_4	Used cooking oil	55	4	3	5	93.64	[19]
commercial zeolite Y	Waste cooking oil	55	1.5	-	-	62	[20]
MS(0.5)	Oleic acid	115	2	3	20	87.57	This work

3.3 Reusability and Structural Stability of Recycled Catalysts

The recyclability of the MS(0.5) catalyst was investigated on four runs in 115 °C, catalyst loading of 3 wt.%, and methanol-to-oil mole ratio of 20, as shown in Figure 9. MS(0.5) catalyst preserved highly conversion effectiveness over all runs, with values of 87.57%, 87.52%, 87.51%, and 87.49% for run 1 to 4, respectively. The negligeable reduction (<0.09%) in conversion on successive use highlights the high recyclability, and obstruction of the catalyst to inactivation. This almost stable performance proposes that the active sites persisted available and the catalyst construction was not meaningfully changed during multiple runs [21]. To supplementary explore the physical integrity of the catalyst afterward recycle, XRD and EDS analyses was carried out on the used catalyst after the fourth run (Figure 10 and Figure 11). The XRD diagram displayed no noticeable alteration in peak location or intensity against to fresh catalyst, proving the conservation of the crystalline phases and absence of leaching. For further assessment of potential leaching, EDS analysis (reported in mol%) was performed. The comparison between the fresh and used MS (0.5 M) samples indicated that the elemental components were largely retained, suggesting no significant leaching under the applied reaction conditions.

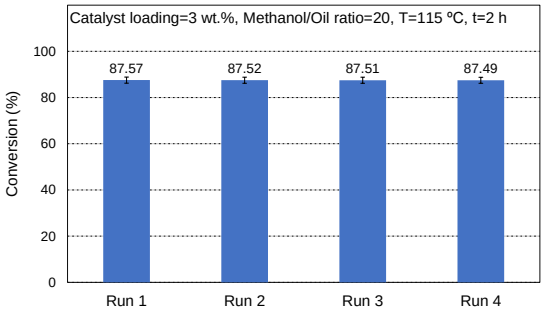

Figure 9. Catalytic activity of MS(0.5 M) catalysts over four successive runs.

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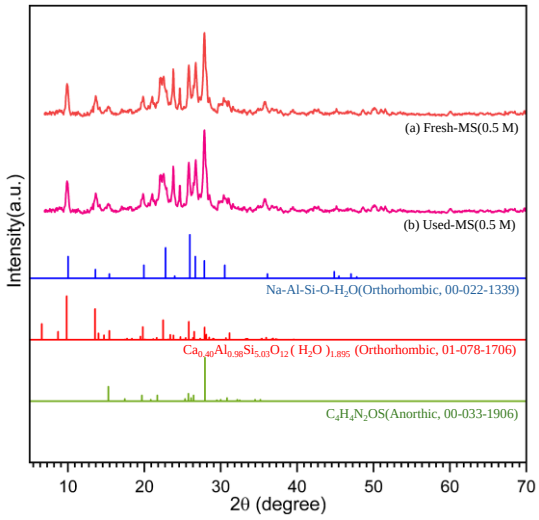

Figure 10. XRD analysis of fresh and used MS(0.5 M) catalyst.

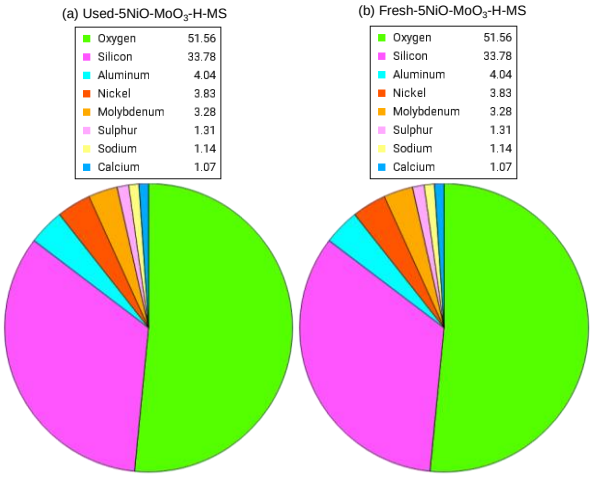

Figure 11. EDS analysis of fresh and used MS(0.5 M) catalyst.

3.4 Reaction Mechanism for Biodiesel Production over MS Catalysts Activated with HCl

As presented in Figure 12 the proposed mechanism for biodiesel production from free fatty acids (FFAs) and methanol over HCl-modified MS catalyst involves five main steps. First, FFAs and methanol diffuse onto the catalyst surface. Second, the reactants penetrate into the internal pores of the catalyst. Third, adsorption occurs, where the acidic sites of the catalyst interact with the reactants, generating carbocation and oxygen anion species to facilitate the esterification reaction. Fourth, the surface reaction proceeds via nucleophilic attack of methanol on the activated carbonyl carbon of FFAs, forming an unstable intermediate. Finally, biodiesel and water are produced through desorption from the catalyst surface via the cleavage of –CO and –OH bonds. The high catalytic performance is attributed to the enhanced acidic strength and structural properties achieved through HCl modification[6].

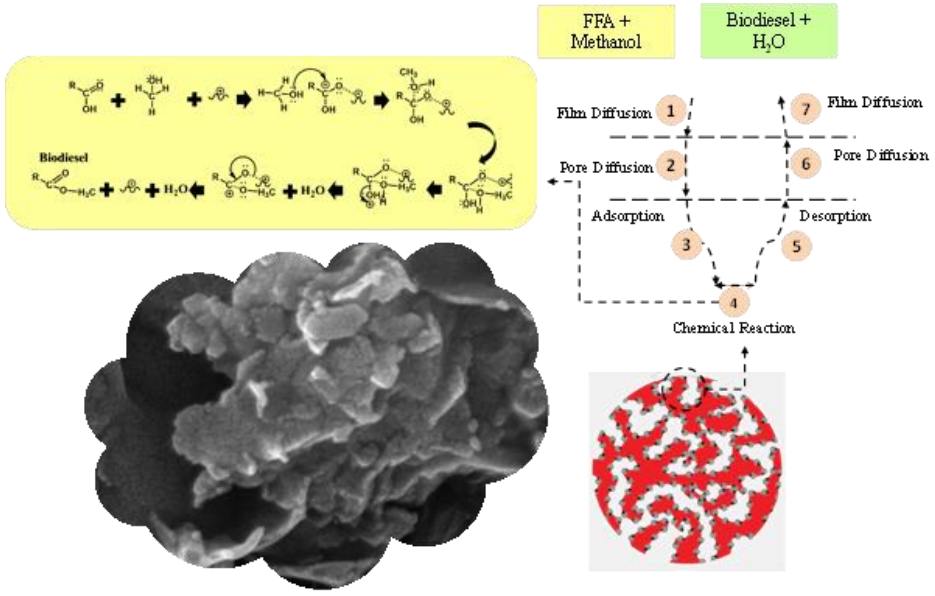

Figure 12. Proposed esterification mechanism of oleic acid with methanol over MS Catalysts Activated with HCl.

4. Conclusions

In this study, HCl-modified Molecular Sieve (MS) catalysts with different acid concentrations (0, 0.25, 0.5, and 1 M) were successfully prepared and evaluated for biodiesel production via esterification of free fatty acids. Characterization analyses indicated that HCl treatment improved the structural properties and enhanced the acidity of the active sites. Among the prepared samples, MS(0.5M) exhibited the highest catalytic perfor-

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mance, achieving a biodiesel conversion of 87.57% under fixed reaction conditions. The results suggest that moderate acid modification is optimal for promoting the esterification reaction, while excessive acid treatment does not further improve catalytic activity. These findings suggest that HCl-modified Molecular Sieve, particularly the MS(0.5M) sample, is a promising, stable, and reusable solid acid catalyst for efficient biodiesel production. It is important to acknowledge that the structural modifications proposed here, particularly regarding the framework vs. extra-framework aluminum distribution, are based on compositional (EDX) and crystallographic (XRD) evidence. While these observations are consistent with established acid-modification mechanisms, definitive confirmation of the framework environment and exact acidity type would require advanced spectroscopic techniques such as Al NMR, NH_3-TPD, and Pyridine-FTIR. These analyses remain a priority for our future work to further elucidate the structure-performance relationship.

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بررسی ساختاری و کاتالیستی غربال‌های مولکولی اصلاح‌شده با هیدروکلریک اسید برای افزایش کارایی استریفیکاسیون اسیدهای چرب آزاد

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چکیده

در این مطالعه، عملکرد کاتالیزوری غربال‌های مولکولی تجاری (MS) از طریق یک فرآیند اصلاح با اسید هیدروکلریک (HCl) در غلظت‌های مولی مختلف (۰/۲۵، ۰/۵و ۱/۰ مولار) افزایش یافت. تأثیر قدرت اسید بر خواص ساختاری، مورفولوژیکی و عنصری کاتالیزورها با استفاده از پراش اشعه ایکس (XRD)، میکروسکوپ الکترونی روبشی گسیل میدانی (FESEM) و طیف‌سنجی پراش انرژی اشعه ایکس (EDX) به طور دقیق ارزیابی شد. نتایج تحلیلی نشان داد که عملیات اسیدی، حذف انتخابی کاتیون‌های اضافی چارچوب و آلومیناسیون چارچوب را تسهیل می‌کند، به طور موثر نسبت Si/Al را تعدیل کرده و اسیدیته سطح را افزایش می‌دهد. تجزیه و تحلیل EDX نسبت بهینه Si/Al برابر با ۴/۵ را برای نمونه تیمار شده با HCl 0.5 مولار تأیید کرد که یکپارچگی چارچوب را حفظ کرده و در عین حال دسترسی به محل فعال را به حداکثر می‌رساند. راندمان کاتالیزوری از طریق استری کردن اسید اولئیک برای تولید بیودیزل ارزیابی شد. کاتالیزور MS-0.5 M عملکرد برتر را نشان داد و در شرایط واکنش بهینه شده (نسبت متانول به روغن ۲۰:۱، ۳ درصد وزنی کاتالیزور و دمای ۹۵ درجه سانتیگراد) به تبدیل ۸۷/۵۷ درصدی اسید چرب آزاد (FFA) دست یافت. در مقابل، غلظت‌های بالاتر اسید (۱/۰ مولار) منجر به تخریب ساختاری و متعاقباً کاهش فعالیت کاتالیزوری شد. این مطالعه نشان می‌دهد که اصلاح اسید با کنترل دقیق، یک رویکرد تحلیلی قوی برای توسعه کاتالیزورهای ناهمگن با عملکرد بالا، پایدار و مقرون به صرفه برای سنتز سوخت‌های زیستی پایدار است.

کلید واژه‌ها

غربال مولکولی؛ اصلاح اسیدی؛ کاتالیز ناهمگن؛ بیودیزل؛ استری شدن؛ توصیف ساختاری.

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