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Sustainable Biodiesel Production via Functionalized Kaolin Catalysis: Performance and Mechanistic Insights

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1. ABSTRACT

This study investigates the catalytic performance of raw kaolin and alkaline-modified kao-lin (t-kaolin) as low-cost, environmentally benign solid acid catalysts for biodiesel produc-tion via the esterification of oleic acid. The modification process, involving alkaline leach-ing with 2M NaOH, resulted in a delaminated and mesoporous structure with enhanced sur-face area (6.8 m^2/g) and high acid density (521.1 µmol NH_3/g). Under optimized conditions (100 °C, 3 wt.% catalyst, 20:1 methanol-to-oil ratio, and 3 hours), the conversion efficiency increased from 81.97% for raw kaolin to 88.34% for t-kaolin. Kinetic studies confirmed that both catalysts follow pseudo-first-order kinetics, with the apparent rate constant (Kapp) in-creasing from 0.097 h^{-1} (raw kaolin) to 0.127 h^{-1} (m-kaolin). A reaction mechanism follow-ing the Eley-Rideal model was proposed, emphasizing the role of the enhanced acidic sites and mesoporous framework. These results underscore the potential of modified kaolin as a sustainable and highly efficient catalyst that bridges the gap between natural minerals and engineered catalysts.

Keywords: Raw kaolin, alkaline-modified kaolin, Oleic Acid, Esterification, Heterogeneous Catalyst, Reaction Mechanism.

2. INTRODUCTION

Kaolin, a naturally occurring non-metallic mineral resource predominantly composed of clay minerals from the kaolinite group, is principally characterized by its layered silicate structure of kaolinite [$Al_2Si_2O_5(OH)_4$] [1, 2]. In a research, the catalytic performance of acid-functionalized kaolin-immobilized $CaO\text{-}ZrO_2$ hybrid nanostructures for one-pot biodiesel synthesis from waste cooking oil through concurrent esterification-transesterification reactions was evaluated [3].

While previous studies have predominantly focused on the efficacy of raw kaolin or highly complex chemically synthesized supports, the impact of controlled alkaline exfoliation on the intrinsic catalytic activity of kaolin remains under-explored. This study aims to fill this gap by comparing the performance of raw kaolin with a modified version (t-kaolin) prepared through a simplified alkaline leaching process. By systematically analyzing the kinetics and reaction mechanisms of both materials, this research provides a comprehensive understanding of how low-cost modifications can significantly enhance the catalytic velocity and conversion efficiency of natural clay minerals for sustainable biodiesel production.

3. MATERIALS AND METHODS

3.1. Materials

Raw kaolin (particle size <5 µm) was obtained from the Zunuz mine (Iran). NaOH (MW=40.00g/mol, purity: EMSURE®) purchased from Sigma Aldrich. Oleic acid with an acid value of 217 mg KOH/g was prepared from Sigma-Aldrich. Methanol (density = 0.791 kg/L, MW = 32.04 g/mol, 99.8% purity) was sourced from Sigma-Aldrich.

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3.2. Material preparation

The modification of raw kaolin was performed via a chemical swelling/exfoliation process using an alkaline leaching method. Initially, a 2M sodium hydroxide (NaOH) solution was prepared by dissolving NaOH pellets in deionized water (DIW). Raw kaolin was then added to the solution. The resulting suspension was subjected to a reflux process at 80 °C for 4 h under continuous stirring to ensure uniform interaction between the hydroxyl ions and the interlayer spaces of the kaolinite. After the treatment, the solid fraction was separated by filtration and washed repeatedly with DIW until a neutral pH was achieved, ensuring the removal of residual alkali. Finally, the treated kaolin (t-kaolin) was dried in an oven at 110 °C for 24 h to obtain a stable powder for further characterization.

4. RESULTS AND DISCUSSION

4.1. XRD

The crystalline phases and structural integrity of the samples were evaluated using X-ray diffraction (Figure 1). The diffraction angles (2θ) recorded for the raw kaolin were:20.97 °, 26.77 °, 36.64 °, 39.55 °, 40.36 °, 42.53 °, 45.87 °, 50.21 °, 54.93 °, 59.98 °, 64.06 °, 67.73 °, 68.34 °, 73.45 °, 75.62 °, 77.66 °, 79.82 °. These peaks are characteristic of the kaolinite mineral structure, the most intense peak at 26.77 ° is usually associated with the (1 0 -1) kaolinite plane or overlapping quartz impurities. A comparative analysis between raw kaolin and treated kaolin (m-kaolin) reveals a systematic shift of the peaks towards lower angles in the entire diffraction spectrum. While the inset in the figure focuses on the reflection of the most intense peak, this downward shift is the same for all identified planes. This shift indicates that the NaOH treatment did not simply affect the surface, but caused a uniform lattice expansion.

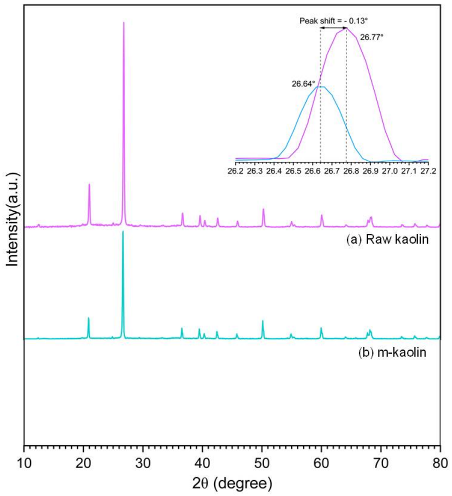

Figure 1. XRD of :(a) raw kaolin and (b) m-kaolin

4.2. FESEM

The surface morphology and microstructural changes were analyzed using FESEM (Figure 2). The FESEM micrographs reveal a transformative change in the kaolin topography: Raw Kaolin: The images show a highly dense and book-like morphology, characterized by thick, rigidly stacked hexagonal platelets. The particles appear as large agglomerates with minimal exposed surface area between the individual layers. Treated Kaolin (m-kaolin): In contrast, the t-kaolin samples exhibit a significant degree of delamination and plate separation. The previously thick stacks have been transformed into thinner, individual nanosheets with increased visible edges. The alkaline treatment has effectively pried apart the layers, resulting in a more porous and disordered structure.

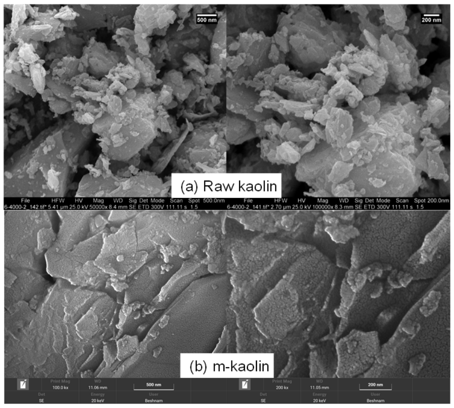

Figure 2. FESEM of :(a) raw kaolin and (b) m-kaolin

4.3. Catalyst evaluation in biodiesel production process

The experimental conditions were kept constant at the optimum: reaction temperature 100 °C, methanol to oil molar ratio 20:1, and catalyst loading 3 wt%. The data show a direct correlation between reaction time and conversion efficiency for both catalysts. For the raw kaolin catalyst, the conversion percentages at times of 0.5, 1, 2, and 3 h were 29.89, 48.37, 68.17, and 81.97%, respectively. In comparison, the m-kaolin catalyst showed significantly higher catalytic activity at all time intervals, achieving conversion values of 39.93, 62.38, 79.23 and 88.34% over the same time periods. This trend indicates that the modification of kaolin effectively improved its catalytic performance. This behavior suggests that the modified catalyst provides more active sites or better accessibility for the reactants, leading to a faster approach to chemical equilibrium under the specified conditions. In this study, the kinetic behavior of the reaction was evaluated using both raw and modified kaolin catalysts. The results of the kinetic study are shown in Figure 3. Based on the linear fit of the experimental data, the reaction follows pseudo-first-order kinetics, which is confirmed by the high linear coefficient of determination ($R^2>0.98$) in Figure 3. The apparent rate constant values of Kapp were calculated from the slopes of the plots (K′) according to Equation 6. The calculated values for Kapp at 100 °C were 0.097 h^{-1} for the raw kaolin catalyst and 0.127 h^{-1} for the modified kaolin catalyst. This increase in the rate constant for the modified kaolin catalyst confirms the superior catalytic efficiency in accelerating the esterification process compared to the unmodified precursor.

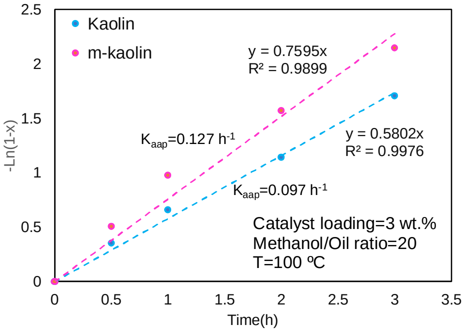

Figure 3. Kinetic evaluation of :(a) raw kaolin and (b) m-kaolin

5. CONCLUSION

This study successfully demonstrates that while raw kaolin possesses inherent catalytic activity for the esterification of oleic acid, its performance can be significantly improved through a simple alkaline modification. The treatment with 2M NaOH effectively transformed the dense, book-like morphology of raw kaolin into a delaminated, mesoporous m-kaolin structure, increasing the conversion efficiency from 81.97% to 88.34%. Kinetic analysis revealed that the modification led to a substantial increase in the apparent rate constant, from 0.097 h^{-1} to 0.127 h^{-1}, while maintaining a pseudo-first-order relationship. This improvement is attributed to the increased accessibility of the strong acidic sites and the reduction of mass transfer limitations within the engineered mesopores. In conclusion, m-kaolin emerges as a highly competitive and sustainable catalyst, offering a superior trade-off between cost, environmental impact, and catalytic efficiency. This work proves that minor architectural tuning of naturally occurring minerals can yield high-performance catalysts for the biofuel industry, providing an economical alternative to expensive synthetic catalysts without sacrificing significant conversion efficiency.

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