

Review

# Modified Bentonite Catalysts: Structure–Property Relationships, Modification Strategies, and Perspectives for Waste Valorization into Hydrogen-Rich Products

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## Abstract

Natural bentonite, dominated by montmorillonite-type layered aluminosilicates, is increasingly considered as an inexpensive and environmentally acceptable support or catalyst for the thermochemical conversion of waste carbon streams. Its relevance to catalysis arises from a combination of cation-exchange capacity, swelling behavior, hierarchical porosity after modification, and the possibility of generating Brønsted, Lewis, redox and metallic active sites. This review critically evaluates bentonite modification strategies—acid activation, alkaline and sodium exchange, inorganic oxide pillaring, transition- and noble-metal impregnation, organosilane or surfactant functionalization, and carbon-based hybridization—with emphasis on their consequences for texture, acidity, thermal stability, metal dispersion and catalytic behavior. The review then connects these structure–property relationships with the emerging application of modified bentonites in plastic-waste thermocatalysis and hydrogen-rich product formation. The recent literature indicates that acid-modified bentonite can substantially improve liquid hydrocarbon formation from polyethylene, binder-free bentonite pellets can operate at kilogram-batch scale for drop-in fuels, and Ni-, Fe- or Ni–Fe-modified bentonite-type catalysts can promote tar cracking, reforming and gas upgrading. However, direct evidence for high hydrogen yields from plastic waste over bentonite remains narrower than the evidence for liquid-fuel production, biomass pyrolysis or model-compound reforming. Therefore, this article distinguishes between direct plastic-waste evidence and transferable evidence from biomass, acetic acid, tar and hydrocarbon reforming studies. The analysis identifies Ni-impregnated acid-activated or pillared bentonite, Ni–Fe/bentonite, and La/Ca-promoted Ni/bentonite as the most promising routes for plastic-derived hydrogen-rich syngas, while acid activation alone is best regarded as a pretreatment rather than a complete catalyst design. Key limitations include catalyst deactivation by coke, metal sintering, chloride poisoning from PVC, inconsistent reporting of gas yields, and insufficient life-cycle and techno-economic analysis. A roadmap is proposed for designing reproducible, scalable bentonite catalysts for circular plastic-waste valorization.



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**Keywords:** bentonite; montmorillonite; clay catalyst; acid activation; pillared clay; plastic waste; pyrolysis; steam reforming; hydrogen production

## 1. Introduction

The conversion of polymer waste into fuels, chemicals and hydrogen-rich gas has become a central challenge in sustainable catalysis. Polyolefins and polystyrene contain high chemical energy but are poorly compatible with conventional mechanical recycling after contamination, ageing, mixing or additive incorporation. Chemical and thermochemical recycling can, in principle, convert these materials into hydrocarbon liquids, light olefins, aromatics, syngas or hydrogen. Among these routes, pyrolysis and catalytic reforming are attractive because they can process mixed carbonaceous feedstocks and can be integrated with existing thermal and refinery infrastructure. However, purely thermal conversion usually gives broad product distributions, waxes, tars and coke, while catalytic conversion requires a stable, inexpensive and regenerable solid that can tolerate large molecules and variable feed composition [1–5].

Zeolites, alumina, silica–alumina, dolomite, CaO, biochar, red mud and supported transition-metal catalysts have all been investigated for plastic and biomass upgrading. Zeolites provide strong acidity and shape selectivity, but their micropores are easily blocked by heavy waxes and coke precursors. Dolomite and CaO are inexpensive and can support tar cracking, but their strength and stability vary. Nickel catalysts are highly active for reforming and dehydrogenation, but they are vulnerable to sintering, carbon deposition and poisoning. These limitations have stimulated interest in natural clays, particularly bentonite, as low-cost and mesoporous catalytic platforms [6–12].

Bentonite is a naturally occurring clay whose main active mineral is montmorillonite. Its 2:1 tetrahedral–octahedral–tetrahedral structure contains exchangeable interlayer cations, structural hydroxyl groups and negatively charged layers generated by isomorphic substitution. These features make bentonite more than an inert support: its interlayer chemistry, surface acidity, swelling capacity and cation-exchange behavior can be exploited to tailor catalytic properties. Through acid activation, alkaline treatment, sodium exchange, pillaring, metal impregnation and organic or carbon functionalization, bentonite can be converted into a family of catalysts and adsorbents with very different physicochemical behavior [13,14].

The present review rewrites and sharpens the previous manuscript by focusing on catalysis rather than only material modification. The aim is not merely to list activation methods but to establish which modifications are mechanistically relevant for hydrogen-rich product formation from plastic waste and which are more relevant to adsorption, membrane fabrication or environmental remediation. A second aim is to separate direct evidence from indirect or transferable evidence. For example, the often-cited 23.4% increase in hydrogen yield over organic-compound-modified Na-bentonite was reported for corn-cob biomass pyrolysis, not plastic-waste pyrolysis [15]. It is useful mechanistic evidence for radical conversion and dehydrogenation over Na-bentonite, but it should not be used as a direct quantitative claim for plastic conversion without additional experiments.

## 2. Bentonite as a Catalytic Platform: Structure, Acidity and Transport

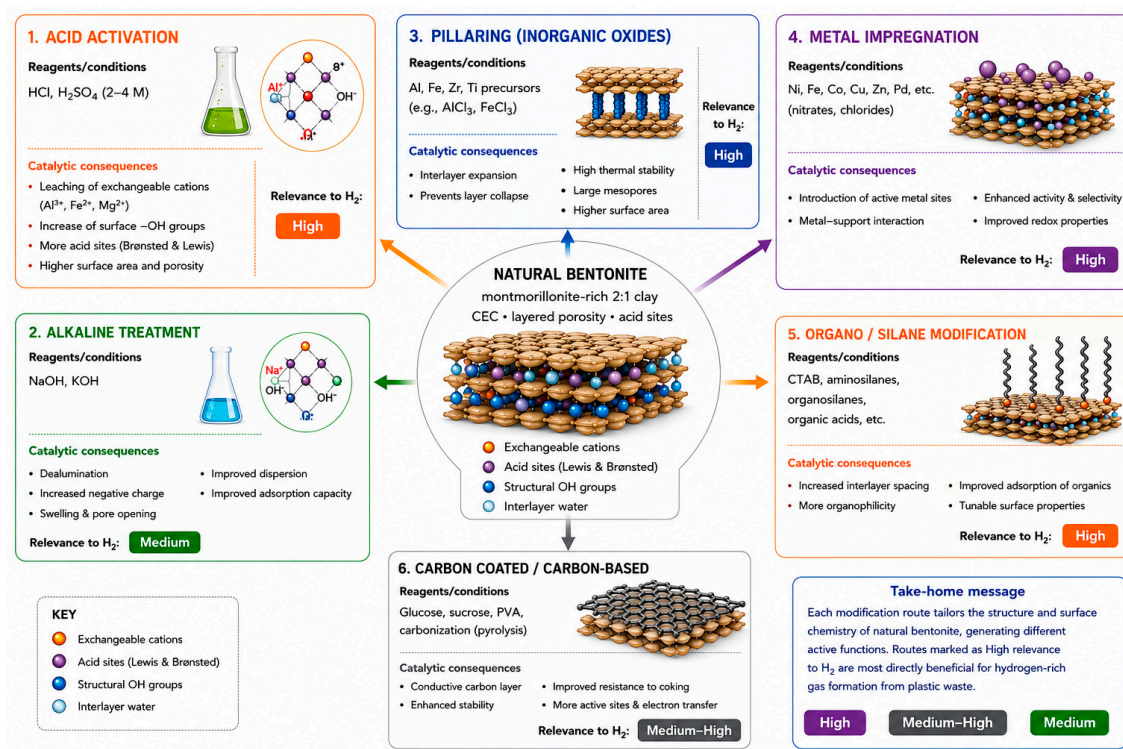
Bentonite is typically composed of 65–85% montmorillonite, together with quartz, feldspars, carbonates, iron oxides and other accessory minerals whose amount depends on deposit origin and beneficiation history. Montmorillonite layers consist of an octahedral alumina sheet between two tetrahedral silica sheets. Isomorphic substitution, such as  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in tetrahedral sheets or  $\text{Mg}^{2+}/\text{Fe}^{2+}$  for  $\text{Al}^{3+}$  in octahedral sheets, generates a net

negative layer charge compensated by exchangeable cations such as  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Mg}^{2+}$  or  $\text{K}^+$ . These cations determine swelling, hydration and interlayer accessibility, while edge hydroxyl groups and structural defects contribute to acidity and adsorption [16–18].

Catalytic behavior is controlled by four interrelated parameters. The first is texture, including specific surface area, pore volume, pore-size distribution and accessibility of interlayer spaces. The second is acidity, including Brønsted acid sites from protonated hydroxyl groups and Lewis acid sites associated with coordinatively unsaturated Al, Fe or transition-metal centers. The third is redox or metallic function, introduced through Fe, Cu, Co, Ni, Pd and related species. The fourth is mass transport, which is especially important for plastic pyrolysis because polymer-derived waxes and oligomers are much larger than the micropores of conventional zeolites. Bentonite can develop mesoporosity after activation or pillaring, which improves diffusion of heavy intermediates and can reduce the probability of pore blockage [19,20].

The catalytic promise of bentonite is therefore not based on natural clay alone. Raw bentonite frequently has modest surface area, limited thermal stability under severe activation, and an insufficient density of controlled active sites. Modification is essential. Acid treatment can leach octahedral cations and increase mesoporosity; pillaring can lock open the interlayer space and increase thermal stability; metal impregnation can introduce reforming, hydrogenation or oxidation functions; and organic or carbon functionalization can tune hydrophobicity, adsorption or conductivity. The best catalyst design for hydrogen production must combine these features rather than rely on a single modification step [21–23].

Several modification strategies can be applied to natural bentonite to tailor its structural and surface chemistry for catalytic applications, as summarized in Figure 1.



**Figure 1.** Main modification routes for natural bentonite and their catalytic consequences. The scheme emphasizes that each route generates a different active function; only some are directly relevant to hydrogen-rich gas formation.

Bentonite possesses several physicochemical properties relevant to its role as a catalyst support and precursor in plastic-waste conversion, including cation-exchange ca-

capacity, Brønsted and Lewis acidity, mesoporosity, thermal stability, and the presence of metallic/redox-active sites. These properties directly influence catalytic activity, product distribution, hydrogen formation, and catalyst stability, and are summarized in Table 1.

**Table 1.** Catalytically relevant properties of bentonite and why they matter in plastic-waste conversion.

| Property                 | Origin in Bentonite                                                                    | Catalytic Role                                                                        | Main Risk If Not Optimized                                        |
|--------------------------|----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------|-------------------------------------------------------------------|
| Cation-exchange capacity | Interlayer $\text{Na}^+$ , $\text{Ca}^{2+}$ , $\text{Mg}^{2+}$ balancing layer charge  | Enables ion exchange and better dispersion of Ni, Fe, Cu, Co or alkaline promoters    | Non-uniform exchange gives heterogeneous metal distribution       |
| Brønsted acidity         | Protonated OH groups and acid-activated sites                                          | Promotes cracking of waxes and oligomers into smaller hydrocarbons                    | Excess acidity promotes aromatics and coke                        |
| Lewis acidity            | $\text{Al}^{3+}$ , $\text{Fe}^{3+}$ , exposed octahedral/tetrahedral sites, Al pillars | Promotes deoxygenation, isomerization and activation of polar intermediates           | Overly strong Lewis sites can bind poisons irreversibly           |
| Mesoporosity             | Acid leaching, pillaring, delamination and interparticle voids                         | Allows transport of bulky plastic-derived vapors and tars                             | Pore collapse or blocking during regeneration                     |
| Thermal stability        | Pillared Al/Fe/Ti/Zr oxide columns; rare-Earth stabilization                           | Allows repeated pyrolysis/reforming cycles at 500–850 °C                              | Natural bentonite can lose structure after severe dehydroxylation |
| Metallic/redox sites     | Impregnated Ni, Fe, Cu, Co, Pd or bimetallic particles                                 | Enable reforming, dehydrogenation, tar cracking and water–gas shift-related chemistry | Sintering, coke encapsulation and metal leaching                  |

### 3. Plastic Waste as Feedstock for Hydrogen-Rich Products

Plastic waste is increasingly recognized as a potential feedstock for hydrogen-rich gas, liquid fuels, and chemicals due to its high carbon and hydrogen content. In this context, hydrogen is considered a sustainable energy carrier that can be produced from waste, biomass, and renewable resources. Electrolysis of water provides high-purity hydrogen; however, it currently accounts for only about 4% of global hydrogen production. The majority is still derived from fossil-based processes, including natural gas reforming (48%), coal gasification (18%), and petroleum refining (30%), which are associated with significant  $\text{CO}_2$  emissions [24].

Pyrolysis of plastic waste is developing, which offers a promising approach to hydrogen production and reducing environmental impact [25]. Plastics can be classified in various ways, including origin, structure, or molecular composition. In addition, plastic recycling technologies are generally classified into four main categories based on the recycling process and the resulting products, as summarized in Table 2.

Common plastics such as polyethylene terephthalate (PET), low-density polyethylene (LDPE), high-density polyethylene (HDPE), polyvinyl chloride (PVC), polypropylene (PP), and polystyrene (PS) are widely used polymers composed of long-chain macromolecules derived from smaller monomeric or oligomeric units [26–28].

Plastic waste therefore represents an attractive alternative resource for hydrogen production. Polyethylene and polypropylene are saturated hydrocarbons and are particularly suitable for thermochemical conversion due to the absence of heteroatoms in their backbone. Polystyrene readily depolymerizes into styrene and aromatic compounds, whereas PET contains oxygen and generates CO,  $\text{CO}_2$ , aromatics, and oxygenated species. PET-derived ethylene glycol has also been investigated as a feedstock for electrocatalytic conversion into value-added chemicals. PVC introduces chlorine and HCl, which can poison catalysts and corrode reactors. Therefore, mixed plastic waste often requires pretreatment or catalyst systems tolerant to impurities [2–5,29,30].

The main thermochemical routes for hydrogen production from plastic waste include pyrolysis with catalytic reforming, direct catalytic pyrolysis, gasification, microwave-assisted pyrolysis, plasma-assisted conversion, and emerging photoreforming and electroreforming processes [30–32]. Among these, pyrolysis-integrated catalytic systems are considered the most technologically mature for handling mixed plastic feedstocks, whereas photoreforming and electroreforming remain limited by catalyst stability, pretreatment requirements, and scalability issues.

Gasification is another important thermochemical route, converting carbon-containing feedstocks such as biomass, coal, and plastic waste into syngas composed of  $H_2$ ,  $CH_4$ ,  $CO$ , and  $CO_2$ . It is widely applied in waste-to-energy systems and industrial energy production, offering a sustainable alternative to fossil fuels [33].

**Table 2.** Classification and characteristics of plastic recycling methods.

| Plastic Recycling                                                                                                                                  |                                                                                                                                                                                             |                                                                                                                                                                       |                                                                                                                                 |
|----------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------|
| Primary<br>(Initial or Sorting)                                                                                                                    | Secondary<br>(Mechanical)                                                                                                                                                                   | Tertiary<br>(Chemical)                                                                                                                                                | Quaternary<br>(Thermal, Incineration)                                                                                           |
| Involves the conversion of plastic waste into products with functionality similar to the source material, in the case of non-contaminated plastics | Includes cleaning, grinding, and remelting plastics to create new products; however, this method often results in low-quality products because many polymers are not processed in this way. | Involves thermal and chemical processes that break down long polymer chains into smaller and adaptable molecules that can be reused to produce new polymers or fuels. | Includes the incineration of plastic waste, which reduces its volume and generates heat that can be used for energy production. |

Pyrolysis and gasification are therefore considered the most practical thermochemical approaches; however, hydrogen yield strongly depends on reaction conditions such as temperature, pressure, residence time, catalyst type, and feedstock composition. In many cases, these processes produce syngas rather than pure hydrogen [34].

Photoreforming of plastics has also been investigated, where physical and chemical pretreatment methods are used to improve catalyst–substrate interaction. However, these methods are generally resource-intensive, slow, and limited to laboratory-scale systems due to feedstock complexity and scalability challenges [35].

The efficiency of plastic pyrolysis can be significantly improved through catalytic process configurations. Among these, catalytic pyrolysis is particularly relevant to the present review because catalyst properties strongly influence cracking activity, product selectivity, hydrogen yield, and catalyst stability. In this context, modified bentonite has attracted increasing attention as a low-cost catalyst support owing to its tunable acidity, mesoporous structure, thermal stability, and high cation-exchange capacity.

Although membrane-assisted reforming can further improve hydrogen purity, catalyst development remains the primary strategy for increasing hydrogen production and process efficiency during plastic pyrolysis and reforming [36–39].

Catalysts play a crucial role in promoting hydrocarbon cracking, reforming reactions, hydrogen formation, and the suppression of undesirable by-products. However, catalyst deactivation caused by carbon deposition, sulfur poisoning, and pore blockage remains a major challenge. Therefore, effective catalyst supports must combine high catalytic activity with excellent thermal stability and resistance to deactivation.

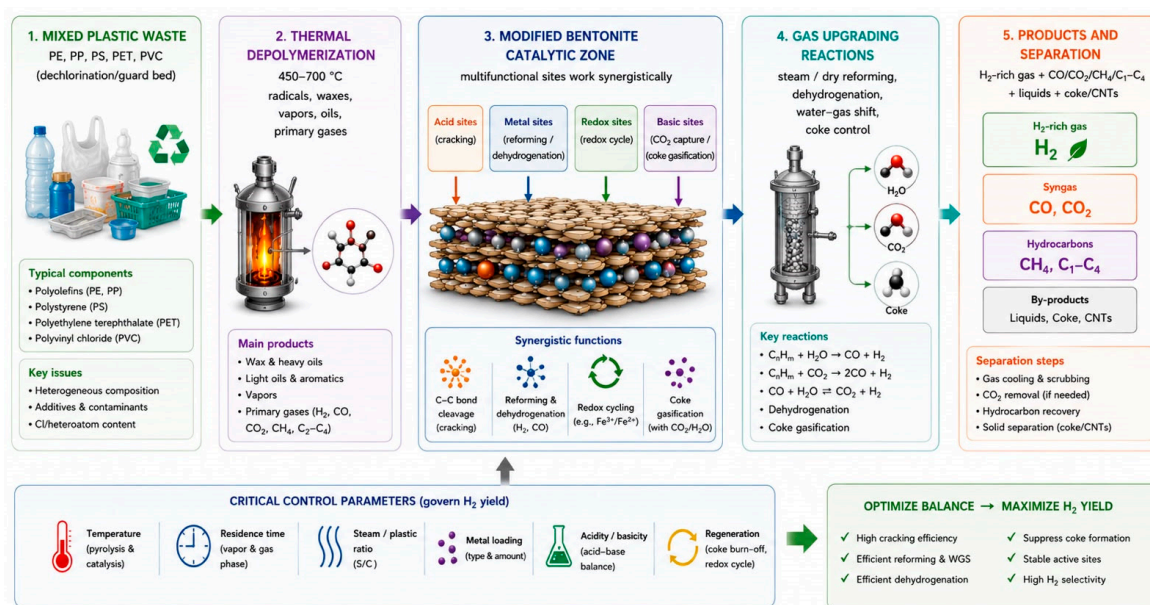
Nickel-based catalysts are widely regarded as the most practical active phase for hydrogen-rich gas production because of their high reforming activity and relatively low cost. In bentonite-supported catalysts, the modified clay acts not only as a support for the dispersion of Ni nanoparticles but also as a source of Brønsted and Lewis acid sites that promote hydrocarbon cracking and facilitate subsequent reforming reactions [40]. Although Pt-based catalysts exhibit excellent catalytic performance, their high cost limits large-scale industrial application.

To improve catalyst durability, various promoters and modified supports have been investigated [41,42]. While oxide-supported systems such as  $\text{NiZnAlO}_x$  exhibit excellent hydrogen production performance, modified bentonite represents an attractive low-cost alternative owing to its natural abundance, adjustable acidity, high cation-exchange capacity, and ability to enhance metal dispersion while suppressing catalyst deactivation. Consequently, modification strategies such as acid activation, pillaring, and metal impregnation play a key role in improving catalyst stability, coke resistance, and hydrogen-rich gas production from plastic waste [43–45].

Although Ni-based catalysts are widely regarded as the most practical option due to their balance of activity and cost, they still suffer from deactivation problems. Therefore, support modification plays a key role in improving catalyst stability and performance.

A two-stage pyrolysis–catalytic reforming system is particularly effective for hydrogen production from plastic waste using bentonite-based catalysts. In the first stage, thermal decomposition produces vapors including waxes, oils, gases, and tars. In the second stage, these vapors undergo catalytic cracking, dehydrogenation, steam reforming, dry reforming, methanation, water–gas shift, and coke-forming reactions. Hydrogen yield is strongly influenced by polymer type, temperature, steam-to-carbon ratio, residence time, catalyst composition, metal loading, acidity, and deactivation behavior. In this context, bentonite has attracted attention as a low-cost and modifiable support material. Previous studies have demonstrated its effectiveness in plastic pyrolysis for liquid fuel production. For example, acid-modified bentonite has been shown to enhance hydrocarbon yields by adjusting the Si/Al ratio [46], while pelletized bentonite catalysts have been successfully applied in large-scale batch pyrolysis systems [19]. However, its role in hydrogen-selective catalytic reforming remains less explored. Nevertheless, catalyst selection significantly affects product distribution, hydrogen yield, and stability.

Therefore, investigating bentonite-supported metal catalysts represents a promising strategy to improve hydrogen production from plastic waste while maintaining cost efficiency and structural stability. The proposed role of modified bentonite catalysts in the conversion of mixed plastic waste into hydrogen-rich products is illustrated in Figure 2.



**Figure 2.** Conceptual pathway for plastic-waste conversion to hydrogen-rich products over modified bentonite catalysts. Hydrogen yield is governed by the balance between cracking, reforming, dehydrogenation, water–gas shift and carbon deposition.

The available literature demonstrates that bentonite- and clay-based catalysts have been investigated in a range of thermochemical conversion processes, including plastic pyrolysis, biomass conversion, steam reforming, and tar reforming. Although not all studies directly target hydrogen production from plastic waste, they provide important mechanistic and catalytic insights relevant to the design of hydrogen-producing systems. The evidence linking these applications to hydrogen-relevant catalyst functions is summarized in Table 3.

**Table 3.** Evidence map connecting bentonite or clay catalysts with plastic/waste/biomass conversion and hydrogen-relevant functions.

| Evidence Type                                    | Representative Studies | Main Finding                                                                                                                                        | Relevance to Plastic-to-H <sub>2</sub> Catalyst Design                                                                  |
|--------------------------------------------------|------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------------------------------------------|
| Direct plastic-to-liquid over bentonite          | [19,20,46]             | Acid-modified or pelletized bentonite can increase liquid hydrocarbon production and improve processability of waste plastics.                      | Strong evidence for plastic cracking and low-cost process integration; weaker direct evidence for H <sub>2</sub> yield. |
| Direct plastic-to-H <sub>2</sub> /syngas reviews | [2–4,29]               | Plastic-to-H <sub>2</sub> routes increasingly combine pyrolysis with catalytic reforming, gasification, membranes or emerging photo/electro routes. | Defines target reactions and performance metrics; supports selecting Ni/Fe sites for reforming.                         |
| Bentonite-supported reforming catalysts          | [47]                   | Bentonite-supported Ni, La and Ca catalysts generate hydrogen-rich gas in acetic acid steam reforming.                                              | Directly informs promoter choice and support-metal interactions for plastic-derived oxygenates/tars.                    |
| Ni-Fe/bentonite for tar reforming                | [48]                   | Ni-Fe-loaded bentonite reduced tar and increased gas yield in catalytic tar reforming.                                                              | Highly relevant to second-stage reforming of plastic pyrolysis vapors and tar management.                               |
| Na-bentonite and hydrogen enhancement            | [16]                   | Organic-compound-modified Na-bentonite increased H <sub>2</sub> production by up to 23.4% in corn-cob biomass pyrolysis.                            | Transferable mechanistic evidence only; not direct proof for plastic waste.                                             |
| Clay catalysts in plastic thermocatalysis        | [1]                    | Clay minerals can provide moderate acidity and mesoporosity favorable to liquid fuels and coke mitigation.                                          | Supports using bentonite as a low-cost alternative or complement to zeolites.                                           |

#### 4. Bentonite Activation

Heterogeneous catalysts are often used in thermochemical conversion of biomass, usually in waste pyrolysis, as their efficiency improves through repeated use. Accordingly, they can be divided into various categories: metal catalysts, metal oxides, mineral aluminosilicate catalysts, etc. Each type of catalyst is selected for the process depending on its respective catalytic activity and selectivity. The recycling of plastic waste, bio-waste, pyrolysis oils and alternative fuels has become possible. However, unlike bentonite-based catalysts, zeolite micropores can lead to coke formation by some macromolecules, limiting their effectiveness of the zeolite micropores. Montmorillonite enriched with iron on a clay basis is of great interest to many researchers due to its low cost and high catalytic effects. The montmorillonite catalyst containing iron has shown that more liquid products can be obtained during the pyrolysis process [49,50]. In contrast, montmorillonite enriched with iron on a clay basis is of great interest to many researchers due to its low cost and high catalytic effects. Using a Box–Behnken statistical design, the effect of iron loading, catalyst-to-biomass ratio, and temperature on product yield was systematically evaluated. It was shown that iron-doped montmorillonite is a viable catalyst for mild pyrolysis vapor upgrading, improving the stability of fast pyrolysis liquids and increasing the formation of alkyl phenols, although further work is needed to assess long-term catalyst stability and regeneration [51].

Clay minerals exhibit layered aluminosilicates with an increase in the interlayer space, a wide range of physico-chemical properties such as cation exchange and a high surface area. Bentonite, used as an acid catalyst, is considered a clay mineral belonging to the smectite group. 65–85% of bentonite consists of montmorillonite and is widely used in

drilling fluids, foundry sands and for granulating taconite iron ores. Bentonite, with the formula  $M_X(Al_{4-X}Mg_X)Si_8O_{20}(OH)_4 \cdot nH_2O$ , consists of 2:1 tetrahedral–octahedral–tetrahedral layers, depending on the arrangement within the layered structure. The tetrahedral layer consists of silicon and oxygen elements forming  $SiO_4$ . Meanwhile, the octahedral layer consists of aluminum, a hydroxyl group and oxygen, which form  $AlO_4(OH)_2$ , respectively. In the structural lattice, due to the formation of Lewis centers, the  $Al^{3+}$  ion is replaced by the  $Si^{4+}$  ion, and the presence of a hydrogen compensator in the formation of Brønsted acid centers means the acidity of bentonite. The silicon ion in the tetrahedral layer can be converted to an aluminum ion, where it replaces the magnesium ion in the octahedral layer or other transition metals with a different electronic potential. Bentonite can be divided into two types: sodium bentonite due to the large number of  $Na^+$  cations and calcium bentonite due to the large number of  $Ca^{2+}$  cations [52–55].

In most cases, various sulfuric acid  $H_2SO_4$ , hydrochloric acid  $HCl$  [56–59], potassium hydroxide  $KOH$  and sodium hydroxide  $NaOH$  [60–62] are used when treating bentonite with acid and alkaline. It increases the surface area and increases porosity, acidity, removes exchangeable cations  $Na^+$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ , cleans impurities and improves adsorption catalytic properties by activating bentonite with acid.

In the study conducted by Khairuddin et al., the activation of bentonite with sulfuric acid was carried out at various molar concentrations, ranging from 0.5 M to 2 M, at different reagent ratios. The optimal activation was achieved with 1.5 M  $H_2SO_4$ . The resulting precipitate was repeatedly washed, and the absence of sulfate ions in the composition was confirmed through comprehensive structural analyses, including X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), and X-ray fluorescence (XRF) methods. XRD analysis revealed shifts in  $2\theta$  values and changes in crystallinity, reflecting significant modifications in the mineral structure, while FTIR analysis identified functional groups such as  $-OH$ ,  $CO_3^{2-}$ ,  $FeO$ , and  $Si-O-Al$  couplings critical for adsorption interactions. XRF analysis further demonstrated reduced impurities, including  $SiO_2$ ,  $CaO$ , and  $TiO_2$ , confirming the effectiveness of the activation process [63].

Natural bentonites generally possess a very low surface area. As reported across several studies, the surface area of natural bentonite ranges from  $9.883\text{ m}^2/\text{g}$  to  $47.370\text{ m}^2/\text{g}$  [64–67]. The study conducted by Wiyantoko et al. demonstrated that the surface area of naturally inactive bentonite was  $22.150\text{ m}^2/\text{g}$ , and after acid activation using sulfuric acid, the value significantly increased to  $213.480\text{ m}^2/\text{g}$ , confirming that acid-activated bentonite exhibits superior surface area and pore volume compared to its natural form. This increase occurs due to the loss of exchange ions and the release of the octahedral layer [68].

As reported by Chen et al., the total surface area of natural sodium bentonite is  $60.371\text{ m}^2/\text{g}$ , while after acid activation the surface area increased significantly to  $379.013\text{ m}^2/\text{g}$  [69]. As reported by Musie and Gonfa, the surface area of natural bentonite corresponds to that of natural montmorillonite at  $57.600\text{ m}^2/\text{g}$ , while activation with 3 M sulfuric acid increased the surface area to  $238\text{ m}^2/\text{g}$  due to more abundant pore formation. Scanning electron microscopy (SEM) analysis revealed that natural bentonite is characterized by dense stacking of layered plates and a relatively smooth surface, whereas acid-activated bentonite exhibits a loosened, heterogeneous and fractured surface. This structural transformation occurs because acid activation removes exchange cations and impurities, increasing porosity and forming additional pores through cation leaching [70].

These findings confirm that acid activation significantly enhances the textural properties of bentonite, resulting in a larger specific surface area and improved pore structure, which are critical factors for catalytic and adsorption applications.

#### 4.1. Acid Activation of Bentonite

Acid activation is one of the most studied and widely used methods of bentonite modification in industry. This chemical treatment consists of the interaction of bentonite with mineral acids under controlled conditions, during which octahedral cations are leached out while maintaining a tetrahedral silica framework, leading to an increase in porosity and specific surface area of the material [71,72].

Sulfuric acid, nitric acid and hydrochloric acid are widely used in the activation of bentonite. However, from the point of view of optimal efficiency and cost ratio, sulfuric acid is the most common. As reported by Yildiz, Aktas and Calimli, treatment of calcium-containing bentonite with  $\text{H}_2\text{SO}_4$  solutions of various concentrations (10–70 wt.%) at a temperature of 97 °C for 6 h leads to a significant improvement in its properties. The specific surface area increased from 43  $\text{m}^2/\text{g}$  to 134  $\text{m}^2/\text{g}$  at a concentration of 40%  $\text{H}_2\text{SO}_4$ . In addition, the total pore volume, including micro- and mesopores, increased by 176% from 0.107  $\text{cm}^3/\text{g}$  to 0.295  $\text{cm}^3/\text{g}$  [18,73].

It has been proven that the optimal concentration of sulfuric acid to increase the surface area is within 2–4 M in many studies. It was investigated that when calcium-containing bentonite is activated with 2 M  $\text{H}_2\text{SO}_4$ , the maximum specific surface area is 240.900  $\text{m}^2/\text{g}$ , and a high concentration of 3–4 M causes structural degradation and a decrease in surface area [18]. Similarly, Balci (2018) demonstrated that when treated with 2 M  $\text{H}_2\text{SO}_4$ , the surface area doubled from 52.770  $\text{m}^2/\text{g}$  to 131.150  $\text{m}^2/\text{g}$ , and the volume of micropores doubled from 0.0139  $\text{cm}^3/\text{g}$  to 0.0340  $\text{cm}^3/\text{g}$  [74]. At an average concentration (2–4 M), selective cation displacement occurs, which leads to mesoporosity, preserving the basic structure of the layer and increasing the surface area. As published by Yildiz, Aktas and Calimli, at higher concentrations (>4 M), excessive activation leads to partial decomposition of the tetrahedral surface and the formation of amorphous silica, which can actually reduce the surface area and catalytic activity [72–74].

The bentonite activation significantly affects the process results. A systematic study of the effect of temperature showed that 90 °C is the optimal temperature for the activation by  $\text{H}_2\text{SO}_4$ , while the specific surface area of bentonite after 120 min of treatment showed a value of about 110  $\text{m}^2/\text{g}$ . Meanwhile, it was noticed that temperatures below 70 °C result in incomplete activation, and temperatures above 120 °C cause excessive degradation of the structure. The mechanism of activation by sulfuric acid includes several related processes. At low acid concentrations (0.5–1 M), the main mechanism is cation exchange, i.e., cations of alkaline Earth metals ( $\text{Ca}^{2+}$ ,  $\text{Na}^+$ ,  $\text{Mg}^{2+}$ ) are replaced by hydrogen ions ( $\text{H}^+$ ).

Sulfuric acid, nitric acid and hydrochloric acid are widely used in the activation of bentonite. According to the research, the activation of bentonite at a temperature of 90 °C for 2 h was compared at an equivalent rate of  $\text{H}_2\text{SO}_4$  and HCl. Both acids enhance the adsorption and catalytic properties of bentonite, but the degree of destruction of the octahedral layer in activated samples ranged from 11.89% to 20.42%. The basal distance  $d(001)$  increased to 16.95 Å during glycolysis and decreased to 9.70 Å during heat treatment at 500 °C, which indicates a successful modification of the interlayer structure [75].

As demonstrated by Szymaszek et al., nitric acid activation yields the best results for materials requiring high catalytic activity. The formation of an aluminum pillar structure was carried out at 95 °C for 2 h using 0.8 M HCl and  $\text{HNO}_3$ , followed by additional acid treatment with 0.12 M oxalic acid ( $\text{C}_2\text{H}_2\text{O}_4$ ) at 80 °C for 2 h. When using  $\text{HNO}_3$ , higher porosity and an increased interlayer distance were observed compared to HCl, leading to greater catalytic efficiency. After treatment with Al-polycations and subsequent impregnation with 5% Cu and Fe, bentonite activated with  $\text{HNO}_3$  showed efficiency comparable to industrial vanadium oxide catalysts, achieving 90% NO conversion at 300 °C in the selective catalytic reduction of nitrogen oxides [76].

Acid activation is the simplest and most cost-effective bentonite modification method, suitable for large-scale industrial application. However, its main trade-off is the risk of irreversible structural damage at acid concentrations above 2–4 M. For hydrogen production applications specifically, acid activation alone is insufficient—it improves surface area and generates acid sites but does not introduce the metallic active sites (e.g., Ni, Fe) required for efficient C–H bond activation and tar cracking. Therefore, acid activation is most valuable as a pre-treatment step before pillaring or metal impregnation, rather than as a standalone strategy for H<sub>2</sub> production catalysts.

#### 4.2. Alkaline Activation of Bentonite

Alkaline treatment represents another effective method for modifying the properties of bentonite. In studies aimed at modeling environmental conditions, Na-bentonite samples subjected to alkaline activation demonstrated positive results in X-ray diffraction (XRD) analysis, as well as in sorption tests evaluating changes in the mineral composition and water retention capacity of the material. As reported by Liu et al., with increasing temperature and duration of alkaline heat treatment, the content of montmorillonite in bentonite gradually decreases, indicating a significant influence of the alkaline medium on the structure and hydration properties of the material [77].

The effect of alkaline treatment of calcium-containing bentonite during geopolymerization was further investigated by Mekhnache et al. [78]), who examined the use of Na<sub>2</sub>SiO<sub>3</sub>, NaOH and their combinations at different concentrations. Unlike studies focused on structural and mineralogical changes such as montmorillonite content reduction, this work specifically evaluated the influence of alkali concentration and silica fume incorporation on the microstructural, mechanical and thermal performance of the resulting geopolymer material [78]. It was found that an increase in the molarity of alkali promotes the dissolution of the aluminosilicate phase of bentonite and the formation of a sodium-aluminosilicate hydrogel. Potassium hydroxide (KOH) and NaOH are also commonly used agents in the alkaline treatment of bentonite [79,80].

Alkaline treatment of bentonite leads to an increase in specific surface area and porosity, the removal of exchangeable cations Na<sup>+</sup>, Ca<sup>2+</sup>, Mg<sup>2+</sup> and purification from impurities, which ultimately improves the adsorption and catalytic properties of the material, as confirmed through structural and textural characterization of the modified samples [81,82].

During pre-treatment of calcium-containing bentonite (Ca-CB) with a Na<sub>2</sub>CO<sub>3</sub> solution, ion exchange processes occur between Na<sup>+</sup> and Ca<sup>2+</sup>, leading to a decrease in calcium content. It has been shown that the resulting sodium-modified bentonite exhibits higher pore volume and specific surface area compared to natural bentonite [83]. It is proved that the modified bentonite has a higher pore volume and specific surface area than the natural bentonite. Such materials are effectively used to purify water from micro-pollutants and dyes. In research for the modification of bentonite are used such compounds as sodium salts: NaCl, Na<sub>2</sub>CO<sub>3</sub>, Na<sub>4</sub>P<sub>2</sub>O<sub>7</sub> and Na<sub>6</sub>(PO<sub>3</sub>)<sub>6</sub> [84].

Compared to acid activation, alkaline treatment has been less extensively studied for catalytic hydrogen production applications. While it effectively modifies the surface chemistry and promotes ion exchange, it does not generate the Brønsted acid sites that are important for hydrocarbon cracking. NaOH-modified bentonite is more promising for adsorption applications and for supporting base-catalyzed reactions. For H<sub>2</sub> production, alkaline activation is best considered as a complementary step rather than a primary modification strategy.

#### 4.3. Technology of Forming Bentonite Pillars

The introduction of “pillars” (pillarization) is considered as a complex modification strategy that radically changes the bentonite structure by introducing stable inorganic oxide

pillars between the clay layers. This approach makes it possible to preserve the layered structure of the starting material, while simultaneously forming a micro- and mesoporous system with a significantly increased specific surface area, thermal stability and catalytic activity. The most common method for obtaining such structures involves the intercalation of large polyhydroxocomplexes into the interlayer space followed by heat treatment at 400 °C, which results in the formation of stable oxide “pillars” separating the layers [85]. Clays with mixed metal pillars have become widespread such as Al–Fe pillared interlayered clay [86–89]. For instance, the molar ratio of active metals in an intercalating solution is selected to optimize their catalytic efficiency in oxidation reactions in the synthesis of bentonites with Al/Fe pillars.

Aluminum columnar structures are among the most studied and widely used due to the high prevalence of aluminum in nature, its low cost and the high thermal stability of the resulting materials. The process of their preparation is based on the formation of polyoxoaluminium cations using solutions of aluminum salts (usually  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  or  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ) and sodium hydroxide. In particular, Keggin-type structures are formed  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$ .

Although the research showed that the surface area of natural bentonite is about 39 m<sup>2</sup>/g, pillared bentonite as a catalyst with high acidity increased to 120 m<sup>2</sup>/g, and the total acidity increased from 0.056 mmol/g to 0.138 mmol/g. It can be noted that inactivated bentonite with a pillar structure collapses at high temperatures while Al-PILC is particularly resistant to heat (above 900 °C). Polycations are dehydroxylated at temperatures from 300 °C to 600 °C, maintaining stable alumina columns in clay layers.

Muntianu et al. demonstrated that optimization of synthesis conditions can be effectively performed using statistical methods including the ratio of aluminum to bentonite [90]. The specific surface area of aluminum-pillared bentonite increases from 31.1 to 152.8 m<sup>2</sup>/g compared with the natural sample under optimal conditions (aluminum content 12.5 mmol/g and calcination temperature 400 °C). The interlayer distance increases to 17.9 Å and the surface acidity more than doubles from 0.180 to 0.443 mmol/g. The Al/bentonite ratio has a decisive influence on the final properties of the material. With an increase in this parameter from 2.5 to 10 mmol/g, it was determined that the maximum specific surface area (203.3 m<sup>2</sup>/g) is reached at 7.5 mmol/g, whereas for the initial Na-montmorillonite it is 40.09 m<sup>2</sup>/g. The interlayer distance ( $d_{001}$ ) increases from 12.95 to 19.13 Å. A significant increase in porosity is observed according to scanning electron microscopy. However, the introduction of Al ions does not lead to a strictly proportional increase in the specific surface area, which is associated with the saturation of available interlayer positions [91].

Columns made of metal alloy (Al/Fe, Ti, Zr) also have a wide range of applications. The additional metals application can give the product special functionality and further improve its properties. The Al/Fe pillared is of particular note when conducting environmental catalysis due to the redox activity of iron compounds. The studies show that developed carbon-coated iron pillared bentonite electrodes for capacitive ionization. The distance between the layers, the specific surface increases, and many mesopores are formed as a result of the iron pillaring. Carbon packaging further improves the electrical conductivity and ion transport ability. Meanwhile, after synthesizing Al/Fe column bentonite in the study, the resulting Al-Fe-PILC catalyst had a basal distance of 17.81 Å (12.4 Å compared to natural bentonite) and a specific surface area of 173.490 m<sup>2</sup>/g, compared to 19.050 m<sup>2</sup>/g for natural bentonite, which is several times higher. Although it was later observed that the surface area decreased to 92 m<sup>2</sup>/g during adsorption of 1% Pd, it provided catalytic activity for hydrochlorination and oxidation reactions. The fact that dehydroxylation took place at a temperature of about 678 °C indicates a higher thermal stability [21,22].

Titanium-pillared clays have been widely studied for photocatalytic and oxidation applications. Bentonite prepared with titanium pillars modified with iron, copper and silver metals is used to remove bisphenol A. The adsorption and catalytic properties of bentonite prepared with titanium pillaring are improved and the surface area is increased through the physical expansion and stabilization of the interlayer space, which prevents layer collapse and creates a permanently delaminated structure with higher Brunauer–Emmett–Teller (BET) surface area and pore volume; the incorporation of metals such as copper and iron further enhances Brønsted and Lewis surface acidity [92]. In some catalytic applications, zirconium pillaring has shown particular effectiveness. Wahyuningsih et al. demonstrate that Zr-pillared bentonite achieves a surface area of 150 m<sup>2</sup>/g compared to 24.470 m<sup>2</sup>/g for raw bentonite, with a corresponding diethyl ether yield of 93.6% [93].

Thermal stability is one of the notable advantages of pillared clays. Valverde et al. demonstrate that this stability can be further enhanced by the intercalation of cerium and lanthanum into Al-pillared smectites, improving their potential utility as catalysts. The increase in heat resistance of pillared smectites by conversion with cerium and lanthanum has been proven by studies. The resulting pillared clays had basal distances of 16–20 Å and a surface area of 239–347 m<sup>2</sup>/g, with a microporosity of 50–80% of the total surface. Cerium and lanthanum transformations have higher thermal and hydrothermal stability compared to other processed clays, and the conversion with Ce metal is effective in the dehydroxylation process. While natural bentonite undergoes irreversible structural disorders at temperatures above 700–900 °C due to dehydroxylation and layered condensation, pillared bentonites retain the expanded interlayer structure and porosity before and after this temperature. Such thermal stability is very important for high-temperature catalytic applications and to be resistant to multiple circulation thermal cycles [94].

The modification of bentonite through metal pillaring represents an effective strategy for developing heterogeneous catalysts with significantly improved structural and functional properties. The introduction of inorganic oxide pillars between clay layers transforms the natural bentonite structure by creating a stable micro- and mesoporous system with increased specific surface area, enhanced surface acidity, and improved thermal stability. Among the various pillaring approaches, aluminum-based pillars are the most widely studied, offering high thermal resistance and substantial increases in surface area and interlayer spacing. The incorporation of additional metals such as iron, titanium, zirconium, cerium, and lanthanum further expands the functional range of pillared bentonites, enabling their application in oxidation, photocatalysis, and environmental remediation. Mixed metal pillars such as Al/Fe systems demonstrate particular promise in environmental catalysis due to the redox activity of iron, while titanium and zirconium pillared clays show effectiveness in photocatalytic and acid-catalyzed reactions. The thermal stability of pillared bentonites, further enhanced by cerium and lanthanum intercalation, makes these materials suitable for high-temperature catalytic applications. Overall, pillared bentonite materials offer a versatile and promising platform for the design of advanced heterogeneous catalysts combining the natural abundance and structural properties of clay with the targeted catalytic functionality of transition metals.

Among the pillaring strategies reviewed, Al/Fe-PILC represents the most promising approach specifically for hydrogen production applications. The combination of aluminum's thermal stability with iron's redox activity enables both structural integrity at high pyrolysis temperatures and active catalytic cracking of hydrocarbons and tars. The main limitation of pillaring—compared to simple acid activation—is the greater complexity of synthesis and cost. However, for applications requiring repeated use at high temperatures (as in plastic waste pyrolysis), the enhanced thermal stability of pillared bentonites (>678 °C for Al/Fe-PILC vs. structural collapse above 700 °C for natural bentonite) clearly

justifies this investment. Cerium and lanthanum intercalation further extends operational stability, making Ce/La-Al-PILC systems the most thermally robust option reviewed, albeit at higher cost.

#### 4.4. Metal Impregnation and Exchanged Transition Metals

The metal impregnation method is the introduction of catalytically active particles into the bentonite structure, either onto its surface or into interlayer spaces. In many cases, the modification strategy combines impregnation with acid activation or the formation of a columnar structure, which makes it possible to obtain multifunctional materials with improved catalytic properties [76].

Bentonite modification is carried out by impregnation using various metals and their oxides. The introduction of metal ions or oxide forms into the surface and interlayer structure of bentonite leads to a change and improvement of its physico-chemical properties. Metals such as Fe, Cu, Ag, Ti, Zn, Mn, Pb, as well as their oxide forms, are most often used for modification. This contributes to an increase in the number of active centers, a change in structural characteristics and an increase in adsorption and catalytic properties. As a result, such materials are widely used in the processes of adsorption, catalysis and environmental purification.

Bentonites modified with noble metals exhibit high catalytic activity in oxidation and hydrogenation reactions. Herrera-Guzmán et al. demonstrate that bentonite can serve as an effective support for palladium-based catalysts in hydrogenation reactions. A Pd/bentonite catalyst was prepared by incipient wetness impregnation of a Pd(II) salt onto bentonite, followed by reduction to Pd, achieving a metal loading of 1.4%. The catalyst proved effective for the partial hydrogenation of soybean oil at low temperatures of 25 °C and 70 °C under a hydrogen pressure of 3.79 MPa, achieving iodine values of 76 and 71, respectively [95].

Silva et al. demonstrate that impregnation of Pd onto Al/Fe-pillared bentonite produces a bifunctional Pd-Al-Fe-PILC catalyst. The basal spacing increased from 12.4 Å in natural bentonite to 17.05 Å in Pd-Al-Fe-PILC, with a corresponding increase in specific surface area, making it a promising material for hydrodechlorination and oxidation catalytic applications [22].

Amadio et al. demonstrate that bentonites from different origins can be successfully functionalized by impregnation with TiO<sub>2</sub>, Ag, Pd, and Au nanoparticles using imbibition or dipping methods, achieving impregnation efficiencies above 90% in all cases. A thermal pretreatment at 700 °C was found necessary to improve impregnation quality, and both methods resulted in suitable distribution and stability of nanoparticles on the bentonite surface [96].

ZnO/bentonite is widely used in photocatalytic and adsorption processes for effective wastewater treatment [97]. Beyond photocatalysis, the adsorption of Pb<sup>2+</sup> and Cd<sup>2+</sup> on modified bentonite composites occurs primarily through siloxane, hydroxyl and carboxyl surface functional groups, with Ca<sup>2+</sup> interlayer ion exchange further enhancing the overall heavy metal adsorption capacity [98].

Alkali and alkaline Earth metals, in either elemental or ionic form, can be introduced into the interlayer structure of bentonite, where an ion exchange process takes place. During this process, native cations such as Na<sup>+</sup> and Ca<sup>2+</sup> are displaced by Sr<sup>2+</sup> ions, contributing to improved adsorption properties of the material. Beyond ion exchange, the surface hydroxyl groups (–OH) of bentonite—which arise from the structural arrangement of silanol (Si–OH) and aluminol (Al–OH) groups on the clay surface—are capable of forming coordination complexes with strontium ions, further enhancing the overall adsorption capacity [99].

Impregnation with transition metals, in addition to pronounced catalytic properties, is considered an economically more accessible alternative to noble metal supports. Cu-containing pillared bentonites demonstrated high efficiency in the selective catalytic reduction of nitrogen oxides. After acid activation with  $\text{HNO}_3$ , Al-pillared bentonite with 5% Cu content showed up to 90% NO conversion at 300 °C, while 50% conversion was achieved at approximately 190 °C. Nitric acid activation promotes increased porosity and accessibility of interlayer spaces, leading to enhanced catalytic activity and reduced copper oxide crystallite size [76].

Fe-modified bentonite also exhibits high activity in oxidation reactions. Al-pillared bentonite with 5% Fe provides comparable NO conversion relative to copper-containing catalysts but is characterized by lower  $\text{N}_2\text{O}$  formation in the 200–350 °C temperature range. This makes it particularly promising for processes where reduction in nitrous oxide emissions is required.

Copper deposited on bentonite is used for the oxidation of organic pollutants in textile wastewater and, under neutral or alkaline pH conditions, can outperform iron-containing catalysts [100]. Cobalt is used as a transition metal in the synthesis of heterogeneous composite catalysts (for example, from  $\text{CoSO}_4$  and  $\text{CoCl}_2$  salts). Such Co/bentonite catalysts demonstrated total organic carbon removal efficiency from textile wastewater of approximately 25% at 40 °C for 60 min [101].

Among the transition metals explored for catalytic applications, Co and Mn have attracted considerable attention due to their oxidative properties. Ghiaci et al. (2012) showed that Co–Mn nanoparticles immobilized on modified bentonite serve as effective catalysts for the oxidation of p-xylene to terephthalic acid [102]. The introduction of various metal ions into the bentonite structure allows its properties to be tailored for a wide range of processes. For example, Ni/bentonite is used for the partial hydrogenation of jatropha oil biodiesel to improve its oxidative stability [103], while cerium introduced into bentonite can act as a promoter for iron-containing catalysts in environmentally significant reactions [85].

The combination of pillaring (formation of a columnar structure) and metal impregnation methods often leads to a synergistic effect. The pillaring process enables the production of supports with high specific surface area, controlled porosity, and thermal stability, while metal impregnation provides specific catalytic properties. The expanded interlayer spaces in pillared clays promote better metal dispersion and prevent their agglomeration during high-temperature reactions. It has been shown that preliminary acid activation of the support prior to the introduction of aluminum pillars, followed by metal impregnation, allows the creation of highly efficient catalysts for benzene alkylation. Acid treatment increases the number of hydroxyl groups, while the presence of pillars maintains structural integrity and prevents pore collapse during catalytic processes [104].

Among the most commonly used cations in bentonite modification,  $\text{Na}^+$  is particularly valued for its ability to enhance swelling capacity and promote the adsorption of organic molecules. Through electrostatic interactions, Na-modified bentonite facilitates hydrocarbon decomposition and can increase hydrogen yield by up to 23.4%. Its sorption properties can be further improved by incorporating organic compounds such as polyphenols, introduced via intercalation or wet impregnation [105], and biopolymers [106], which broaden the sorption spectrum and improve the environmental safety of the material.

$\text{Fe}^{3+}$  modification introduces Lewis acid sites, increases surface acidity and conductivity, and enables effective reuse of the material due to its low cost and non-toxicity. Iron-modified bentonite has been successfully applied in water treatment and dye removal, including Rhodamine B [107,108], and exhibits high adsorption and photocatalytic performance as a nano-adsorbent [109].

$\text{Al}^{3+}$  similarly generates Lewis acid sites and enhances surface acidity, resulting in strong catalytic activity across diverse processes. Al-modified bentonite demonstrates high selectivity and efficiency, particularly in fluoride removal through enhanced electrostatic interactions and the formation of additional adsorption sites [110].

$\text{Ca}^{2+}$ , naturally abundant in bentonite, stabilizes its structure and increases the number of surface functional groups, providing high adsorption capacity for heavy metals such as  $\text{Pb}^{2+}$  and  $\text{Cr}^{6+}$  [111,112].

Titanium ( $\text{Ti}^{4+}$ ) imparts high photocatalytic activity, promoting free radical generation and facilitating the decomposition of dyes, pesticides, and phenolic compounds [113]. Although unmodified bentonite lacks photocatalytic activity, titanium incorporation improves interfacial contact, and  $\text{TiO}_2$ /bentonite composites have been shown to outperform pure  $\text{TiO}_2$  in photocatalytic efficiency [114].

Transition metals such as  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Ni}^{2+}$ , and  $\text{Co}^{2+}$  possess pronounced redox properties and, upon ion exchange, alter chemical mobility within the interlayer spaces while generating new active sites. These catalysts are notable for their environmental compatibility, reusability, high activity and selectivity, and reduced reaction times [115,116]. Bentonites modified with Ni, Co, and Fe ions are widely applied in hydrogenation, pyrolysis, cracking, methane production, dry methane reforming, and steam reforming of ethanol. Systems incorporating Ni, La, and Ca ions have also been explored in the steam reforming of acetic acid, where bentonite-based materials showed promise as catalysts [47]. Finally, modification with noble metals such as platinum (Pt), palladium (Pd), and ruthenium (Ru) yields materials with high activity in hydrogenation, isomerization, and selective oxidation, combining excellent chemical and thermal stability with cost-effective physicochemical properties through the use of nanoparticles [117].

Among all impregnation-based modifications, Ni-impregnated bentonite stands out as the most relevant for  $\text{H}_2$  production from plastic waste pyrolysis. Nickel's strong capacity for C–H bond activation and its ability to catalyze steam reforming of tars and residues make it the most effective and economical transition metal for this application. The key advantage of bentonite as a Ni support—compared to conventional  $\text{Al}_2\text{O}_3$  or  $\text{SiO}_2$  supports—is its mesoporous structure that helps prevent coke accumulation, combined with its cation exchange capacity that facilitates better Ni dispersion. However, long-term stability under repeated pyrolysis cycles and the risk of Ni sintering at high temperatures remain critical challenges that require further investigation.

#### 4.5. Organic, Silane and Carbon-Based Functionalization

Functionalization with carbon materials is regarded as a new direction in modification that addresses the limitations of traditional bentonite systems, particularly low electrical conductivity and hydrophobicity. This approach opens broad opportunities for application in electrochemical systems and in the adsorption of organic pollutants [118].

Combining a carbon coating with pillared bentonite provides not only high specific surface area and well-developed porosity but also improved electrical properties and chemical stability. Such materials are used to enhance ion conductivity and transport, as well as to increase surface area while preserving the mesoporous structure.

The carbon coating serves several functions: it increases electrical conductivity for electrochemical applications and protects the clay structure from chemical degradation under harsh conditions. In addition, owing to enhanced adsorption properties toward organic molecules, these materials are effectively used for the purification of water from organic pollutants, dyes, and heavy metals.

Modification through the introduction of organic cations (for example, via silylation processes) enables the production of highly hydrophobic organobentonites, which are

effectively used as adsorbents for the removal of organic and inorganic pollutants, including pesticides, herbicides, and pharmaceutical compounds [118,119].

Organosilanes are widely used in the chemical modification of clays due to their ability to hydrolyze with the formation of reactive silanol groups (Si–OH). These groups interact with hydroxyl groups located at the layer edges and outer surface of the clay, forming Si–O–Si (siloxane) bonds between the silane molecules and the clay surface, thus establishing strong covalent linkages with the material. As a result of the modification, new functional groups are introduced, leading to increased surface hydrophobicity.

Bentonite, with its layered structure and swelling capacity, serves as a favorable matrix for the incorporation of silane compounds. Such modification affects pore size, surface hydrophobicity, and adhesion to the substrate, which in turn improves the properties of composite membranes. The study illustrates that bentonite was first treated with aluminum polyoxocations and then silylated with alkylchlorosilanes, yielding silylated pillared clays (SPILC) with high thermal stability. The thermal stability temperatures were 508 °C for octadecyltrichlorosilane (OTS-Al-PILC) and 214 °C for trimethylchlorosilane (TMCS-Al-PILC), which are significantly higher compared to conventional organobentonites [120].

Basak et al. used fluoroalkylsilanes to modify the surface of bentonite membranes in order to increase their hydrophobicity. This chemical fixation ensures reliable anchoring of the silane to the surface. The resulting materials exhibit enhanced hydrophobicity and improved performance in oil-water emulsion separation within composite membranes [121].

Santos et al. noted that compounds such as 3-propylethylenediamintrimethoxysilane and 3-propyldiethylenetriamintrimethoxysilane are relatively rarely used in the silylation of bentonite, whereas 3-aminopropyltriethoxysilane is employed considerably more frequently.

Both aminosilanes are capable of enhancing complexation with metal ions due to the presence of chelating groups. Changes to the clay surface at the molecular level are assessed by various methods, and the resulting materials are used, in particular, for the introduction of Zn(II) ions to create catalysts with antibacterial activity. Although the antibacterial properties of Zn-containing bentonites have long been known, it is suggested that the incorporation of metals into silylated clays may further enhance the effectiveness of such materials [122].

A number of studies have shown that modification of bentonite with quaternary alkylammonium cations significantly enhances its adsorption properties. The use of various modifying compounds—such as hexadecyltrimethylammonium, dodecyltrimethylammonium, and tetramethylammonium—with varying alkyl chain lengths affects the interlayer spacing, structural characteristics, and organophilicity of bentonite. It has been established that the determining factor in adsorption efficiency is not so much the specific surface area as the organophilicity of the material. Bentonite demonstrates high capacity for the removal of both dyes and metal ions from aqueous solutions [123,124].

The use of cetyltrimethylammonium bromide (CTAB) as an organic modifier of natural bentonite for the removal of phenol from aqueous solutions has also been investigated [125]. Among cationic surfactants, CTAB is currently widely used, as its long hydrophobic alkyl chain increases the hydrophobicity of bentonite and promotes the adsorption of organic pollutants. Through intracrystalline swelling and expansion of the polymer matrix, the interlayer spacing increases, which improves the material's properties upon modification with hydrophobic compounds. Among its advantages are cost-effectiveness and an increase in the cation exchange capacity of bentonite [48,126]. Furthermore, the hydroxyl groups present in the structure of bentonite facilitate effective silylation, and several studies have confirmed the successful modification of bentonite with silane compounds using various analytical methods [127]. Overall, the surface modification of bentonite—whether through

cationic surfactants or silane compounds—represents a promising approach for enhancing its adsorption capacity and expanding its applicability in water treatment and composite membrane fabrication.

The functionalization of bentonite with carbon materials and organic compounds represents a versatile and effective strategy for tailoring its physicochemical properties to meet specific application requirements. Carbon coatings enhance electrical conductivity, chemical stability, and adsorption capacity, making modified bentonite suitable for electrochemical systems and the removal of organic pollutants, dyes, and heavy metals. Organosilane modification introduces hydrophobic functional groups through stable covalent Si–O–Si bonds, significantly improving surface hydrophobicity and membrane performance. The use of quaternary alkylammonium cations and cationic surfactants such as CTAB further expands the adsorption capabilities of bentonite by increasing interlayer spacing and organophilicity. Aminosilane-modified bentonites demonstrate additional potential in metal ion complexation and the development of antibacterial materials through the incorporation of Zn(II) ions. Collectively, these modification approaches—whether carbon-based, silane-based, or surfactant-based—substantially broaden the functional versatility of bentonite, establishing it as a promising material for advanced applications in water treatment, membrane fabrication, and environmental remediation.

Carbon-based and organic modification strategies are less relevant for hydrogen production applications compared to acid activation, pillaring, and metal impregnation. Their primary value lies in environmental remediation and membrane fabrication. However, carbon-coated Fe-pillared bentonite electrodes represent an interesting emerging direction where conductivity enhancement could potentially benefit electrochemical hydrogen production pathways. Organomodification should therefore not be considered a competing strategy for H<sub>2</sub> production but rather a complementary approach for multifunctional bentonite composites.

## 5. Comparative Analysis of Property Improvements

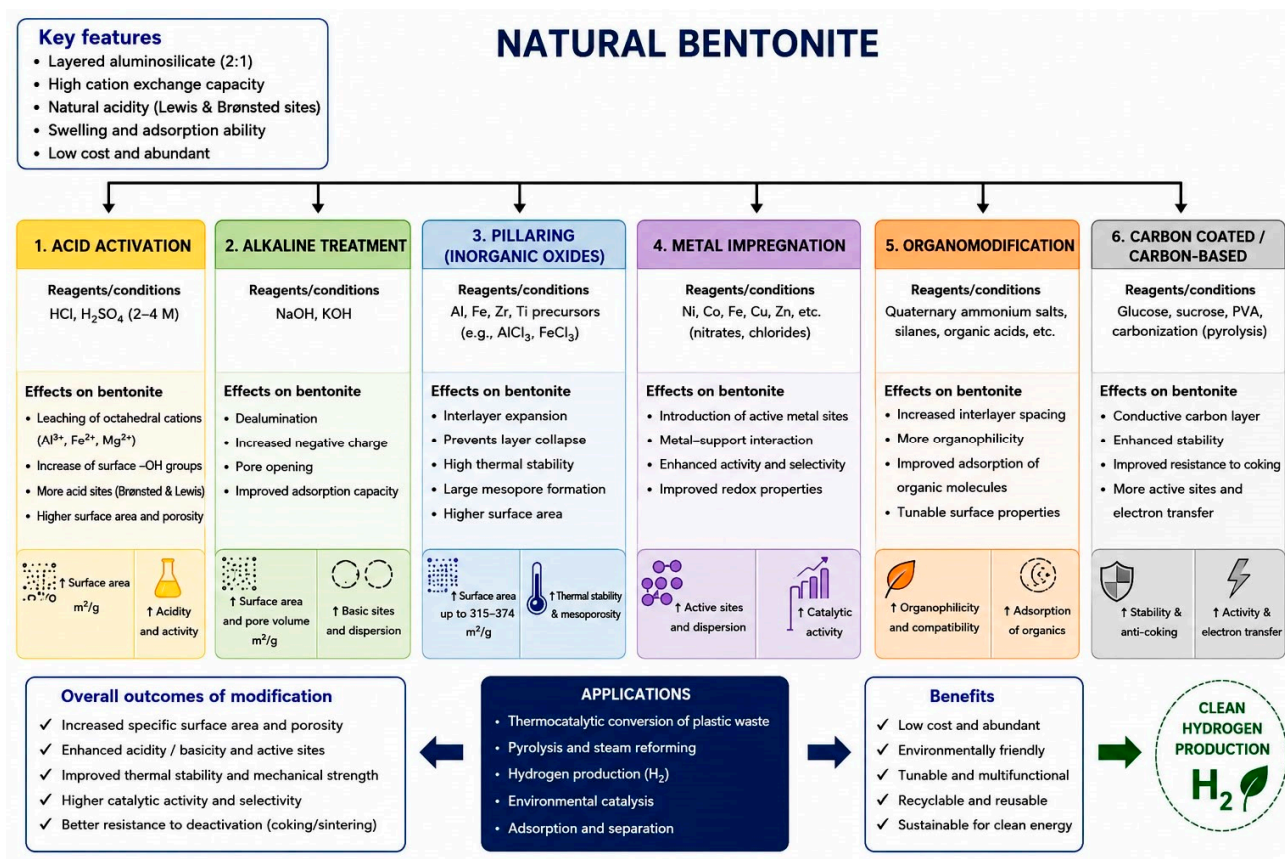
### 5.1. Property Improvements Induced by Bentonite Modification

Bentonite, owing to its widespread natural occurrence, low cost, chemical and mechanical stability, high specific surface area, and favorable structural characteristics, is a promising material for use as an adsorbent, catalyst, and component of composite systems. Its high adsorption properties, cation exchange capacity, and swelling ability make it particularly attractive for a wide range of applications.

In the context of plastic waste conversion, these intrinsic properties determine the suitability of bentonite as a catalyst support by influencing hydrocarbon cracking, reforming reactions, hydrogen formation, and catalyst stability. To enhance the functional characteristics of bentonite, various chemical modification methods are employed, including metal impregnation and organic modification using cationic surfactants. These approaches make it possible to improve structural properties, increase surface hydrophobicity and organophilicity, and enhance the catalytic and adsorption characteristics of the material.

Figure 3 illustrates the main modification strategies of bentonite used to enhance its physicochemical and catalytic properties. The modification routes include acid activation, alkaline treatment, pillaring with inorganic oxides, metal impregnation, organomodification and carbon-based functionalization. Acid activation increases the specific surface area and generates additional Brønsted and Lewis acid sites through the removal of octahedral cations. Alkaline treatment promotes delamination and pore opening, improving adsorption properties and surface charge characteristics. Pillaring with metal oxides such as Al, Fe, Ti, and Zr stabilizes the layered structure, expands the interlayer spacing, and enhances thermal stability and mesoporosity. Metal impregnation introduces catalytically

active sites and improves redox and catalytic performance, particularly for thermocatalytic conversion reactions. Organomodification using surfactants and silane compounds increases hydrophobicity and affinity toward organic molecules, while carbon coating enhances electrical conductivity, resistance to coking, and structural stability. Overall, these modification strategies significantly improve the catalytic performance of bentonite by tailoring acidity, porosity, redox properties, and metal dispersion, thereby enhancing its suitability for plastic waste conversion into hydrogen-rich gas.



**Figure 3.** Overview of bentonite modification strategies, including acid activation, alkaline treatment, pillaring, metal impregnation, organomodification, and carbon-based functionalization, and their effects on the physicochemical and catalytic properties of bentonite.

Comparative analysis of the reviewed studies shows that organic modification of bentonite—particularly silylation and quaternary ammonium treatment—significantly enhances hydrophobicity and adsorption capacity toward organic pollutants [121,124], while metal-modified bentonites demonstrate superior catalytic activity and redox properties suitable for oxidation and reduction reactions [102,108]. Thus, the selection of modification method directly determines the functional properties of the resulting material and should be guided by the specific requirements of the target application [13,56].

To clearly correlate bentonite modification strategies with catalytic performance in plastic waste conversion, Table 4 summarizes the principal physicochemical changes and their implications for hydrogen-rich gas production. It provides a systematic comparison of all modification methods reviewed in this article, including their effects on Brunauer–Emmett–Teller (BET) surface area, active site generation, H<sub>2</sub> production performance, thermal stability, and key limitations. Because the reported BET surface areas vary considerably among different bentonite deposits and activation protocols, the values summarized in Table 4 should be regarded as representative literature ranges rather than fixed values. The reported values depend on the origin of bentonite, acid type, acid concentration, activation

temperature, and treatment time. H<sub>2</sub> production performance is evaluated relative to unmodified bentonite. This comparison is intended to assist researchers in selecting the most appropriate modification strategy for hydrogen production from plastic waste and other catalytic applications.

**Table 4.** Comparative summary of bentonite modification methods for catalytic and hydrogen production applications.

| Modification Method                                    | Representative BET Surface Area (m <sup>2</sup> /g) | Main Active Sites Generated | Evidence for Plastic-to-H <sub>2</sub> Production | Representative Catalytic Role                                                                                         | Key Limitation                                            |
|--------------------------------------------------------|-----------------------------------------------------|-----------------------------|---------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------|
| Acid activation (H <sub>2</sub> SO <sub>4</sub> , HCl) | 130–379                                             | Brønsted + Lewis acid sites | Indirect                                          | Improves polymer cracking and serves as pretreatment before metal loading                                             | Structural damage at excessive acid concentration         |
| Alkali treatment (NaOH, KOH)                           | Moderate increase                                   | Basic sites                 | Limited                                           | Surface modification and catalyst precursor preparation                                                               | Few studies on plastic-to-H <sub>2</sub> conversion       |
| Al-pillaring                                           | 120–203                                             | Strong Lewis acid sites     | Indirect                                          | Stabilizes porous structure and facilitates diffusion during cracking                                                 | Complex synthesis                                         |
| Al/Fe-pillaring                                        | ~173                                                | Lewis acid + redox sites    | Limited–Direct                                    | Enhances tar cracking and reforming through combined acidity and redox activity                                       | Possible Fe leaching                                      |
| Acid activation + pillaring                            | 315–374                                             | Brønsted + Lewis acid sites | Indirect                                          | Highly porous support for subsequent metal impregnation                                                               | Multi-step preparation                                    |
| Ni impregnation                                        | Variable                                            | Metallic Ni + redox sites   | Direct                                            | Steam reforming, dry reforming and dehydrogenation for hydrogen-rich gas production                                   | Coke formation and metal sintering                        |
| Na-modification                                        | Moderate                                            | Ion-exchange sites          | Indirect (biomass evidence)                       | Improved hydrogen formation reported for biomass pyrolysis (+23.4% H <sub>2</sub> ); plastic evidence remains limited | Plastic-to-H <sub>2</sub> data are scarce                 |
| Organomodification (silylation, CTAB)                  | Moderate increase                                   | Organic functional groups   | No direct evidence                                | Adsorption and polymer compatibility                                                                                  | Unsuitable for high-temperature H <sub>2</sub> production |
| ZnO/TiO <sub>2</sub> composite                         | Moderate increase                                   | Photocatalytic/redox sites  | Emerging                                          | Photocatalytic reforming and oxidation                                                                                | Requires UV irradiation                                   |

BET surface area values are representative literature ranges and depend on bentonite mineralogy, acid concentration, activation temperature, and treatment conditions. The “Evidence for plastic-to-H<sub>2</sub> production” column reflects the level of direct experimental support available in the reviewed literature rather than a quantitative ranking of catalytic performance.

The comparison presented in Tables 4 and 5 demonstrates that bentonite modification governs hydrogen-production performance primarily through changes in acidity, pore architecture, thermal stability, metal dispersion, and catalyst deactivation resistance.

**Table 5.** Critical comparison of bentonite modification strategies for catalysis and hydrogen-rich gas formation from plastic waste.

| Modification                         | Primary Physicochemical Effect                                                          | Mechanistic Role in Plastic-to-H <sub>2</sub> Conversion                                                                              | Principal Catalytic Application                                                   | Suitability for Plastic-to-H <sub>2</sub>                                     | Key Limitation                                                                         |
|--------------------------------------|-----------------------------------------------------------------------------------------|---------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|-------------------------------------------------------------------------------|----------------------------------------------------------------------------------------|
| Acid activation                      | Leaching of octahedral cations, increased mesoporosity, stronger Brønsted/Lewis acidity | Promotes polymer cracking and formation of light hydrocarbons that are subsequently reformed to H <sub>2</sub>                        | Cracking, esterification, alkylation, pretreatment before metal loading           | Medium as a support pretreatment; Low as a standalone H <sub>2</sub> catalyst | Excessive acid treatment damages the layered structure and may increase coke formation |
| Na exchange/alkaline treatment       | Swelling, ion exchange, increased basicity and surface charge                           | Improves dispersion of active metals and facilitates catalyst preparation but contributes only indirectly to H <sub>2</sub> formation | Adsorption, rheology modification, base catalysis, catalyst precursor preparation | Low–Medium; mainly useful as a preparatory step                               | Limited direct evidence for plastic-to-H <sub>2</sub> conversion                       |
| Al pillaring                         | Expanded interlayer galleries, enhanced Lewis acidity, improved thermal stability       | Improves diffusion of pyrolysis vapours and stabilizes catalyst structure during high-temperature reforming                           | Solid-acid catalysis, stable catalyst supports                                    | Medium–High, particularly with Ni catalysts                                   | Synthesis complexity and reproducibility                                               |
| Al–Fe/Ti/Zr/Ce–La pillaring          | Mesoporosity combined with redox, photocatalytic or oxygen-storage functions            | Enhances tar cracking, reforming reactions and catalyst durability through combined acidity and redox activity                        | Oxidation, tar cracking, high-temperature catalysis                               | High for Al–Fe/Ni systems; Medium for other pillared materials                | Metal leaching, higher synthesis cost                                                  |
| Ni impregnation                      | Metallic reforming and dehydrogenation sites                                            | Catalyzes steam reforming, dry reforming, methane reforming and dehydrogenation, directly increasing H <sub>2</sub> production        | Plastic pyrolysis–reforming, tar cracking, H <sub>2</sub> -rich syngas production | Very High when coke formation is controlled                                   | Coke deposition, sintering, poisoning by Cl and S compounds                            |
| Ni–Fe or promoted Ni                 | Bimetallic reforming sites, improved oxygen mobility, modified carbon formation         | Enhances reforming and water–gas shift reactions while suppressing coke formation and improving catalyst stability                    | Plastic pyrolysis–reforming, tar conversion                                       | Very High; currently the most promising approach                              | Requires optimization of metal ratio, preparation method and regeneration              |
| Organosilane/surfactant modification | Increased hydrophobicity and organophilicity                                            | Improves adsorption of organic molecules but contributes little to thermocatalytic H <sub>2</sub> generation                          | Adsorbents, membranes, polymer nanocomposites                                     | Low for high-temperature H <sub>2</sub> production                            | Organic modifiers decompose at elevated temperatures                                   |
| Carbon coating/carbon hybrids        | Improved conductivity, hydrophobicity, potential coke suppression                       | May improve electron transfer and catalyst stability; evidence for plastic-to-H <sub>2</sub> conversion remains limited               | Electrochemical systems, adsorbents, hybrid catalyst supports                     | Emerging; requires further validation                                         | Carbon coating may partially block active clay sites                                   |

### 5.2. Mechanistic Relationship Between Bentonite Modification and Hydrogen-Rich Gas Production

The catalytic role of modified bentonite depends on both the modification strategy and the chemical composition of the plastic feedstock. Acid activation generates additional Brønsted and Lewis acid sites that promote protonation of olefins, carbenium-ion formation,  $\beta$ -scission, and isomerization reactions. For polyolefins such as polyethylene (PE) and polypropylene (PP), these reactions accelerate depolymerization into lighter hydrocarbons that are subsequently reformed over metallic active sites to produce hydrogen-rich gas. However, excessive acidity may also promote secondary aromatization and coke formation, thereby decreasing catalyst lifetime.

Metal impregnation, particularly with Ni or Ni-Fe, provides active reforming and dehydrogenation sites that catalyze steam reforming, dry reforming, methane reforming, and the water-gas shift reaction. Consequently, Ni-modified bentonite exhibits the greatest potential for hydrogen-rich gas production from PE and PP because it combines efficient hydrocarbon cracking with rapid conversion of light hydrocarbons into  $H_2$ .

Pillared bentonites improve catalytic performance mainly through structural stabilization. Expanded interlayer galleries and increased mesoporosity facilitate diffusion of waxy intermediates, reduce diffusion limitations, and improve dispersion of impregnated Ni particles. These effects are especially beneficial during continuous plastic pyrolysis-reforming, where catalyst stability and resistance to pore blockage are critical.

The influence of catalyst modification also depends on polymer chemistry. Polystyrene (PS) readily forms aromatic compounds that tend to generate coke on highly acidic catalysts; therefore, moderate acidity combined with well-dispersed Ni or Ni-Fe particles is preferable. Polyethylene terephthalate (PET) produces oxygenated compounds that can undergo steam reforming and water-gas shift reactions, whereas polyvinyl chloride (PVC) releases HCl during decomposition, which may poison metallic active sites and therefore requires dechlorination or chlorine-tolerant catalyst systems.

Overall, the available evidence demonstrates that acid activation primarily enhances hydrocarbon cracking, whereas Ni- or Ni-Fe-modified acid-activated or pillared bentonites provide the most effective combination of acidity, metal dispersion, reforming activity, coke resistance, and catalyst stability for hydrogen-rich gas production from plastic waste.

### 5.3. Catalytic Pathways for Plastic Waste Conversion over Modified Bentonite

Plastic conversion over modified bentonite involves a network of thermal and catalytic steps. Polyolefins initially undergo random chain scission, producing macroradicals, waxes, alkanes and alkenes. Acid sites can protonate alkenes, generate carbenium-ion intermediates, and promote beta-scission, isomerization, oligomerization and aromatization. These reactions decrease molecular weight and can increase gasoline-range hydrocarbons. However, strong acidity or long residence time can also increase aromatics, polyaromatics and coke.

Hydrogen-rich gas formation requires additional reactions beyond cracking. Steam reforming of hydrocarbons and oxygenates produces  $H_2$  and CO; the water-gas shift reaction converts CO and water into  $H_2$  and  $CO_2$ ; dry reforming consumes  $CO_2$  and hydrocarbons to form syngas; dehydrogenation releases  $H_2$  from hydrocarbons but may leave carbonaceous residues; and methane cracking can produce  $H_2$  and solid carbon. Nickel catalyzes many of these transformations, explaining why Ni-modified supports dominate hydrogen-production studies. Iron can influence water-gas shift and carbon morphology, while basic promoters such as Ca, Mg or La can enhance  $CO_2$  adsorption, coke gasification or metal dispersion [8–12,47,48,128].

Bentonite contributes through support effects. Mesoporosity provides diffusion paths for waxy intermediates. Acid sites crack large molecules before they reach metallic reform-

ing sites. Cation-exchange capacity and hydroxyl groups can anchor metal precursors. Pillars can keep the pore structure open during high-temperature treatment. These properties can improve the balance between cracking and reforming. If acidity is too low, heavy waxes and tars may pass through unconverted. If acidity is too high, coke may form before vapors reach Ni sites. If Ni particles are too large, methane formation and carbon deposition may dominate. Therefore, the optimal catalyst is likely to have moderate acidity, accessible mesoporosity and well-dispersed reducible Ni or Ni-Fe sites.

Hierarchical pore architecture is also essential for efficient mass transfer during plastic pyrolysis. Macropores facilitate transport of bulky polymer-derived waxes, mesopores improve diffusion of intermediate hydrocarbons, and micropores provide abundant catalytic active sites. Optimizing this hierarchical pore network reduces diffusion limitations, suppresses secondary coke formation, and improves contact between hydrocarbons and metallic reforming sites. Therefore, future catalyst design should focus not only on increasing BET surface area but also on tailoring pore-size distribution to maximize hydrogen productivity.

Catalyst deactivation by coke remains one of the principal challenges in plastic-to-hydrogen processes. Coke originates from secondary polymerization and condensation of aromatic intermediates formed during cracking, particularly from styrene-rich vapors derived from PS. Strong Brønsted acidity accelerates aromatization and polycondensation, whereas insufficient metal dispersion slows reforming reactions and promotes carbon accumulation. Acid-activated bentonite alone therefore tends to exhibit faster deactivation than Ni-modified systems. The incorporation of Ni or Ni-Fe facilitates continuous reforming of carbonaceous intermediates into CO and H<sub>2</sub>, thereby suppressing coke formation. Nevertheless, excessive metal particle growth or pore blockage during prolonged operation may eventually reduce catalyst activity.

The mechanism also depends on polymer identity. PE and PP require C–C and C–H activation and generate saturated/unsaturated hydrocarbons. PS produces aromatics and styrene-rich vapors, which can coke rapidly on strong acid sites. PET introduces oxygenates and CO<sub>x</sub>; its reforming may benefit from catalysts developed for acetic-acid or bio-oil model compounds. PVC, even at low concentrations, releases HCl and requires dechlorination or guard beds. Mixed plastic feedstocks therefore require catalyst systems, not a single catalyst: a pretreatment/dechlorination stage, a pyrolysis stage, a cracking/reforming catalyst and possibly a membrane or pressure-swing adsorption stage for H<sub>2</sub> purification.

Besides coke formation, catalyst poisoning by chlorine and sulfur compounds represents another important challenge. During PVC pyrolysis, HCl released from the polymer can react with metallic Ni sites to form nickel chlorides, decreasing reforming activity and accelerating catalyst deactivation. Sulfur-containing impurities similarly poison active metal sites by forming stable sulfides. Current studies therefore emphasize feed pretreatment, dechlorination, sulfur removal, and the development of chlorine-tolerant catalyst formulations as important directions for industrial application.

To complement the qualitative comparison presented in Tables 4 and 5, Table 6 summarizes representative experimental studies on hydrogen-rich gas production from plastic waste over bentonite-based catalysts. Because the reported hydrogen performance is expressed using different metrics (e.g., H<sub>2</sub> concentration, yield, or selectivity) and was obtained under different reactor configurations and operating conditions, the data are presented as reported in the original publications rather than being directly compared quantitatively.

As summarized in Table 6, bentonite- and montmorillonite-based catalysts demonstrate a clear relationship between catalyst modification strategy and hydrogen-production performance. Within the Co/Ni-modified montmorillonite series, bimetallic Co/Ni-

pillaring produced the highest reported hydrogen performance (42.0 vol% H<sub>2</sub> concentration), corresponding to an approximately 1.9- to 2.3-fold improvement compared with the respective monometallic Co- (18.0 vol%) and Ni-modified (22.0 vol%) catalysts under identical feedstock and reaction conditions (post-consumer film waste, 480 °C). This result highlights the synergistic effect of bimetallic pillaring on hydrogen formation. Similarly, within the metal oxide-modified bentonite series, MnO<sub>2</sub> modification resulted in the highest reported hydrogen performance (15.544 vol% H<sub>2</sub> concentration), approximately four times higher than that of unmodified bentonite (3.811 vol%) and 3.2 times higher than that of TiO<sub>2</sub>-modified bentonite (4.885 vol%) under identical HDPE pyrolysis conditions at 750 °C, indicating a substantially stronger promotion of hydrogen-generating pathways. In contrast, Fe-pillared montmorillonite (Fe-PILC) exhibited the highest reported hydrogen performance among all catalysts summarized in Table 6 (47.7 vol% H<sub>2</sub> concentration). However, because this result was obtained using a different feedstock (mixed plastics including PS and PET) and different reaction conditions, it should not be directly compared quantitatively with the other catalyst systems. Nevertheless, it demonstrates the strong potential of Fe-based pillared bentonite catalysts for hydrogen-rich gas production.

**Table 6.** Representative studies reporting hydrogen-rich gas production over bentonite- and montmorillonite-based catalysts.

| No. | Catalyst                    | Plastic Feedstock        | Process             | Temperature (°C) | Reported H <sub>2</sub> Performance Metric | Main Findings                                                       | Ref.  |
|-----|-----------------------------|--------------------------|---------------------|------------------|--------------------------------------------|---------------------------------------------------------------------|-------|
| 1   | Co/MMT                      | Post-consumer film waste | Catalytic pyrolysis | 480              | 18.0 vol% H <sub>2</sub> concentration     | Higher H <sub>2</sub> concentration than non-catalytic pyrolysis    | [129] |
| 2   | Ni/MMT                      | Post-consumer film waste | Catalytic pyrolysis | 480              | 22.0 vol% H <sub>2</sub> concentration     | Higher H <sub>2</sub> concentration than Co/MMT                     | [129] |
| 3   | Co/Ni-PILC                  | Post-consumer film waste | Catalytic pyrolysis | 480              | 42.0 vol% H <sub>2</sub> concentration     | Synergistic effect of bimetallic pillaring                          | [129] |
| 4   | Bentonite                   | HDPE                     | Catalytic pyrolysis | 750              | 3.811 vol% H <sub>2</sub> concentration    | ≈3.3-fold increase vs. thermal pyrolysis                            | [130] |
| 5   | TiO <sub>2</sub> /Bentonite | HDPE                     | Catalytic pyrolysis | 750              | 4.885 vol% H <sub>2</sub> concentration    | Higher than raw bentonite                                           | [130] |
| 6   | MnO <sub>2</sub> /Bentonite | HDPE                     | Catalytic pyrolysis | 750              | 15.544 vol% H <sub>2</sub> concentration   | Highest H <sub>2</sub> concentration among oxide-modified catalysts | [130] |
| 7   | Fe-PILC                     | Mixed plastics (PS, PET) | Catalytic pyrolysis | 500              | 47.7 vol% H <sub>2</sub> concentration     | Highest reported H <sub>2</sub> concentration in this comparison    | [131] |

Note: Different studies report hydrogen performance using different metrics, including H<sub>2</sub> concentration (vol%), H<sub>2</sub> yield (mol kg<sup>−1</sup> plastic or wt%), H<sub>2</sub> selectivity, or gas composition. Therefore, the values presented in this table are reported exactly as given in the original publications and are not directly comparable quantitatively.

Catalyst regeneration is another important consideration for practical application. The limited studies currently available indicate that bentonite-based catalysts can recover a substantial proportion of their catalytic activity after oxidative coke removal; however, repeated regeneration cycles may gradually decrease acidity, reduce surface area through partial pore collapse, and promote metal sintering. Consequently, catalyst lifetime and regeneration stability remain insufficiently investigated for plastic-to-hydrogen processes and represent an important direction for future research.

These within-series comparisons demonstrate that, although the reviewed studies report hydrogen performance using different metrics (e.g., H<sub>2</sub> concentration, yield, or

selectivity) and different reactor configurations, meaningful quantitative comparisons can be made when identical reaction conditions are employed. Therefore, the relative improvements associated with specific modification strategies, such as bimetallic pillaring or transition-metal oxide loading, provide a more reliable basis for evaluating catalyst effectiveness than qualitative descriptors alone.

## 6. Deactivation, Regeneration and Stability

Modified bentonites demonstrate high efficiency in environmental catalysis, particularly in air and water purification. In selective catalytic reduction processes, they play an important role in controlling NO<sub>x</sub> emissions from stationary sources and diesel engines. Pillared bentonites with mixed Al–Fe oxides function as Fenton-type catalysts in the oxidation of organic water pollutants in the presence of H<sub>2</sub>O<sub>2</sub>, where iron provides redox activity while the pillared structure ensures high specific surface area and stability [23]. Beyond these applications, they are also employed in catalytic wet peroxide oxidation of organic pollutants; for example, acid-activated bentonite treated with sulfuric acid showed high efficiency in phenol oxidation, where the increase in specific surface area, porosity, and acidity contributes to enhanced catalytic activity [74].

In industrial organic synthesis, these materials are widely used in the alkylation of benzene with olefins to produce linear alkylbenzenes—key precursors for surfactants. Acid-activated aluminum-pillared bentonites provide an optimal combination of acidity and surface properties, enhancing catalytic activity [104].

In esterification reactions used in the production of flavoring agents and polymers, organobentonites modified with quaternary ammonium salts are effective catalysts. For example, such materials increase acetic acid conversion by 20–30% in esterification with n-butanol. Optimal performance was achieved at 130 °C with an alcohol-to-acid molar ratio of 2.5:1, a reaction time of four hours, and a catalyst loading of 0.4 g [132].

Owing to their high specific surface area, thermal stability, and acidity, pillared bentonites can be considered as an alternative to conventional solid acid catalysts [133]. In addition, metal-modified bentonites are actively used in hydrocracking and hydroconversion processes, for example, in the conversion of vegetable oils to bio-gasoline and in hydroconversion reactions of n-decane.

Acid-activated bentonites are widely used for bleaching vegetable and animal oils as well as beverages. Treatment with H<sub>2</sub>SO<sub>4</sub> simultaneously increases specific surface area and porosity, which improves the bleaching properties of the material. A number of studies confirm that it is the activation process that determines the enhanced adsorption efficiency of such clays [90].

A generalized analysis of the research shows that optimal modification strategies depend to a large extent on the intended application and the required properties of the material. For tasks requiring high specific surface area and well-developed porosity, the most effective method is acid activation of bentonite, which allows for a significant increase in specific surface area values. In the preparation of pillared bentonites, the choice of metal should be guided by specific catalytic requirements: aluminum is used for acid catalysis, iron for redox reactions, and titanium for photocatalytic processes. For the remediation of environments contaminated with organic and inorganic substances, organobentonites are the most effective, providing high adsorption capacity. Combined systems that integrate pillaring (to increase specific surface area and structural stability) with organic modification (to enhance affinity for organic compounds) can be regarded as versatile adsorbents for environmental remediation tasks [122]. Silylated pillared clays offer particular advantages in cases where high thermal stability of organic functional groups is required [125]. Acid activation of clays on its own provides significant improvement of physicochemical prop-

erties at minimal cost, including a manifold increase in specific surface area, making this method suitable for large-scale application [134,135].

Catalyst deactivation is the decisive barrier between promising laboratory conversion and industrially useful plastic-to-hydrogen technology. In plastic pyrolysis and reforming, deactivation occurs through coke deposition; pore blockage; metal sintering; oxidation/reduction cycling; poisoning by chlorine, sulfur, nitrogen additives or metals; and mechanical attrition. Bentonite-based catalysts are not immune to these problems. Their advantage is the possibility of using a low-cost support with larger pores and ion-exchange anchoring, but stability still has to be demonstrated quantitatively [9–12].

Coke can be beneficial or harmful depending on its morphology and process objective. Encapsulating coke blocks metal particles and acid sites. Filamentous carbon can leave metal tips exposed for longer and may form valuable carbon nanotubes in some Ni-Fe systems, although this is not always desired in a hydrogen process. The support and promoter can influence which carbon form dominates. Fe, Ni-Fe interactions, La or Ca basicity, and oxygen storage components can all shift coke behavior. Therefore, spent catalyst characterization by thermogravimetric analysis (TGA), Raman spectroscopy, TEM/SEM, XRD and temperature-programmed oxidation should be routine.

Regeneration should not be treated as a minor experimental detail. Industrial pyrolysis/reforming catalysts require repeated cycles of coking and oxidation or steam regeneration. Acid-activated bentonite may lose crystallinity under severe treatment. Pillared bentonite is more stable but may suffer metal migration. Organomodified bentonites are generally unsuitable for repeated high-temperature regeneration because the organic moieties decompose. A strong review article should therefore recommend standard reporting as follows: time-on-stream curves, at least three regeneration cycles, post-regeneration BET/XRD/TPR data, metal particle-size changes, coke amount and gas composition after each cycle.

## 7. Kazakhstan and Regional Relevance of Bentonite-Based Catalysts for Plastic Waste Valorization

The motivation for studying low-cost bentonite catalysts is particularly strong in regions where plastic waste management, petrochemical development and natural clay resources intersect. Kazakhstan has growing polymer consumption and developing petrochemical capacity, while plastic waste disposal remains environmentally challenging. A national or regional strategy for circular plastics cannot rely only on mechanical recycling because mixed, contaminated and aged plastics require chemical or thermochemical routes. Bentonite-based catalysts are attractive because they may be sourced, modified and regenerated at lower cost than many synthetic supports, while aligning with local mineral-resource utilization.

For Kazakhstan and the Caspian region, the most practical near-term application is unlikely to be pure hydrogen from mixed plastics in a single step. A more realistic pathway is staged valorization: sorting and dechlorination; pyrolysis of polyolefin-rich fractions; catalytic upgrading of waxes and vapors over acid-activated or pillared bentonite; reforming of gases and light liquids over Ni- or Ni-Fe/bentonite; and purification of hydrogen-rich gas using established separation technologies. This pathway also allows integration with existing oil-refining, gas-processing and petrochemical infrastructure.

The environmental argument must be supported by life-cycle analysis. Acid activation consumes mineral acid and produces acidic wastewater. Metal impregnation uses nickel salts and requires reduction. Regeneration produces CO<sub>2</sub> and may release pollutants if chlorine-containing plastic is present. Therefore, bentonite catalysts should be evaluated not only by activity but also by acid consumption, wastewater treatment, catalyst lifetime,

recoverable metal content and net greenhouse-gas balance relative to incineration, landfill, mechanical recycling and conventional hydrogen production.

## 8. Research Gaps and Future Directions

Research gaps and future directions stemming from this study include the following:

1. Direct plastic-to-H<sub>2</sub> evidence over bentonite is still limited. Most bentonite studies focus on liquid fuels, adsorption or model compounds. Future work should test PE, PP, PS, PET and mixed plastic feeds under identical conditions and report H<sub>2</sub> yield in comparable units.
2. Catalyst design should move from single modification to integrated architecture. The most promising systems are likely acid-activated or pillared bentonite with well-dispersed Ni or Ni-Fe and suitable promoters such as La, Ca, Ce, Mg or Zn.
3. Acidity must be optimized, not maximized. Strong acid sites can improve cracking but also accelerate aromatization and coke formation. Pyridine-FTIR, NH<sub>3</sub>-temperature-programmed desorption (TPD) and product analysis should be used to define optimal Brønsted/Lewis acid balance.
4. Bentonite origin and purification need standardization. Clay mineralogy, accessory minerals and exchangeable cations strongly affect modification. Papers should report XRF/XRD/CEC and purification methods before comparing catalysts.
5. Poly(vinyl chloride) (PVC) and additives must be addressed. Real waste contains chlorine, sulfur, nitrogen, fillers, pigments and metals. Catalyst tolerance and guard-bed strategies should be studied explicitly.
6. Regeneration and scale-up should be included early. Kilogram-scale pellet studies are valuable, but hydrogen-focused work also needs shaped catalysts, attrition resistance, pressure drop, regeneration cycles and pilot reactor data.
7. Sustainability metrics must accompany catalytic metrics. Techno-economic analysis and life-cycle assessment should include catalyst synthesis, acid neutralization, metal recovery, reactor heat demand and H<sub>2</sub> purification.
8. Electrochemical plastic waste conversion represents an emerging complementary pathway for plastic valorization and should be further explored alongside established thermochemical technologies. The potential use of bentonite-based materials in such systems may also be considered in future studies.

## 9. Conclusions

This review provides a comprehensive analysis of bentonite modification strategies and their application in heterogeneous catalysis, with particular emphasis on hydrogen production from the thermocatalytic conversion of polymer waste. Bentonite, owing to its layered aluminosilicate structure, high cation exchange capacity, natural abundance, and low cost, represents a highly promising platform for the development of advanced heterogeneous catalysts and adsorbents.

Among the modification approaches examined, acid activation—particularly with sulfuric acid at concentrations of 2–4 M—remains the most widely adopted and cost-effective pretreatment, enabling a two- to fivefold increase in specific surface area, from approximately 40–53 m<sup>2</sup>/g in natural bentonite to 131–241 m<sup>2</sup>/g in activated forms. Pillaring with aluminum-based and mixed metal oxide systems further raises the surface area to 120–374 m<sup>2</sup>/g while improving thermal stability and broadening the functional range to include redox, photocatalytic, and high-temperature applications. Metal impregnation, especially with Ni and Ni-Fe combinations, constitutes the most directly relevant strategy for hydrogen-rich gas formation, as it introduces active reforming and dehydrogenation sites. Organic and silane functionalization, while valuable for adsorption and

environmental remediation, are generally not primary strategies for high-temperature hydrogen production.

The comparative analysis presented in this review demonstrates that the catalytic performance of modified bentonite in plastic waste conversion is governed by the synergistic effects of surface acidity, pore structure, metal dispersion, and thermal stability. These properties collectively determine hydrocarbon cracking efficiency, reforming activity, hydrogen yield, catalyst stability, and resistance to coke formation.

In catalytic applications, modified bentonites have demonstrated performance comparable to or exceeding those of conventional industrial catalysts across selective catalytic reduction, esterification, alkylation, and Fenton-type oxidation processes. From the perspective of hydrogen production specifically, Ni-modified and Na-modified bentonite variants have shown particular promise; Na-modified bentonite increased hydrogen yield by up to 23.4% in biomass pyrolysis, while NiZnAlO<sub>x</sub>-type formulations supported on bentonite offer a compelling direction for deactivation-resistant catalysts in large-scale plastic waste valorization.

Nevertheless, the evidence base for direct plastic-to-H<sub>2</sub> production over bentonite remains incomplete. Long-term stability and regenerability under industrial conditions require further systematic investigation, and the optimization of multi-step modification protocols remains sensitive to the mineralogical composition of the starting material. Furthermore, because the reviewed studies were conducted using different bentonite sources, modification procedures, reaction conditions, and characterization methods, a direct quantitative statistical analysis was not feasible. Therefore, the comparative assessment presented in this review is qualitative and based on critical evaluation of the published literature. Future research should prioritize Ni- and Ni-Fe-modified acid-activated or pillared bentonite systems, hierarchical pore engineering, the optimization of acid-metal synergy, resistance to chlorine and sulfur poisoning, and catalyst regeneration over multiple reaction cycles. In addition, standardized reporting of hydrogen-performance metrics (yield, selectivity, gas composition, and carbon balance), together with rigorous comparison under unified experimental protocols, will be essential for enabling meaningful quantitative assessment of catalyst performance. Techno-economic analysis and life-cycle assessment should also be integrated into future studies to evaluate the industrial viability of bentonite-based catalysts for circular plastic waste valorization. Only through such evaluation can bentonite advance from an attractive low-cost support to a fully validated catalyst platform for circular plastic waste valorization and sustainable hydrogen production.

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