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Advancing Green Chemical Catalysis: The Role of Pillared Interlayered Clays

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Abstract: Pillared Interlayered Clays (PILCs) have gained significant attention in recent years due to their versatile applications, particularly in adsorption and catalysis. These advanced materials leverage the unique nanostructure of clay minerals, offering tailored interlayers and active sites for catalytic processes. The strategic modification of clays has led to the development of various catalytic systems, including ion-exchanged catalysts, acid-activated clays, intercalated and pillared catalysts, as well as hybrid organic-inorganic and hierarchically structured catalysts. Their effectiveness in green chemical catalysis is attributed to their high surface area, tunable acidity, and thermal stability. This review highlights the role of PILCs in sustainable catalytic applications, emphasizing their significance in eco-friendly and efficient reaction pathways.

Keywords: Pillared Interlayered Clays, Green Catalysis, Heterogeneous Catalysts, Montmorillonite, Chromium-Pillared Clays, Iron-Pillared Clays, Zirconium-Pillared Clays, Adsorption, Environmental Catalysis

I. INTRODUCTION

Catalysis plays a pivotal role in ensuring the sustainability and efficiency of chemical production processes. The global demand for catalysts spans several million tons annually, and their handling during use, as well as disposal after exhaustion, poses significant environmental challenges. Many conventional heterogeneous catalysts employed in organic transformations suffer from toxicity, lack of specificity, and intricate preparation procedures. Additionally, their use, recovery, and disposal require specialized care, leading to increased energy consumption and operational costs. This has fueled the ongoing search for environmentally friendly catalysts that can enhance reaction efficiency while minimizing waste generation and energy input.

An ideal green catalyst is one that is non-hazardous, facilitates reactions at lower temperatures with higher efficiency, maximizes desired product yield while reducing by-products, and is easily separable and reusable. Traditional heterogeneous catalysts such as metals, metal oxides, solid acids, low-dimensional solids, and ion-exchange resins have been extensively used in organic synthesis. Although only a few of these meet the criteria of an ideal green catalyst, recent advancements in catalyst modifications have demonstrated improved yields, selectivity, and recyclability, supporting the development of greener chemical processes [1].

A growing trend in the chemical industry is the transition toward environmentally benign catalysts, ensuring easy handling and sustainable disposal. Among the promising materials explored for green catalysis, clay-based materials have gained significant attention due to their availability, cost-effectiveness, and potential for modification. The development of high-performance solid catalysts is crucial for replacing polluting homogeneous catalysts with reusable heterogeneous alternatives [2]. Furthermore, engineered solid catalysts have the potential to drive innovations in fuel and chemical production from sustainable biomass-derived feedstocks [3]. Clays, as naturally occurring inorganic layered compounds, offer an excellent platform for developing functional catalysts due to their unique structural and

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compositional attributes. Over the past four decades, research has focused on designing and optimizing clay-based catalysts for applications in green and sustainable catalysis, spanning chemical, photonic, electronic, and biological domains.

II. CLAYS IN CATALYSIS

Clays are regarded as green catalytic materials due to their natural abundance and minimal processing requirements. They possess non-corrosive properties, plasticity for easy fabrication into various shapes and sizes, efficient separability from product streams, and environmentally safe disposal after use. Among the different types of clays, montmorillonites are the most extensively utilized in chemical transformations.

Various surface modification techniques have been employed to enhance the catalytic properties of montmorillonite, including:

- Ion Exchange with Multivalent Inorganic Cations and Coordination Complexes: This approach introduces redox-active species and generates acidic centers within the clay structure.
- **Organic Cation Exchange and Intercalation:** The incorporation of long-chain organic species expands the interlayer spacing, modifying the clay's catalytic properties.
- **Pillaring with Inorganic Hydroxyl-Oligomeric Species:** Thermal treatment after pillaring results in stable, thermally resistant materials with enhanced Lewis acidity.
- Acid and Surfactant Treatment: This process tailors porosity and acidity by incorporating mineral and organic acids.
- **Dealumination of Structural Aluminum:** Mild acid treatments create additional porosity and introduce mixed Brønsted acid sites in the interlayer region.
- Incorporation of Polymeric Hydrated Metal Species: This strategy, followed by thermal treatment, results in porous clay heterostructures.
- Impregnation of Metal Salts and Reduction: Produces supported metal and metal oxide catalysts for specific organic transformations.
- **Microwave-Assisted Reactions:** Due to their intrinsic bipolarity, clays efficiently absorb microwave energy, facilitating rapid and selective reactions [4].

Modified clays exhibit remarkable stability, retaining their catalytic characteristics even after multiple cycles of use. Numerous reviews in recent years have explored the modifications and applications of clay-based catalysts in organic synthesis. However, many of these studies overlook the crucial relationship between surface modifications and catalytic performance. Recent research has demonstrated that clay catalysts can facilitate a wide array of organic transformations, including addition, condensation, alkylation, rearrangement, isomerization, cyclization, ring-opening and closure, oxidation, hydrogenation, dehydrogenation, hydroboration, and protection-deprotection reactions [5,6].

III. STRUCTURAL AND PHYSICOCHEMICAL CHARACTERISTICS OF CLAYS

At the microscopic level, clay minerals consist of ultrathin crystalline aluminosilicate layers (~1.0 nm thick) interspersed with hydrated ions. These structures are broadly classified into two types:

1:1 Type (T-O Layers): Composed of one tetrahedral silica (Si–O) sheet bonded to one octahedral aluminum (Al–O) or magnesium (Mg–O) sheet.

2:1 Type (T-O-T Layers): Consists of one octahedral sheet sandwiched between two tetrahedral sheets via chemical bonds [7].

Interlayer spaces and T-O-T layers are held together by electrostatic and hydrogen-bonding forces. Isomorphous substitution of central metal ions (e.g., Mg for Al in octahedral sheets or Al for Si in tetrahedral sheets) generates negatively charged layers, necessitating the presence of compensatory cations within the interlayer space [8]. These cations, along with the negatively charged sites on broken layer edges, endow clay minerals with distinctive physicochemical properties, including high surface area, swelling capacity, ion exchange ability, and active M-O bonds. These characteristics make clay minerals highly suitable for adsorption and catalysis applications.

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The structural versatility of clays enables their transformation into various functional catalysts, including:

- Ion-Exchanged Catalysts
- Acid-Activated Clay Catalysts
- Intercalated Catalysts
- Pillared Interlayer Clay Catalysts
- Clay-Supported Catalysts
- Composites and Hybrids
- Hierarchically Structured Catalysts [9,10].

Clays function as solid acidic catalysts capable of exhibiting both Brønsted and Lewis acidity. Their submicron-sized particles (<2 mm diameter) yield extensive surface areas (\sim 23,000 cm²/g), allowing effective catalytic activity. Structurally, clays are crystalline hydrous aluminosilicates that also incorporate diverse cations. Based on their crystal structure and chemical composition, clays are classified into four primary groups:

- Illite
- Smectite
- Vermiculite
- Kaolinite

Among these, montmorillonite, a subgroup of smectite clays, is particularly valuable for catalytic applications due to its superior adsorption, swelling, and ion-exchange properties. Recent research underscores the potential of montmorillonite-based catalysts for a wide range of organic transformations, supporting the broader objective of green and sustainable chemistry.

Pillared Clays

Pillared clays have gained significant attention due to their enhanced catalytic and adsorption properties. Rightor et al. [34] successfully synthesized a series of CuO-supported Zr-pillared CeO₂-modified montmorillonite (MMT) catalysts, which demonstrated superior catalytic performance for the total oxidation of volatile organic compounds (VOCs) such as toluene, acetone, and ethyl acetate. The Ce–Zr/MMT support was identified as a crucial factor in enhancing VOC combustion efficiency.

Rachid et al. [35] explored sulfated zirconium montmorillonite-supported 1 wt.% palladium as an effective catalyst for hydroisomerization of light naphtha. The high activity and selectivity were attributed to the strength of acid sites and the hydrogenation ability of palladium, preventing hydrocarbon residues from blocking active sites. Similarly, Mishra et al. [36] investigated Zr-pillared clays with different pillar densities, starting from Ni²⁺-exchanged clay, and characterized them using XRD, TGA, IR, UV–VIS-DRS, and sorptometric studies. The acidity of these materials, determined via TG analysis of adsorbed n-butyl amine, correlated well with their alkylation activity. The catalysts demonstrated selective O- and C-alkylation of phenol with methanol, with lower pillar density favoring anisole production due to controlled acidity.

Bineesh et al. [7] synthesized titania- (Ti-PILC) and zirconia-pillared (Zr-PILC) clays, demonstrating their catalytic efficiency for the selective oxidation of H_2S to elemental sulfur. The superior performance was attributed to high surface area and the presence of Brønsted and Lewis acid sites. Ahmad et al. [8-9] examined Fischer-Tropsch (FT) synthesis over cobalt nanoparticles supported on modified Zr-pillared montmorillonite. Their findings indicated increased selectivity for C_2 - C_{12} hydrocarbons and reduced methane and higher molecular weight hydrocarbon production.

Further applications of pillared clays were explored by Kavitha and Sugunan [10], who synthesized zirconium pillared and rare-earth exchanged zirconium pillared montmorillonite for Friedel–Crafts benzylation. These catalysts, particularly at room temperature, exhibited high efficiency in catalyzing benzene benzylation with benzyl chloride. Similarly, Zhoua et al. [11] synthesized Fe- and Zr-pillared montmorillonites for Cr(VI) adsorption, demonstrating their potential in wastewater treatment.

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Palinko et al. [12-15] developed Fe, Al, and Cr, Al-mixed pillared clays and characterized them using mid- and far-FTIR and Mössbauer spectroscopy. Catrinescu et al. [13] further investigated AlFePILCs to correlate their catalytic properties with their active phases. Luo et al. [14-17] examined Fe-Al pillared clays for Fenton oxidation of phenol with hydrogen peroxide, analyzing factors affecting catalytic activity, induction periods, and reaction kinetics.

Bouchenafa-Saïb et al. [15-20] synthesized microporous chromium-aluminum pillared montmorillonite, demonstrating superior cadmium adsorption capacity. Yuan et al. [16] introduced iron pillared clays with a meso-microporous delaminated structure, providing novel insights for catalyst and adsorbent development. Choy et al. [17-21] synthesized chromia-pillared clay using Na-montmorillonite and trimeric chromium oxyformate, while Zhao et al. [18] prepared CrAl PILCs with enhanced thermal stability and acid site density.

Kurian et al. [19] explored the use of shape-selective iron pillared clays for Friedel–Crafts alkylations, emphasizing the role of surface acid sites in catalytic performance. Kar et al. [20] synthesized Cr-pillared montmorillonite (Cr-PM) for the solvent-free, microwave-assisted synthesis of octahydroxanthenes, highlighting its efficiency as a heterogeneous catalyst. Thomas et al. [21] investigated metal cation-exchanged montmorillonite (Ce³⁺, Fe³⁺, Al³⁺) for acetalization of carbonyl compounds under ambient conditions, outperforming conventional catalysts like Y-zeolites and γ -Al₂O₃.

Paranjape et al. [22] applied Fe³⁺-exchanged montmorillonite K10 in Friedel–Crafts acylation of arenes, demonstrating favorable yields with polymethylated benzene derivatives. Ellias and Sugunan [23] synthesized aluminum and ironaluminum pillared clays, incorporating cerium for enhanced phenol hydroxylation selectivity. Roulia et al. [24-30] developed chromium pillared clays with basal spacings of 2.45 nm, optimizing synthesis parameters such as pH, intercalation time, and chromium concentration. Zhou further detailed the role of clays and modified clays in a variety of organic transformations, including alkylation, oxidation, and cyclization reactions.[31-35]

IV. FUTURE PERSPECTIVES

The strategic design of clay-based catalysts is expected to play a crucial role in the catalytic conversion of biomassderived feedstocks. With the depletion of fossil fuels and increasing greenhouse gas emissions, sustainable catalytic processes for biofuels production, such as lignocellulosic biomass conversion, have gained prominence [52]. Drop-in hydrocarbon fuels derived from grass, wood, or algae biomass via liquefaction, pyrolysis, or gasification are anticipated to meet the growing energy demands.

Beyond biofuels, petrochemicals remain essential for manufacturing pharmaceuticals, plastics, and fine chemicals. The shift toward bio-derived feedstocks, such as lignocellulose [53,54], saccharides [55], lactic acid, and glycerol [56], necessitates the development of efficient catalysts. Clay-based catalysts offer promising solutions for these transformations, enabling eco-friendly chemical synthesis.

The catalytic potential of clay minerals extends to various organic reactions, including Friedel–Crafts alkylation, oxidation, and transacetalization. The use of solid acids over conventional homogeneous Lewis acids enhances reaction efficiency while minimizing environmental impact. Partial oxidation of hydrocarbons remains integral to pharmaceutical and agrochemical industries, while hydrogen peroxide-based catalytic systems continue to attract attention for oxidation reactions.

Glycerol, a byproduct of biodiesel production, represents a valuable renewable feedstock. Its valorization through transacetalization enables the production of fuel additives and surfactants, with methanol as the only byproduct. The growing interest in glycerol-based acetals and ketals underscores the relevance of clay-based catalysts in sustainable chemistry.

As heterogeneous catalysis evolves, interdisciplinary research will drive advancements in catalyst design, enabling cost-effective, high-purity production with reduced environmental hazards. Clay-based catalysts are poised to play a pivotal role in this transformation, offering sustainable and efficient solutions for the future of organic synthesis and industrial applications.

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