The Catalytic Potential of Modified Clays: A Review

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Abstract: The need for innovative catalysts and catalytic support materials is continually growing due to demanding requirements, stricter environmental demands, and the ongoing development of new chemical processes. Since about 80% of all industrial processes involve catalysts, there is a continuing need to develop new catalyst materials and supports with suitable qualities to meet ongoing industrial demands. Not only must new catalysts have tailored properties, but they must also be suitable for large-scale production through environmentally friendly and cost-effective processes. Clay minerals, with their rich history in medicine and ceramics, are now emerging as potential catalysts. Their transformative potential is exemplified in applications such as hydrogenating the greenhouse gas CO$_2$ into carbohydrate fuel, a crucial step in meeting the rising electrical demand. Moreover, advanced materials derived from clay minerals are proving their mettle in diverse photocatalytic reactions, from organic dye removal to pharmaceutical pollutant elimination and photocatalytic energy conversion through water splitting. Clay minerals in their natural state show a low catalytic activity, so to increase their reactivity, they must be activated. Depending on the requirements of a particular application, selecting an appropriate activation method for modifying a natural clay mineral is a critical consideration. Traditional clay mineral processing methods such as acid or alkaline treatment are used. Still, these have drawbacks such as high costs, long processing times, and the formation of hazardous by-products. Other activation processes, such as ultrasonication and mechanical activation routes, have been proposed to reduce the production of hazardous by-products. The main advantage of ultrasonication and microwave-assisted procedures is that they save time, whereas mechanochemical processing is simple and efficient. This short review focuses on modifying clay minerals using various new methods to create sophisticated and innovative new materials. Recent advances in catalytic reactions are specifically covered, including organic biogeochemical processes, photocatalytic processes, carbon nanotube synthesis, and energy conversion processes such as CO$_2$ hydrogenation and dry reforming of methane.

Keywords: clay minerals; activation; catalyst; photocatalyst; nanomaterial; CNT synthesis

1. Introduction

Clay minerals, as defined by the International Association for the Study of Clays and the Clay Minerals Society committees, are layered silicate minerals whose properties, such as flexibility and hardness, can be altered through dehydration or heating [1]. Based on their formation routes, clays can be divided into two groups: transported clay and residual clay. Rocks and shales undergo surface weathering to produce residual clays. Transported clays, also called sedimentary clays, have been eroded from their original location and deposited in a new, potentially distant location via fluid transportation. Clay minerals make up most soils and often consist of ultra-fine particles of <2 µm in size. In nature, clays occur in a wide variety of types and, being one of the most abundant natural minerals, clays and clay-derived products are utilized in many different applications such as building materials, medicines, environmental pollution adsorbents, catalysts, and catalyst supports for various chemical reactions. More than 80% of all manufacturing reactions require...
Minerals are known to display catalytic activity for hydrocarbon degradation, but there is an ongoing need to develop cheaper and environmentally friendly catalysts for many other synthetic reactions. The uniqueness, geological genesis, chemical composition, and crystal structure of the various clay minerals all have a significant impact on their applications. To understand basic differences in the physicochemical properties of clay minerals, it is necessary to consider their crystal structures and chemical compositions. Based on their layer type and interlayer species, clay minerals are divided into seven groups: kaolin-serpentine, pyrophyllite-talc, smectite, vermiculite, mica, chlorite, and mixed-layer (interstratified) clay minerals [2].

With the world’s population growth, energy demands are increasing exponentially. The generation of renewable energy is increasing only gradually, and at present, it provides only 25% of electricity generation, with the remainder coming from fossil fuel combustion. Coal combustion produces more than 60% of the greenhouse gas CO₂ in the atmosphere [3]. For this reason, sustainable energy production demands an efficient and environmentally friendly method of producing electrical energy. CO₂ hydrogenation is one of the methods for addressing the increasing demand for electrical energy and the environmental problem of CO₂. This technology captures CO₂ from the atmosphere and converts it to hydrocarbon fuels such as CH₄, ethanol, and CₓHᵧ [4]. However, CO₂ reduction is a thermodynamically unfavorable reaction that requires a catalyst. Instead of expensive noble metal catalysts, naturally abundant, eco-friendly clay mineral-based catalysts are excellent alternatives for these reactions [5,6]. Another major issue in today’s world is the environmental pollution caused by industrial wastes such as organic pollutants from textile factories or pharmaceutical manufacturers [7]. Pollutant degradation and energy conversion processes, such as water splitting, necessitate efficient photocatalysts. However, pure metal oxides such as titanium dioxide and zinc oxide, which are typically used to catalyze these reactions, have drawbacks, including cost and high demand due to their increased use in a range of other applications [8]. Numerous studies are currently being conducted on using clay mineral composites with commonly used metal oxides as catalysts for photocatalytic reactions.

Many new discoveries and advances are being made in science and technology. Carbon nanotubes (CNTs) and their alternatives, such as carbon nanospheres, carbon black nanoparticles, graphite, graphene oxide, and their composites, are examples of these new materials. These carbon-based materials are versatile due to their high surface area, unique morphology, and good thermal conductivity [9,10]. To meet the demand for these materials, an efficient and cost-effective catalyst is needed for their synthesis. Clay mineral-based catalysts and catalyst supports have recently received attention for the synthesis of nanocarbon materials [11,12]. In contrast to the use of clay minerals in photocatalytic reactions, their use in the synthesis of CNTs has the advantage of being able to be used without additional admixtures.

Although there are numerous publications on the catalytic activity of clay minerals, there is a lack of a clear and comprehensive review of their use in advanced catalytic reactions such as photocatalysis, CO₂ conversion, and CNT synthesis. This short review gathers fundamental data on natural clay minerals and their unique physicochemical properties, as well as the pros and cons of their activation and modification to create new materials. This review also covers the role of clay-derived catalysts’ roles and the parameters that affect their catalytic activity in a number of reactions including energy conversion reactions, photocatalytic reactions, and the synthesis of carbon nanotubes.

2. Clay Mineral Properties
2.1. Genesis and Classification of Clay Minerals

The formation of the vast majority of clay minerals requires the interaction of rocks with fluids, gases, or steam. Molten rocks and weathered rocks on a hillside are examples of these, as are the sediments at the bottom of lakes and oceans. The most typical sedimentary rock is shale, which is principally formed from clay. Silicate-containing rocks undergo lengthy chemical weathering to form clay minerals. The research has provided a complete
list of the most significant and common clay minerals based on their genesis [13]. According to their data:

- Micaceous minerals such as illite are typically obtained from parent rocks or other substances that are formed under pressure/temperature conditions other than those found on the Earth’s surface.
- Smectite formation in soils is facilitated by a number of environmental factors, including but not limited to the presence of parent rocks rich in bases, poor drainage, low-lying terrain, an alkaline pH, high silica activity, and an abundance of alkali cations.
- Vermiculite is created when micas, primarily biotite (trioctahedral vermiculite) or muscovite, are weathered, which releases interlayer K\(^{+}\) and oxidizes structural Fe\(^{2+}\). Chlorite is a common inherited clay mineral found in soils and weathered crusts that readily transform into vermiculite or interstratified chlorite–vermiculite. Another diagenetic method for chlorite formation intercalates aluminum hydroxides into a smectite, vermiculite, or interstratified minerals.
- Kaolinite is a mineral found in soils that can be newly formed, modified, or inherited. Rainy and well-drained conditions assist its formation. Halloysite is a mineral that is commonly found in weathered crusts on acidic volcanic rocks. Fibrous clay minerals such as palygorskite and sepiolite are more likely found in fossil soils than in topsoil. Thus, weathering and biogeochemical reactions in nature can convert most clay minerals into each other.

Because of the similarities in clay crystal structures, these are complex systems; for this reason, it is critical to understand their categorization based on their crystal structures. A helpful nomenclature and distinctions between the various clay minerals are outlined in Figure 1, based on a revised classification of clay minerals from the literature [2]. Figure 1 summarizes the structure type, crystallinity, lattice properties, and dimensional variations between various clay minerals.

![Figure 1. Classification of clay minerals based on their crystallinity.](image-url)

Clay minerals comprise tetrahedrally coordinated cations (Si\(^{4+}\), Al\(^{3+}\), Fe\(^{3+}\)) and octahedrally coordinated cations (Al\(^{3+}\), Fe\(^{3+}\), Fe\(^{2+}\), Mg\(^{2+}\)). These cations are arranged in sheets or chains. The fundamental structural components of layer silicates are sheets of silica and sheets of brucite or gibbsite. Figure 2 shows the basic building units of the crystal structures of the clay minerals, in which a hexagonal network is formed by SiO\(_4\)^{2-} tetrahedra that are joined at three corners in the same plane. The apices of the tetrahedra all point in the same direction. The brucite or gibbsite sheet is formed from a plane of magnesium or aluminum ions, which are octahedrally linked by two planes of hydroxyl ions. The term “octahedral sheet” refers to this component. By combining these sheets, two-thirds of the hydroxyls are replaced by oxygens at the corners of the tetrahedra that stretch into the hydroxyl
plane in the octahedral sheet, creating a layer structure from these combined sheets [14,15]. Clay minerals of type 1:1 consist of tetrahedral and octahedral sheets with a thickness of about 7Å. Clays with a 2:1 structure have two tetrahedral silica sheets enclosing an octahedral sheet, resulting in a thickness of about 10Å. The most common 1:1 clay minerals include kaolinite, serpentine, saponite, chamosite, greenalite, amesite, and cronstedtite. All the kaolinite minerals are hydrous aluminum silicates. Replacing two-thirds of the properties of the mineral, and the choice of a suitable processing method depends on providing a sufficient layer charge to cause shrinkage and the creation of biotite mica or the smectite. Unlike the high-Fe²⁺ clays, all the rich-Mg clays have a 2:1 structure, possibly due to the difficulty of the two silica sheets in accommodating a sizable Fe-octahedral layer. A considerable degree of aluminum replacement is required to adjust the single silica layer of 1:1 clay to the large octahedral sheet. This is mitigated in the 1:1 clay by exchanging Al³⁺ for Fe³⁺ in the octahedral sheet. It is likely that the silica sheets in a 2:1 iron-rich clay would have sufficient aluminum substitution to adjust to the size of the octahedral sheet, providing a sufficient layer charge to cause shrinkage and the creation of biotite mica or the attachment of a positively charged brucite sheet to form chlorite.

Figure 2. Schematic illustration of tetrahedral/octahedral unit cell structures of the major clay minerals.

2.2. Chemical Composition and Physico-Chemical Properties

Since the composition of the parent rock and climate affects the formation of a clay mineral, the chemical composition of the clay is influenced by local weather patterns and local geological features. Being a phyllosilicate mineral, clay primarily contains silica, which accounts for about 50% of its weight, together with aluminum (10–30% by weight), potassium, calcium, and magnesium (1–10%). The remaining trace elements may include copper (Cu), zinc (Zn), rubidium (Rb), selenium (Se), strontium (Sr), molybdenum (Mo), manganese (Mn), lead (Pb), arsenic (As), and cadmium (Cd). Table 1 is compiled from information from the literature on the principal chemical elements of several natural clay minerals. The ratio of Si:Al plays an essential role in determining the physicochemical properties of the mineral, and the choice of a suitable processing method depends on this ratio. This is because silica dissolution occurs mostly under alkaline conditions, and aluminum dissolution occurs in acidic media (although aluminum also dissolves in alkaline media to a lesser degree). In addition, consideration must be given when selecting an appropriate method for activating and modifying a particular clay mineral to the nature of the desired product and the removal of impurities such as Fe, Mg, Ca, and Ti.
Table 1. Typical chemical composition of clay minerals.

<table>
<thead>
<tr>
<th>Mineral Name</th>
<th>SiO2</th>
<th>Al₂O₃</th>
<th>Fe₂O₃</th>
<th>MgO</th>
<th>K₂O</th>
<th>CaO</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Kaolin</td>
<td>49.0</td>
<td>37.0</td>
<td>0.4</td>
<td>0.2</td>
<td>1</td>
<td>0.1</td>
<td>[16]</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>63.2</td>
<td>16.2</td>
<td>5.98</td>
<td>3.67</td>
<td>0.25</td>
<td>5.29</td>
<td>[17]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>46.84</td>
<td>38.32</td>
<td>1.16</td>
<td>0.14</td>
<td>0.39</td>
<td>0.16</td>
<td>[18]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>47.97</td>
<td>34.74</td>
<td>1.46</td>
<td>0.14</td>
<td>0.08</td>
<td>0.16</td>
<td>[19]</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>55.76</td>
<td>32.02</td>
<td>0.03</td>
<td>0.14</td>
<td>0.24</td>
<td>-</td>
<td>[20]</td>
</tr>
<tr>
<td>Phlogopite</td>
<td>38.4 (atm. %)</td>
<td>14.5 (atm. %)</td>
<td>3.5 (atm. %)</td>
<td>33.4 (atm. %)</td>
<td>10.2 (atm. %)</td>
<td>-</td>
<td>[21]</td>
</tr>
<tr>
<td>Serpentine</td>
<td>51.00</td>
<td>0.38</td>
<td>0.38</td>
<td>47.32</td>
<td>-</td>
<td>0.92</td>
<td>[22]</td>
</tr>
<tr>
<td>Bentonite</td>
<td>61.0</td>
<td>17.1</td>
<td>1.6</td>
<td>6.6</td>
<td>0.07</td>
<td>4.4</td>
<td>[23]</td>
</tr>
<tr>
<td>Montmorillonite</td>
<td>65.0</td>
<td>21.5</td>
<td>-</td>
<td>3.0</td>
<td>-</td>
<td>-</td>
<td>[24]</td>
</tr>
</tbody>
</table>

Typically, soil clay is defined as having a particle size of <2 µm, providing plasticity in water. Clays are differentiated from other fine-grained soils in terms of their particle size and mineral composition, although many natural deposits contain both silts and clays. The cation exchange capability and strong chemical stability of natural clay minerals make them hydrophilic. On the other hand, 2:1 trioctahedral or dioctahedral minerals such as talc and pyrophyllite show hydrophobic properties by virtue of the unsubstituted nature of their tetrahedral layers. Since they also have electronegative surface features and cation exchangeability [25], natural clay minerals are efficient adsorbents for removing heavy-metal cations and many other positively charged organic contaminants.

### 3. Activation and Modification Methods

In general, the potential applications of clay minerals are influenced by their elemental composition and surface characteristics. In addition to using clay minerals in their native form, activation and modification techniques have been developed for various applications since the latter part of the last century. Activation of the clay surfaces through mechanical, chemical, and/or thermal treatment or a combination of these can be used to alter the clay surface characteristics. Acid activation and mechanochemical activation are the most widely used techniques for this purpose due to their low cost and excellent effectiveness. Acid activation has been used for many years to produce bleaching earth for decolorizing various types of oils [26]. Modern approaches such as microwave and ultrasound treatments are now being developed. The following is a summary of the techniques that have proved effective for modifying and activating clay minerals to create useful advanced materials. Figure 3 illustrates the benefits of commonly used methods for clay mineral activation and modification.

![Figure 3. Clay mineral activation and modification processes and their advantages.](image-url)
3.1. Acid Activation

In the acid activation process, clay minerals are reacted with a mineral acid solution, typically hydrochloric or sulfuric acid and, to a lesser extent, nitric acid \[27\], to partially dissolve their octahedral layer, increasing their specific surface area, porosity, and surface acidity. In addition, acid treatment forms partially coordinated Al\(^{3+}\) species, which create Brønsted acid sites, and cation exchange of the alkaline or alkaline-earth cations by H\(^+\) in the interlayer regions increases the number of acid sites. The research was conducted on the acid dissolution of the three non-swelling minerals: kaolin, sepiolite, and illite \[28\]. The dissolution sequence of the octahedral cations was reported to be Mg > Fe > Al, and the dioctahedral clay minerals exhibited a greater resistance to acid attack than the trioctahedral clay minerals. The release of octahedral cations resulted in a lighter material, the formation of micropores, and an increase in the specific surface area. Further research on the acid activation of swelling clay minerals by \[29\] indicated that the chemical composition and initial crystallite size determined the diversity of the clay mineral structures. The octahedral sheets were destroyed by acid through an attack on their interlayers and edges. The degree of Mg or Fe substitution in the octahedral sheets helped to break down these layers and produce a silica-rich phase. In contrast with the swelling smectites and vermiculites, it is interesting that the dissolution and breakup of the particles of non-swelling clays required longer reaction periods. Strong acid treatment resulted in a significant increase in pore volume and a widening of the pore size distribution \[25,30\]. Acid treatment does not always result in improvement of the properties; acid-treated Na-montmorillonite, palygorskite, and kaolinite all inhibited the decomposition of C\(_x\)H\(_y\) via various pathways, whereas untreated saponite had no effect on the reaction \[31\]. The same group of researchers conducted another study on HCl-treated clays, including kaolinite, palygorskite, saponite, and montmorillonite, and compared the behavior of these clays towards the removal of polycyclic aromatic hydrocarbons (PAH) during biodegradation in microcosm testing with the performance of the clays unmodified with acid \[32\]. The acid-activated clays and unmodified kaolinite were less effective in the biodegradation of the PAHs than the unmodified clays. Another study tracked changes in the layer charge that had undergone acid treatment \[33\]. A decrease in the CEC (cation exchange capacity) following the acid attack corroborated the findings that all the studied systems exhibited a decrease in the layer charge. The authors \[34\] demonstrated that the 5M sulfuric acid activated bentonite clay’s catalytic properties and remarkably enhanced diester preparation using succinic acid and ethanol. The acid-leached bentonite showed a high activity with, 63% of the conversion of succinic acid at yield (73%) and selectivity. The cost of acid-treated bentonite was $400/t, which confirms an economically viable and environmentally benign porous catalyst preparation procedure.

In summary, while acid-activated clay minerals offer potential improvements in specific properties, the direct and universally positive impact on practical applications remains contentious. The correlation between structural alterations induced by acid treatment and their applicability in various industrial or environmental scenarios warrants further critical examination and clarification.

3.2. Alkali Activation

Although alkali activation of clay minerals is less frequently used than acid activation, it offers the benefit of generating fewer byproducts and less acidic waste. It is crucial to understand the structural alterations of clays following alkali activation. Akali-activated clay minerals, also called geopolymers, are commonly used as building and construction materials \[35–37\]. Alkali activation of montmorillonite and illite was reported in the literature \[38\] and confirms the potential use of alkali-activated clay minerals as cement stabilizers for building materials such as those used in walls. This geopolymer is produced as a primary product of alkali activation of uncalcined montmorillonite; its amount increases with increasing molar ratios of sodium to aluminum in the system. To gain a better understanding of how alkali activation affects the structure and chemical composition of
clay minerals and their use in advanced applications such as catalysis and water treatment, it is necessary to conduct research on their structural characterization, optimal setting conditions, and changes in their surface properties as in the following recent studies.

Phase formation in alkali-activated mixtures of the common clay minerals kaolinite, montmorillonite, and illite was investigated in the literature [39], where researchers compared the behavior the clay mixtures with those of the individual clays. To establish a connection between the behavior of the individual clays and complex soil systems, this study adopted a methodical approach, finding that in terms of reactivity, montmorillonite dominated the entire kaolinite–montmorillonite series, whereas kaolinite determined the phase formation in these systems. In the case of phase formation in the montmorillonite–illite series, it was concluded that montmorillonite predominated over illite. In the illite–kaolinite series, both reactivity and phase formation were controlled by kaolinite rather than illite.

The structural changes due to alkali activation of calcined kaolin and illite clay are described in reference [40]. Alkali-activated binders based on metakaolin containing up to 55.9% reactive components have an amorphous structure reflecting the changes (restructuring) of the metakaolin under saturated alkaline conditions. Unlike kaolin-based binders, illite-based binders have 2.5 times fewer reactive components and a less distinct amorphous configuration. It is possible to generate an alkali-activated binder with a high OH-ion leaching rate by incorporating a glass additive into the mix, and this alkali-activated material can be used for passive pH fixation in wastewater treatment processes that ideally operate in the pH range of 9 to 11. A unique nanotubular-structured halloysite was formed, and it was reported by the authors [41] that pre-heating at 650 °C–850 °C could tune the crystal structure and improve the mechanical characteristics of the geopolymer product. Thermal treatment increases the alkali activation efficiency of phlogopite [42]. After thermal treatment, their most soluble phlogopite sample released 45% Si and 33% Al into the solution, which was significant compared to the highly soluble metakaolin (26% Si and 40% Al). Various acid and alkaline leaching of clay minerals and their mechanical treatment for the preparation of various nanoporous and composite materials for advanced applications were published in a review paper [43]. The studies focused on the chemical leaching of clay minerals and their utilization as templates for further applications. One such important paper studied the preparation of γ-alumina with a uniform pore size distribution via KOH leaching of calcined kaolin minerals. The resulting product showed a high thermal stability and good catalytic properties [44]. The chemical composition of the clay used in the alkali activation process and the potential uses of the resulting product in water purification systems was significant [45].

In addition to their traditional use as building materials, alkali-activated clays may also have applications in cutting-edge applications such as adsorbents for water treatment.

3.3. Mechanochemical Activation

Mechanical activation is a versatile tool for chemical transformations ranging from polymorph transitions to solid-state reactions [46] and is now attracting more interest because of the potential for the synthesis of a new compound and improved reactivity through green chemistry without solvents [47].

Clays of the 2:1 type, such as talc and pyrophyllite, have structures in which the oxygen atoms reside only in the spaces between their octahedral layers, resulting in relatively low cation-exchange capacities. They thus exhibit hydrophobic properties and very slow leaching characteristics. Leaching of talc for 14 days by 2M H₂SO₄ at 150 °C produced flaky particles with a SiO₂ content of 91% and a specific surface area of <40 m²/g [48]. For this reason, it is necessary to choose a different method for modifying the surface of an unsubstituted 2:1 clay mineral. Mechanochemical activation is a method that can be used in many chemical synthesis processes due to its simplicity and efficiency in increasing a system’s chemical and physical energy in one step. The milling environment, material
properties, grain size, and total system viscosity all have an impact on the effectiveness of mechanochemical activation.

The mechanochemical consistency of trioctahedral clays (hectorites and saponite) and dioctahedral clays (montmorillonites) was investigated using a short-time high-energy grinding method [49]. In general, trioctahedral clays are amorphized and dehydroxylated more readily than dioctahedral smectites under these conditions. It is essential to note that the use of mechanical activation to increase the efficiency of clay minerals in further applications is dependent on their crystal structure. The effects on the production of cordierite due to amorphization brought about by milling composites of talc, clay, and gibbsite using different milling parameters (milling, calcination, amorphization) have been studied [50]. The destruction of the crystalline phases and enhancement in reactivity that occurred during milling facilitated the formation of the cordierite minerals. Cordierite was the steady-state phase formed when the mixture was calcined at lower temperatures (900–1200 °C). According to an FTIR study [51], the hydroxyls in the kaolinite structure were depleted after 10 h of grinding. The most important finding was that the kaolinite crystals could be tuned using dry mechanical milling without the use of a solvent.

Some authors determined that mechanically induced amorphization of the kaolinite structure is accelerated by a higher concentration of quartz impurity because of the high hardness of quartz, which could act as the milling medium [51]. The author of [52] studied methods for mechanically activating kaolins during intense grinding (supergrinding). Disintegration, aggregation, and agglomeration caused the kaolin powders to alter their morphological features. Disintegration dominates short-term activation, while aggregation, and agglomeration determine long-term activation. After grinding, dispersity initially reduces, and kaolin–water elasticity declines. It has been shown that a highly defective kaolinite can be produced through mechanochemical processing [53], which also decreases the dehydroxylation temperature and increases the amount of adsorbed/coordinate water. An increase in the grinding time increases the dehydration temperature. The authors of [54] studied mechanically activated Tsagaan-tsav (Mongolian) zeolite and found that after grinding for 2–20 min, the amorphous structure of the raw zeolite was increased, together with a corresponding increase in its cation exchange capacity. A similar study on kaolinite showed that mechanical milling can increase its degree of amorphization and change its plate morphology [55,56]. Talc has also been subjected to mechanical activation to alter its surface hydrophobicity and structural distortion. Mechanical milling prior to acid activation has been found to increase the surface area and porosity of talc and a pyrophyllite-based porous material [57,58]. Kameda and Owari have observed mechanoradical formation on activated kaolinite powders via wet-grinding in ethanol using a free-radical scavenger (2,2-diphenyl-1-picrylhydrazyl; DPPH) [59]. Such active mechanoradicals on the kaolinite surface could lead to industrial applications for preparing nanocomposite and powder surface functionalization.

A unique copper removal technique has been reported by the authors of [60], in which the hydrated magnesium silicate serpentine was mechanically activated, increasing its reactivity to that of Mg hydroxide and thereby enabling it to extract Cu (II) from wastewater. In another study carried out by the authors of [61], phlogopite, a trioctahedral mica, was activated via solvent-free ball milling, allowing its direct use as a slow-release potassium fertilizer. The precipitation of cesium as struvite via a new process that uses an insoluble magnesium source (CsMgPO₄·6H₂O) has been reported by the authors of [62]. With only basic agitation at an ambient temperature, a mixture of phosphoric acid and activated antigorite (Mg₃Si₂O₅(OH)₄) was mixed with cesium chloride to form struvite in a nearly stoichiometric ratio. Since other alkali metals such as K and Na do not form stable struvite phases but remain in solution, it is intriguing that by comparison, cesium is removed with a very high selectivity. The adsorption of fluoride by activated kaolinite clay has been reported by the author of [63], who found that the surface area of the clay was doubled after mechanochemical activation. In order to find the best equilibration conditions, these authors performed batch adsorption studies on raw and activated kaolinites.
A combination of two mechanical milling and acid treatments was used by the authors of [64] to study mechanochemically activated kaolinites with both moderate and severe defects, followed by treatment with sulfuric acid. The disordered and adequately deformed phases in the mechanochemically amorphized samples reacted with sulfuric acid, and the specific surface areas of the leached samples of the partly or completely amorphized materials were found to be higher than those of the thermally amorphized samples. In the partially amorphized materials, as opposed to completely amorphized samples, the acid treatment increased the total pore volume. A more complete study on mechanochemically assisted acid activation of 1:1 and 2:1-structured clay minerals has been performed by the authors who previously reported that mechanochemical treatment destroys the template-type structure of the clay minerals and is not beneficial for a uniform pore size distribution of the resulting silica [55,65]. A more detailed description of nanoporous material preparation via acid and alkaline leaching of raw, thermally, or mechanically treated various clay minerals was reported and concluded in the references [43,66]:

- Thermally amorphized kaolinite favours mechanically treated kaolinite in terms of its high surface area;
- It is necessary to destroy the layer-lattice structure of non-substituted 2:1 clay minerals (talc, pyrophyllite) for successful acid activation;
- Acid leaching of the 2:1 layer lattice initially removes interlayer cations, followed by octahedral cations;
- With acid leaching of 2:1 lattice clay minerals form 2 types of pores, a smaller slit shape formed between tetrahedral sheets, and a larger framework structure was formed via the polycondensation of slit-shaped pores or the polycondensation of porous structures.
- The structural composition of the 2:1 lattice clay minerals controls the porous properties of the materials formed via acid leaching of the 2:1 layer lattice of the clay minerals.

3.4. Microwave and Ultrasound-Assisted Activation

Ultrasound and microwave-assisted modifications have the advantage of being easier and making it faster to obtain the required products than using traditional techniques. The authors of [67] studied the activation of smectite clay using microwave (MW) irradiation and “traditional or conventional” heating. This study showed that although both conventional heating and microwave irradiation produced small pores in the prepared materials, conventional activation required about 8 h to complete, whereas microwave irradiation only required 20 min at 500 W of power to produce a highly porous structure. The authors of [68] compared the surface acidity of montmorillonite exposed to a conventional hydrothermal acid treatment with ultrasonic and microwave-assisted acid digestion. This semi-quantitative study assessed the Brønsted acidity produced via acid digestion and found that hydrothermal, ultrasonic, and microwave-assisted acid digestion all produced robust Brønsted acid sites. An interesting study carried out by the authors of [69] suggested that clay minerals might be activated without a solvent utilizing ultrasoundsonication. This work investigated the intercalation of a low-molecular-weight poly (ethylene glycol) with a montmorillonite-type Anatolian clay soil to create a new type of organoclay with outstanding thermal characteristics. This suggests that ultrasound sonication in a solvent-free environment is a potential method for intercalating montmorillonite using environmentally benign polyethylene glycol with excellent biocompatibility during the synthesis of organoclays.

Thus, combining conventional techniques such as microwave and acid treatment seems feasible. Interesting research by the authors of [70] was carried out on the effects of microwave-assisted acid treatment on the configuration and composition of kerolitic clays, sepiolites, and dioctahedral (montmorillonite) and trioctahedral (saponite) smectites. This showed that in the case of the smectites, the chemical composition of the octahedral sheet has a significant impact on the effectiveness of the process, whereas in kerolitic clays, it is the amount of the upgradeable phase in the mixed-layer series that is important. By
contrast, it is the diameter of the natural fibers that controls the reactivity of sepiolites. Microwave-assisted acid treatment produces a large increase in the specific surface area within 16 min.

4. Catalytic Activity

4.1. Naturally Occurring Catalysts for Organic Reactions

Clays can be used directly in their natural form, without modification or special equipment, to catalyze many reactions, including modifying the hydrocarbon constitution of crude oils, heavy oil degradation, petroleum cracking, decarboxylation of fatty acids, diamondoid formation, kerogen degradation, and alkane cracking. According to the authors of [71], clay minerals are crucial due to their chemical activity and widespread availability. Clay minerals, in their natural state, form an adsorbed phase with a variable number of layers of water molecules and polar organic molecules. This phase is capable of undergoing a wide variety of chemical transformations that may be catalyzed by surface constituents as well as adsorbed water. To better understand the actual geological processes occurring in nature, some interesting research has been conducted under simulated laboratory conditions. The authors of [72] investigated the effects of the catalyst, activation period, catalyst loading, and thermal effects on a variety of products formed via mineral-catalyzed reactions of isoprenoid hydrocarbons under geological conditions. The purpose of this work was to gain a better understanding of the various resulting products. It would be beneficial to improve our understanding of the role of clay catalysts in converting organic matter in nature if more simulation studies of this type were made. The catalytic properties of the clay minerals, namely cationic or anionic clay minerals, are of interest to catalyst scientists [73]. In addition to the crystalline structure, the clay minerals, due to their chemical properties, can also be grouped as cationic clays, which are very common in nature, or anionic clays, which are rare in nature. Therefore, they can be synthesized easily in laboratory conditions, and their cost of synthesis is relatively low.

One of the most comprehensive descriptions of clay minerals as catalysts is shown by the authors of [74]. The origin of catalytic activity is explained in terms of the following factors:

- Size effects caused by size such as a high specific surface area, chemical nature, low dimensionality, and increased local concentration of reactants;
- The acidic nature of the original or acid-activated clays, which causes structural characteristics imparting activity;
- A pillared structure is usually formed via the intercalation of other cations or larger molecules between the clay layers, which also influences the shape/size selectivity;
- In addition to the organic reactions, the clay minerals can also catalyze inorganic reactions by acting as a base catalyst by removing protons from the solution;
- Since clay minerals show a high specific surface area with various active sites, they can act as supports for reagents and co-catalysts. For this type of research, supporting and keeping the active surface of clay minerals with a surface modifier such as 3-aminopropyl triethoxysilane is becoming an interesting topic.

A comprehensive review describes the application of clay-supported metal oxide nanoparticles in advanced oxidation processes (AOPs) [75]. AOPs are applied for catalytic oxidation, catalytic wet peroxidation, photocatalysis, and photooxidation, and they have demonstrated a high efficiency in the removal of recalcitrant compounds from pollutants. The authors stressed the lower cost of clay-supported catalysis compared to other inorganic support materials and the importance of their utilization at an industrial scale, with a clear aim to reduce the water requirements for their synthesis.

The authors of [76] described that hydrocarbon generation and migration may occur during illite and smectite diagenesis due to catalytically active diagenetic illite, a fluid release mechanism, and geo-pressure development. The presence of illite with a high surface area in reservoir sandstones may indicate chemical modifications of crude oil. Since the composition of clay, including its exchangeable cations, influences its catalytic
properties, reaction mechanisms, and formation pathways, these factors must be considered when assessing clay catalysts for the generation of hydrocarbons.

The catalytic impact of montmorillonite and calcite was investigated on oil breakdown in closed combustion systems [77]. In addition to measuring the thermodynamic parameters, these researchers measured the chemical constituents of gaseous hydrocarbons and the isotopic ratios of carbon. The authors of [78] investigated the role of minerals in the thermal cracking of heavy oil in water. Their findings demonstrated that the process is accelerated by the presence of clay minerals, which also reduced the viscosity and molecular weight of the oil. The authors of [79] used DFT (density-functional theory) simulations to study how the model fatty acid propionic acid (C_2H_5COOH) converts into an alkane (C_2H_6) in the presence of pyrophillite with isomorphic aluminum substitution. These results demonstrated that an electrically neutral structure with a sodium counterion best catalyzes the decarboxylation of Al-doped pyrophillite. The authors of [80] evaluated the catalytic impact of montmorillonite, aluminosilicate, kaolinite, and illite on the decomposition of kerogens by reacting them at 340 °C for 72 h under anhydrous and hydrous pyrolysis conditions. When the ratio of minerals to kerogen is 15:1, thermal degradation slows due to the mineral surfaces being saturated with organic precursors, decreasing the yield of diamondoids.

4.2. CO₂ Conversion Catalysts

As stated in the introduction, energy consumption is increasing, requiring the development of environmentally friendly and efficient electrical energy production methods. CO₂, one of the most abundant air contaminants, could be exploited as a precursor/source for fuel production via the CO₂ hydrogenation process. The use of CO₂ as a starting compound for the synthesis of important chemicals, especially cyclic carbonates, has been extensively researched to mitigate greenhouse gas emissions. A benefit of using clay minerals for CO₂ conversion processes is their ability to adsorb and capture carbon dioxide at ambient pressures and temperatures [5].

Methane dry reforming (MDR) involves the reaction of two important greenhouse gases, methane and carbon dioxide, to form syngas (a mixture of CO + H₂). This is a resource for high-added-value products such as long-chain hydrocarbons produced via the Fischer–Tropsch reaction or oxygenated chemicals such as acetic acid. MDR is highly endothermic (ΔH° 298 K = +247 kJ·mol⁻¹) and is therefore thermodynamically favorable only at high temperatures. As a potential CO₂ conversion catalyst, the nickel-bearing phyllosilicate clay minerals hydrotalcite, laterite, and attapulgite are of significant interest to many researchers. The authors of [5] reported that a nickel and magnesium-containing hydrotalcite clay was an efficient, cost-effective catalyst that was competitive with conventional commercial nickel-bearing catalysts for the conversion of carbon dioxide to methane at 860–890 °C. Furthermore, the stability of the clay-based catalyst exceeded that of the commercial catalyst. Previous authors investigated the catalytic performance of a nickel-bearing one-dimensional nanomaterial produced from natural nickel lateritic ores from Niquelândia (Brazil) and used this catalyst in the methane dry-reforming process at 800 °C [81]. These authors studied the effects of the position of the nickel in the structure of the clay, both without treatment (Ni in octahedral sites) and in a clay treated with Na and exchanged with Ni (Ni in the exchange sites). The results indicated that the natural clay produced syngas with a reasonable yield and minimal deactivation without pretreatment. The tests conducted on the exchanged clay fractions confirmed a very strong effect of the reduction temperature of the catalysts. After reduction at 700 °C, the Na-Ni-clay was inactive towards H₂ production, but pre-reduction at 500 °C maximized its catalytic efficiency. At lower temperatures, the presence of Ni in structural and exchange positions is beneficial. Reduction at 700 °C produced large Fe-Ni-containing particles that were highly inactive in the dry-reforming reaction and favored H₂ utilization via the methanation of carbon dioxide or the RWGS (reverse water gas shift) reaction. Like the previous authors, using the Tunisian natural clay minerals for dry reforming methane using a Ni catalyst is
systematically studied by the authors of [82–84] while changing support elements and dry-reforming temperatures. The main conclusions drawn from their research are as follows:

- Ceria or zirconia modification of Cu or Fe-pillared clays increased the number of medium and weak basic sites, which favors CO₂ adsorption and desorption on the catalyst surface, leading to enhanced catalytic activity.
- The catalysts prepared using the Cu-modified clay yielded the highest CO₂ and methane conversions every time.
- La, Al, and Mn promoters resulted in smaller Ni⁰ crystallite sizes and further promoted Ni dispersion for the Fe-modified clay-supported Ni catalyst. Al showed better Ni reducibility in comparison to La and Mn-promoted catalysts.
- The moderate temperature reduction of the Fe and Cu-modified natural clay-supported Ni catalyst contained larger crystals of Ni than that reduced at higher temperatures, thus enhancing its catalytic activity.

Figure 4 shows the catalytic reaction mechanism for these Ni/Mg phyllosilicates with a 23 wt.% Ni content. Attapulgite is another potentially useful clay mineral catalyst for the CO₂ conversion process.

![Figure 4](image_url)

**Figure 4.** Schematic diagram of the CO₂ dry-reforming methanation reaction using a Ni-bearing clay mineral catalyst. Reproduced with the permission of Elsevier from reference [81].

A study on nanomaterials derived from attapulgite showing their potential as a low-cost, abundant resource for CO₂ capture and conversion is performed in reference [85]. The facile production of an efficient catalyst from silver-doped attapulgite for the synthesis of non-symmetric carbonate was reported by the authors of [86]. Another study of a nickel-bearing catalyst reported improved catalytic activity by adding Ce to a clay mineral and applying microwave energy to synthesize the modified catalyst [87]. Increasing amounts of Ce from 3–10 wt.% improved both the degree of conversion and the catalytic selectivity. These authors reported that an increase in the Ce content of the clay catalyst improved its catalytic performance. Instead of using a natural mineral as a catalyst, [6] reported the synthesis of Ni-containing 1:1 and 2:1 phyllosilicates and tested their catalytic performance for CO₂ conversion. This study’s important finding is that dry reforming and RWGS occur simultaneously. Due to the reaction between H₂ and CO₂, carbon dioxide conversion is greater than methane conversion. This type of research into the development of synthetic clay catalysts is equally as important as the use of natural minerals which require time-consuming purification. Natural 2:1-structured clay minerals with swelling properties, such as vermiculite and montmorillonite, are often used as catalytic support materials [88,89]. Therefore, it can be suggested that the swelling properties of the clay minerals, which
ease the pillaring structure, are one of the main requirements for their application as catalyst supports.

4.3. Light-Driven Catalysts

The authors published an excellent review article on light-driven catalysts (light-driven C1 transformation) [90]. Although the authors did not give special attention to the choice of catalyst support materials, many of them were based on natural or synthesized clay-type hydrotalcite minerals such as LDH (layered double hydroxides).

4.3.1. Photocatalysts

The word “photocatalyst” comes from the words “photo,” meaning “light,” and “catalyst,” meaning “to hasten or retard” chemical reactions. Therefore, photocatalysts are substances that, when exposed to light, speed up chemical reactions [91]. In 1972, the authors published the idea of photocatalysis by investigating the electrochemical photolysis of water using a semiconductor electrode [92]. This investigation led to the development of this concept. More often than not, photocatalysts are semiconductors. There are two distinct types of photocatalysts, distinguished by the type of light source being used to excite electrons and form electron–hole pairs; these are UV light photocatalysts and visible light photocatalysts [93]. UV light photocatalysts are a well-known industry, but they require energy to create artificial UV light for the reaction. On the other hand, visible light photocatalysts have been attracting increased attention lately, since they can be used with no light source other than sunlight, making them applicable to real-life situations.

Metal oxides such as titanium, iron, zinc, and manganese are extensively used as photochemical catalysts. These generally have a band gap energy of 2–4 eV and can be used in either UV or visible light-assisted processes. Although metal oxides can catalyze most photochemical processes, they are constrained by low surface areas and high manufacturing costs. However, clay minerals, which are cheap and abundant, can also be used as photocatalysts, either on their own or in combination with metal oxides. The photocatalytic activity of clay mineral-derived nanocatalysts and composites is appropriate for a diverse range of applications [94]. The following section will briefly address the two categories of clay mineral-derived catalysts in terms of their ability to operate as (a) UV light photocatalysts (<400 nm) and (b) visible light photocatalysts (>400 nm).

4.3.2. UV Light Photocatalysts

Under UV light, natural clay in its purest form can be used as a photocatalyst without the addition of any other compounds. Some research examples of the use of UV photocatalysts derived from pure minerals are provided below. Natural pillared clays (aluminum–copper and aluminum–iron-containing smectites) are used as heterogeneous photocatalysts, together with hydrogen peroxide, to purify winery wastewater containing a large number of polyphenolic compounds [95]. The photocatalytic activity is greatly influenced by the metallic ions immobilized in the clay mineral structure, according to the findings of this study. Due to its greater surface area and porosity, the copper-doped catalyst demonstrated greater activity than the iron-doped catalyst. The preparation and characterization of a new type of low-cost natural metal oxide-based catalyst derived from a clay mineral from Inner Mongolia (China) is reported in a research article [96]. The photocatalytic activity of the catalyst was assessed in terms of its photocatalytic water-splitting behavior and the photodegradation of wastewater pollutants such as Na2S-Na2SO3, CH3OH, and TEOA (Triethanolamine) in an aqueous suspension. This research found that natural clay-derived photocatalysts have a greater catalytic activity than commercial P25-TiO2 catalysts.

Since TiO2 is a well-known UV catalyst, numerous researchers have investigated clay–TiO2 composite photocatalysts. Here, we highlight some of the latest findings. Sepiolite clay, both unmodified and modified with exchanged Zn or Cu ions combined with nanostructured anatase (titanium dioxide) for the synthesis of sepiolite-based nanocomposites, were tested in the photocatalytic oxidation of NOx gases [97]. Under UV irradiation,
sepiolite, and particularly Zn-modified sepiolite-based nanocomposites, demonstrated superior photocatalytic activity for the oxidation of NOx compared with the reference photocatalyst (P25 titania). Bentonite was delaminated with TiO$_2$ and utilized to remove phenol from aqueous solutions under UV light [98]. The homogeneous substitution of iron in the anatase structure lowered its bandgap and increased its photocatalytic performance when Fe$^{3+}$ and Ti$^{4+}$ were added to the bentonite that was intercalated with iron-doped TiO$_2$ nanoparticles. The practical significance of this study was that it reduced the amount of TiO$_2$ required compared with conventional photocatalytic processes. Hectorite–TiO$_2$ and kaolinite–TiO$_2$ composites were used under mild conditions without the use of stabilizing agents or heat treatment [99]. The photocatalytic efficacy of these composites in the removal of indoor pollutants, such as hydrophobic volatile organic compounds (VOCs), toluene, and D-limonene, was evaluated. This research showed that the structure of clay minerals influenced the formation of the clay-TiO$_2$ composite. The porous and amorphous structure of anatase in hectorite-induced morphological changes in the hectorite-TiO$_2$ composite, resulting in an uptake of Ti by up to 36 wt.%, markedly expanded the specific surface area and enhanced VOC adsorption and photocatalytic degradation. The kaolinite–TiO$_2$ composite exhibited no structural change and had four times less surface area than the hectorite–TiO$_2$ composite due to its rigid crystalline structure, but the photocatalytic activity increased marginally. A study carried out by the authors of [100] showed that as the amount of titanium dioxide in an artificial hectorite–TiO$_2$ composite was increased, the specific surface area decreased as a result of the formation of a delaminated layer structure. These authors also synthesized a lamellar aggregated montmorillonite–TiO$_2$ composite to compare its photodegradation of a chloroacetanilide herbicide (dimethachlor) in an aqueous medium. Both catalysts exhibited higher catalytic activities than pure TiO$_2$ (PS25, a commercially available photocatalyst). These authors emphasized that the simple recovery of nanocomposites from aqueous streams via filtration or sedimentation is an important practical advantage of these nanocomposites.

Another study carried out by the authors of [101] showed that a mixed phase of TiO$_2$ and a clay mineral influences the catalytic activity of the composite. These authors synthesized kaolinite–TiO$_2$ composites with mixed TiO$_2$ phases of anatase–brookite and anatase–rutile by introducing polymeric Ti cations into the kaolinite structure at low temperatures (50–200 °C). The catalytic activity of the kaolinite–TiO$_2$ composite was significantly greater than those of kaolinite and commercial P25 for the removal of acid red G (ARG) and 4-nitrophenol (4-NP) when exposed to UV light. Initially, the high specific surface area of the kaolinite-TiO$_2$ composites allowed for more adsorptive and photocatalytic active sites for the degradation of the organic molecules, which was advantageous for the photocatalytic reaction. The high photocatalytic activity of the kaolinite-TiO$_2$ composites may be attributable to the heterojunction microstructures of the anatase–brookite and anatase–rutile, which can suppress the recombination of electron and hole pairs by altering the electronic properties of TiO$_2$, thereby increasing the photocatalytic activity. The degradation efficiency of palygorskite–TiO$_2$ composite for Orange G dye in aqueous media was investigated by varying the photocatalytic system parameters (pH, loading mass, dye concentration) [102]. According to these authors, the system pH has a significant effect on the photocatalytic performance of the palygorskite–TiO$_2$ composites, with a greater catalytic activity occurring at pH < 4 or pH > 8 due to surface charge effects. This research is expected to be crucial for future applications. A novel cationic surfactant-modified montmorillonite–TiO$_2$ composite was studied for its photocatalytic degradation of a hydrophobic contaminant (BDE 209) [103]. Their results showed that the photocatalytic efficiency of this composite increased with increasing titanium dioxide immobilization on the clay. Electron transfer and hydroxyl radical reaction pathways were suggested to be the main reaction processes in BDE 209 removal under these particular experimental conditions. By modifying the cationic surfactant and attaching TiO$_2$, this research suggests a method for enhancing the adsorption capacity of clay minerals to produce composites that could be used selectively for the photocatalytic removal of cationic pollutants during
wastewater treatment. A composite of titanium dioxide and fibrous sepiolite clay with a high surface area was applied to the photocatalytic oxidation of Eosin Y anionic dye under UV illumination. According to these authors, attachment of the titanium dioxide can occur as follows: the TiO$_2$ forms from small colloidal Ti(OH)$_4$ particles that precipitate on the surface of the sepiolite and interact with the surface hydroxyls of the fibers, thereby incorporating the TiO$_2$ particles [104]. According to these results, the high surface area of the composite allows a large number of organic dye molecules to be adsorbed. When a system containing the sepiolite–TiO$_2$ composite in the presence of contaminants is exposed to UV light, the light-induced formation of OH and O$_2$−• radicals on the surface of the composite can oxidize the organic contaminants.

In view of the excellent photocatalytic performance of iron and zinc oxides and their natural abundance, nanoparticles of these oxides are also considered promising photocatalysts in the form of clay–nanoparticle composites. One example of recent research on clay–Fe$_3$O$_4$ and clay–ZnO composite photocatalysts includes a bentonite–Fe$_3$O$_4$ catalyst. The authors investigated its photocatalytic activity for the treatment of rhodamine B from wastewater under UVA light exposure [105]. These authors hypothesized that the magnetite enhances the photocatalytic activity of the clay via a synergistic effect, and that also increases the number of times the catalyst can be reused by preventing its loss and coaggregation. The physicochemical properties of a vermiculite–Fe$_3$O$_4$ nanocomposite and the effects of heat treatment on its formation and photocatalytic efficiency for carbon dioxide reduction were revealed in [106]. These authors claimed that treatment of the composite at a temperature of 500 °C produced greater catalytic activity than treatment at 700 °C. This result may be due to a slightly greater specific surface area, a smaller crystallite size, and an abundance of oxygen vacancies in the lower-temperature sample. These authors also noted that this magnetic composite has the advantages of a good dispersion ability and simple magnetic separation from aqueous media. The synthesis and characterization of natural montmorillonite–ZnO and synthetic saponite–ZnO composites were reported [107]. According to these authors, the particle size and pH of the system exert a significant impact on the photocatalytic efficiency of the composites in the degradation of methylene blue dye. Innovative ZnO/clay composite structures based on smectites such as a commercial montmorillonite, an iron-rich smectite from Gafsa (Tunisia), and sepiolites from Madrid (Spain) were created [108]. The resulting nanoporous materials were tested as photocatalysts for the decomposition of methylene blue dye (a model for contaminants in water) to evaluate their potential application for environmental remediation. The most important finding of this study was that the bandgap energy of the ZnO particles can be decreased by combining them with clay minerals; thus, the bandgap of ZnO (3.21 eV) is lowered to 2.80 eV in sepiolite–ZnO. Furthermore, the surface area of 14 m$^2$/g and pore volume of 0.017 cm$^3$/g of the zinc oxide nanoparticles were increased to 103 m$^2$/g and 0.36 cm$^3$/g, respectively, by combining them with the clay mineral. These results indicate a significant improvement in the photocatalytic performance of the composite clay–ZnO material. The recent review provides a comprehensive analysis of clay-based photocatalysts for wastewater treatment, emphasizing their potential through specific examples, such as TiO$_2$ and g-C$_3$N$_4$ composites. It emphasizes their ability to hinder the accumulation of particles and enhance the degradation of pollutants [109]. Future research should prioritize the investigation of scalable applications and long-term environmental consequences. This can be achieved by exploring hybrid materials and innovative synthesis methods to improve overall efficiency.

4.3.3. Visible Light Photocatalysts

Clay minerals containing introduced cations have been widely studied as visible light catalysts. The authors of [110] investigated the formation of smectite–cation catalysts from Wyoming smectite clay minerals modified by Ag$^+$, Zn$^{2+}$, Ti$^{4+}$, and Ag$^+$/Zn$^{2+}$ cations. The resulting materials were tested as surface water disinfectants based on their photocatalytic reactions under a sodium lamp visible light to destroy bacteria. This study
showed that smectite–Ti catalysts have the highest overall disinfection efficiency, followed by smectite–Ag/Zn catalysts, smectite–Ag catalysts, and smectite–Zn catalysts. The high degree of disinfection potency of the smectite–Ti catalytic activity, is likely due to its extreme superhydrophilicity. In addition, the weight percentage of metal cations in the composite had a significant impact on its catalytic activity; with low Ti contents, the formation of OH and O$_2^-$ and shielding effects reduced the photocatalytic activity. When the Ti content of the smectite–Ti composite reached 0.06 wt.%, its photocatalytic activity increased and the amount of byproduct decreased.

The photocatalytic activity to remove phenanthrene of series of clay mineral catalysts containing the cations Fe$^{3+}$, Cu$^{2+}$, Ca$^{2+}$, K$^+$, and Na$^+$ was tested [111]. The negative structural charge of smectite had a greater influence on the photocatalytic activity than in kaolinite and vermiculite minerals, as did its expandable structure, containing cation exchange sites in both the interlayers and the tightly packed outer surface layers. Initiation of the photochemical oxidation of phenanthrene in the presence of the transition metal ions was hypothesized to occur via direct electron transfer from the excited singlet state of phenanthrene to molecular oxygen, yielding singlet oxygen, which readily reacts with another molecule of phenanthrene to give endoperoxide. Subsequent irradiation of phenanthrene and endoperoxide results in the formation of other, smaller compounds. Understanding the mechanism of the photodegradation of organic contaminants in the presence of sunlight is essential for studies such as this.

Graphitic carbon nitride (g-C$_3$N$_4$) is gaining interest as a constituent of clay mineral-based visible light photocatalysts due to its high surface area and small band gap of 2–3 eV, which is suitable for visible light photocatalytic reactions. A composite photocatalyst of kaolinite with bismuth oxychloride and g-C$_3$N$_4$ showed a high activity for the degradation of rhodamine B dye [112]. The high photocatalytic efficiency of this composite was said to be due to several factors, including the combination of g-C$_3$N$_4$ and kaolinite, which improves the trapping of visible light; exfoliation of the bismuth oxychloride to form an ultrathin nanostructure with a “sandwich” configuration that dramatically increases the number of reactive sites; and the formation of bismuth oxychloride/g-C$_3$N$_4$/kaolinite heterojunctions that facilitate photo-generated charge carrier migration and separation.

Photocatalytic reactions depend on the presence of reactive oxidative species, especially H$.^+$ Research was conducted on the synthesis of an innovative kaolinite-g-C$_3$N$_4$ composite prepared via a straightforward mechanochemical method [113]. This material exhibited enhanced visible light-driven photocatalytic activity for the photo-degradation of rhodamine B in water. The kaolinite-g-C$_3$N$_4$ composite exhibited a greater capacity for rhodamine B adsorption than CN due to its stronger electrical attraction for rhodamine B. It was proposed that the enhanced photocatalytic activity of KA/CN composites is due to the increased dispersity of g-C$_3$N$_4$ and the enhanced movement efficiency of the photo-induced electrons. Two visible light-driven composite photocatalysts, kaolinite–g-C$_3$N$_4$ and illite–g-C$_3$N$_4$ composites, relied heavily on the presence of holes and O$_2^-$ and the intimate interface contact between g-C$_3$N$_4$ and the layered minerals, which improves dispersion, charge separation, and adsorption, thereby increasing the photoactivity of the composite [114]. The kaolinite–g-C$_3$N$_4$ composite showed greater photocatalytic activity than the illite–g-C$_3$N$_4$ composite and pure g-C$_3$N$_4$ because the negative charge of the kaolinite attracted the rhodamine B molecules to create an efficient adsorption–degradation system.

The synthesis of a maifanite–g-C$_3$N$_4$ composite and its photodegradation of rhodamine B in the presence of humic acid was studied [115]. This research showed that the photodegradation of RhB in the presence of humic acid and a composite of maifanite–g-C$_3$N$_4$ produced fewer byproducts than a photocatalyst of pure reduced graphitic carbon nitride. The authors of [116] synthesized a novel 2D kaolinite–g-C$_3$N$_4$ composite using a heating method and used it to photocatalytically degrade orange II dye under visible light. This composite showed a high catalytic efficiency by degrading orange II dye within just 10 min. In addition, the incorporation of the cyano group within the structure of g-C$_3$N$_4$ has been shown to drastically improve the absorption of visible light and facilitate electron–hole
separation when tested in kaolinite dehydroxylation. The defect site “-CN” can trap the electron of a photo-generated charge carrier in the conduction band of g-C$_3$N$_4$ and suppress charge recombination via a charge transfer mechanism, thereby promoting the production of reactive oxygen species and providing exceptional photocatalytic activity.

Metal sulfide particles are also becoming interesting for producing photocatalytic composites with clay minerals. CdS nanoparticles were loaded on to the nanosheets of kaolinite clay to construct a kaolinite–CdS photocatalyst [117]. Their natural kaolinite starting material contained only a trace amount of iron oxide (0.476 weight percent), but it exhibited definite photo-response characteristics that were similar to those of a semiconductor. The semiconducting property of the kaolinite nanosheet and its capacity for oxygen adsorption were primarily responsible for the improved photocatalytic performance of these composites. In another study [118], the authors hydrothermally loaded MoS$_2$ onto the surface of montmorillonite clay and successfully synthesized montmorillonite–MoS$_2$ nanosheets with hollow microspheres. The catalytic activities of these composites were evaluated in the photodegradation of an aqueous solution of the anionic dye methyl orange under visible-light irradiation. This was explained in terms of the synergistic effects of the unique hollow structure, the vertically aligned and thinner MoS$_2$ nanosheets that greatly boosted their light-utilization efficiency, the density of the active sites, and the separation between the photoelectrons and vacancies. An important aspect of this study was this catalyst’s excellent stability over several cycles, due primarily to the inhibition of MoS$_2$ oxidation by the montmorillonite during the photocatalytic process.

A montmorillonite–MoS$_2$ nanosheet structure’s catalytic performance can also be enhanced with the doping effect of W, thus becoming useful as an electrocatalyst for the H$_2$ evolution reaction [119]. The authors found that doping with W could facilitate the reactivity of catalytic active sites.

4.4. Carbon Nanotube (CNT) Synthesis Catalysts

In the modern world, technological advancements are increasingly demanding materials with physical strength, good chemical activity, a high degree of stability, and abundance. Materials based on carbon are increasingly being recognized as a good fit for the demands of contemporary technology, including the need for new catalysts. Since the discovery of graphene and carbon nanotubes, carbon materials have gained popularity. These new graphene forms are synthesized via chemical and mechanical exfoliation, chemical synthesis, and pyrolysis. The three primary techniques for producing carbon nanotubes are chemical vapor deposition (CVD), laser ablation, and carbon arc discharge. CVD has come to be accepted as a standard method for CNT synthesis due to the product’s high purity and good output and the simple control of the synthesis environment. CVD involves the catalytic degeneration of a carbon source, such as hydrocarbons or alcohol, or the reduction of carbon monoxide in the presence of a nanocomposite transition metal catalyst such as copper, nickel, iron, or a silica-based clay mineral catalyst. The reaction temperature for CVD is typically 600–1000 °C. Interactions between the substrate and the catalytically active metallic particles play an important role in the synthesis of carbon nanotubes (CNTs). Some of the catalysts for CNT synthesis include natural unmodified clay minerals or minerals functionalized with organic composites.

Naturally occurring volcanic minerals containing abundant iron oxide particles can serve as natural catalysts for the production of carbon nanotubes and carbon nanofibers without the need for wet chemical treatments or additional additives [120]. The authors observed that due to the presence of iron in a wide range of minerals, clays, and soils, a new era of cheap mass production of carbon nanomaterials may be opening up. Their study also suggests that CNT/CNF (carbon nanofibers) can form naturally on a mineral in the presence of a carbon source. A similar study reported on using natural untreated bentonite clay to synthesize carbon nanotubes and studied their application for the oxidative dehydrogenation of ethylbenzene to produce styrene (a vital monomer in the polymer industries) [121]. Their reaction requires an induction period, possibly for O$_2$-assisted
functionalization of the graphitic surface with oxygenated surface groups as the active sites. During a model reaction, ethylbenzene conversion, styrene selectivity, and the yield of bentonite–CNTs was virtually unchanged, indicating that the composite can produce a high volume of product.

A simple ion exchange and impregnation technique was used to incorporate iron into the montmorillonite structure to form a montmorillonite–Fe catalyst for CNT synthesis [122]. The results indicated that the clay was enlarged and exfoliated by the intercalation of the iron ions into the clay interlayers, thereby permitting the growth of CNTs on the clay platelets via CVD. Magnesite clay was used as a catalyst for the synthesis of single-walled carbon nanotubes (SWNTs) that were successfully grown on the magnesite crystals [123]. In contrast to the CVD method, these authors used pyrolyzed methane gas under moderate conditions, demonstrating the possible formation of naturally occurring SWNTs. Three different clay minerals (kaolinite, nontronite, and sepiolite) in the formation of clay–iron catalysts were used in the synthesis of CNTs to compare the effects of differences in the structure and morphology of the product CNTs due to the different catalysts. In the case of the kaolinite catalyst, the nanotubes were interspersed between single crystallites and grew throughout the entire volume, forming three-dimensional grids. In both the nontronite and sepiolite catalysts, the CNTs grew throughout the mineral volume; however, on nontronite, the CNTs were not aligned, whereas on sepiolite, they were aligned. This observation is extremely beneficial because it enables the selection of specific clays for the production of CNTs with specific characteristics for use in particular applications. In a similar approach to the synthesis of catalysts, synthesized carbon nanotubes (CNTs) were formed over an iron-doped muscovite catalyst, then the muscovite–CNTs were to form a composite polymeric film with polylactic acid [124]. These authors determined the elasticity, electric properties, and thermal and mechanical properties of the film and found that the composite filler prevented the mechanical stability of the PLA from decreasing and formed a tangled interconnected system of polymer network and hybrid filler, thereby sustaining chain cleavage and maintaining the mechanical consistency of the samples up to incredibly high radiation exposure periods. A new nanoarchitectural method for designing functional nanomaterials from natural aluminosilicate (halloysite) was described by the authors of [125]. They prepared structured silica and zeolite using nanotube templates and hybrid core-shell systems with metallic or organic molecules in aluminosilicate walls. Al$_2$O$_3$/SiO$_2$ chemistry in 50 nm halloysite tubes provides structure and site-dependent properties, biocompatibility, environmental safety, and abundant availability. The research suggests scaling these functional systems for industrial catalysis, biomedical applications, and environmental remediation.

Clay materials and their composites with carbon nanomaterials are pivotal catalysts due to their enhanced properties. These materials offer superior mechanical strength, reactivity, and tunable functionality, which are critical for various applications [126]. Their importance lies in their ability to overcome the limitations of traditional catalysts, opening avenues for more efficient catalytic processes in industries such as wastewater treatment, energy production, and chemical synthesis. A novel clay–carbon nanotube composite showed high catalytic activity toward decomposition of acetylene over clay–iron centers formed on montmorillonite surfaces via impregnation [127] (Figure 5).

Although iron is the most commonly studied component of clay composite catalysts used to form CNTs, some researchers have studied the effects of other metals for this purpose. The authors used a natural nickel–laterite catalyst, also containing Mg, Al, Si, Cr, Fe, and Au, to synthesize carbon nanostructures at temperatures of 700 °C, 800 °C, and 900 °C [128]. This study indicated that the reaction temperature greatly affects the formation of carbon nanotubes or carbon nanospheres. Carbon nanotubes are the dominant product at lower temperatures, but at higher temperatures, carbon nanospheres are mostly formed. Iron and nickel oxide clusters can be fragmented and reduced to nanometer-sized metal-containing particles that nucleate and develop CNTs. Carbon nanospheres grow as a result of the breakdown of undiluted ethylene at higher temperatures, insulating
the catalytic fragments with amorphous carbon Fe from two different salts and Ni and Co as dopants on montmorillonite and using these to produce clay–carbon nanotube composites with varying carbon nanotube contents and qualities [11] or synthesized on montmorillonite clay by using FeCo nanoparticles [129]. They reported that the optimum synthesis temperature is 700 °C, and that the nitrate salts supported on montmorillonite produced CNTs that were virtually free of metal carbide impurities, in contrast to the chloride salts. Most notably, the catalyst-containing nickel nitrate produced high-quality CNTs with few defects. An in-depth investigation was conducted into the effects of the transition metals Cr, Mn, Fe, Co, Ni, Cu, and Zn loaded onto laponite and montmorillonite clays as catalysts for forming carbon nanostructures [130]. The origin of the transition metal was found to have a vital influence on the synthesized carbon nanostructures’ yield, structural quality, and morphological characteristics. Apart from the chromium and zinc-containing clay catalysts, all the other metal–clay catalysts produced carbon nanostructures at 700 °C. Cobalt and copper formed the most highly graphitized carbon nanostructures when associated with laponite and montmorillonite, while nickel was the most active catalyst and yielded the most product. Nickel-supported laponite yielded twice the carbon yield compared with nickel-supported montmorillonite. The nickel used in another study demonstrates a new method for producing Ni-pillared clay (Ni-PILC) by utilizing a specific nickel complex as a catalyst. It effectively showcases the use of Ni-PILC in the synthesis of carbon nanotubes (CNTs) [131]. This study highlights the substantial influence of the concentration of nickel complexes on both the amount and characteristics of the carbon nanotubes (CNTs) produced. This indicates a promising approach to improve the efficiency and properties of CNT synthesis.

Figure 5. Schematic illustration of the clay–carbon nanotube composite. Reproduced with the permission of Elsevier from reference [127].

5. Conclusions and Possible Future Directions for Research

The wide range of crystal structures and chemical compositions of clay minerals make them excellent starting materials for activation and modification to produce advanced products. The basic crystal structure units are tetrahedral silica sheets and octahedral...
alumina sheets in a 1 tetrahedral to 1 octahedral configuration (1:1 lattice) and 2 tetrahedral to 1 octahedral configuration (2:1 lattice). The interlayers of the crystal planes can also contain charge-balancing ions (Fe$^{2+}$, Na$^+$, Mg$^{2+}$) and associated water molecules. Acid treatment can remove interlayer cations and water molecules and dissolve octahedral cations, resulting in a porous silica-based structure. Alkali treatment dissolves the silica from the mineral and assists in the synthesis of new highly porous products, together with an aluminum residue. In comparison with traditional processing methods, modern procedures such as ultrasonication and microwave treatment enhance the surface properties of the clay mineral-derived product and reduce the required processing time.

Since natural clays catalyze the decomposition of numerous types of environmental hydrocarbons, the catalytic activity of clays offers limitless opportunities. In addition to studies of the catalytic activity of natural clays and their derivatives, numerous studies have been reported in an effort to expand the application of natural clays in a variety of catalytic processes, including CO$_2$ hydrogenation, water splitting, photocatalysis, and carbon nanotube synthesis. The catalytic activity of clays and clay minerals depends on their distinct crystal structures, interlayer cations, surface area, pore size, and surface charge. For instance, surface properties such as a specific surface area, pore size, surface charge, etc., play a crucial role in the photocatalytic activity of these materials. Interlayer cations (Ni$^{2+}$, Co$^{2+}$, Fe$^{2+}$, or Fe$^{3+}$) and the thermal stability of the clay and clay mineral catalyst play a crucial role in CO$_2$ hydrogenation and CNT synthesis catalytic reactions. However, the effects of such variations are not fully understood; consequently, it is necessary to study the performance of various clays and clay minerals under varying reaction conditions.

Future possibilities of massive catalyst production can go in either two directions: using natural clays and their derivatives, with or without additional processing, or synthetic clay minerals. Because of the complex structure and composition of natural clays, it is difficult to determine the precise mechanism of catalytic reactions and predict the intermediate and final products of the reaction. Additionally, natural clays require more time and effort to purify than synthetic clay minerals. On the other hand, synthetic clay minerals are more manageable and allow for the determination of the effect and efficiency of the catalyst in catalytic reactions. However, the massive production of synthetic clay minerals is restricted in some cases, particularly in developing countries, due to their high price and limited availability. Therefore, it is evident that natural and synthetic clay minerals can be used in various catalytic reactions, with the objective of using different minerals depending on the application or scientific findings. The combination of the various clay structures to form a composite clay template for further processing could be another topic of interest to scientists working in this field.

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