

Clay mineral supports in NaBH₄-based hydrogen generation: From surface chemistry to electrochemical performance

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Abstract: Clay minerals have attracted increasing attention as low-cost, abundant, and structurally tunable catalyst supports for hydrogen generation reactions. In particular, sodium borohydride (NaBH₄)-based hydrogen generation provides an important platform for evaluating how mineral-derived supports influence catalytic activity, stability, metal dispersion, and interfacial reaction behavior. Among various hydrogen production routes, NaBH₄ hydrolysis and related catalytic hydrogen release processes have gained attention within the broader framework of green hydrogen technologies. In this system, catalyst support design plays a critical role in determining surface accessibility, active-site distribution, charge-transfer behavior, and long-term catalytic performance. This review examines the structural, morphological, physicochemical, and electrochemical roles of clay minerals in clay-supported catalytic systems for hydrogen generation, with particular emphasis on NaBH₄-based systems. The structural classification of phyllosilicates including 1:1 vs. 2:1-layer types, is discussed in relation to their corresponding morphologies, such as plate-like kaolinite, tubular halloysite, and swelling montmorillonite. Particular attention is given to morphology- and surface-chemistry-dependent catalytic mechanisms in NaBH₄ hydrolysis, where surface accessibility, interlayer characteristics, cation exchange capacity, metal-support interactions, and interfacial charge-transfer processes influence hydrogen generation performance. A comparative analysis of reported clay-supported systems published between 2020 and 2025 reveals that while tubular and high-cation-exchange-capacity structures may enhance metal dispersion, reactant diffusion, and catalytic stability. However, catalytic performance is not governed by morphology alone. Instead, metal distribution, thermal treatment effects, surface activation, support conductivity, and structural evolution during catalyst preparation frequently dominate the observed activity trends. By integrating mineralogical structure with catalytic and electrochemical function, this work provides a mechanistic framework for evaluating clay-based systems and discusses their future potential in photocatalytic, UV-responsive, and electrochemically hydrogen generation platforms. The findings highlight that rational catalyst design should consider both intrinsic clay architecture and processing-induced transformations to advance sustainable, mineral-derived catalytic materials for next-generation green hydrogen technologies.

Keywords: sodium borohydride, clay mineral supports, hydrogen generation, phyllosilicate structure, surface chemistry

1. Introduction

The accelerating impacts of climate change and the continuous growth in global energy demand have intensified the transition toward clean and sustainable energy systems. According to recent reports by the International Energy Agency (IEA, 2024), energy-related CO₂ emissions reached record levels in 2023–2024, reinforcing the urgency of low-carbon energy technologies. In this transition, hydrogen has emerged as a strategic energy carrier because of its high gravimetric energy density and its potential to

decarbonize hard-to-abate sectors, including steel production, chemical manufacturing, and transportation (IEA, 2024; Mehtab et al., 2024).

Green hydrogen, commonly defined as hydrogen produced using renewable energy sources, primarily through water electrolysis, plays a central role in this framework (IEA, 2024). Although water electrolysis remains the dominant pathway for green hydrogen production, alternative hydrogen generation routes, such as the catalytic hydrolysis of sodium borohydride (NaBH_4), have gained increasing attention because they enable controllable hydrogen release under relatively mild conditions. With a high theoretical hydrogen storage capacity of 10.8 wt%, NaBH_4 is particularly attractive for portable and on-demand hydrogen generation systems due to its chemical stability under alkaline conditions and manageable reaction kinetics in the presence of suitable catalysts (Nguyen-Dinh et al., 2026). From a safety perspective, on-demand hydrogen generation can also reduce the amount of gaseous H_2 stored within the system and thereby limit some of the fire and explosion hazards associated with high-pressure hydrogen storage. Nevertheless, because the generated hydrogen remains highly flammable, appropriate ventilation, leak detection, and controlled hydrogen release remain essential for safe operation (Abohamzeh et al., 2021). In these systems, catalyst design critically determines the hydrogen generation rate, activation energy, operational stability, and long-term performance.

Among advanced catalytic materials, transition-metal-based catalysts, metal-organic frameworks (MOFs), ZIF-derived materials, and hybrid nanostructures have attracted significant attention due to their high surface area, tunable active sites, and enhanced catalytic efficiency (Saleh et al., 2023). However, increasing attention has also been directed toward the role of catalyst supports, particularly naturally abundant clay minerals, because of their structural diversity, surface chemistry, ion-exchange capacity, and economic feasibility (Bergaya & Lagaly, 2013; Murray, 2007). In supported catalyst systems, the support material does not merely act as an inert carrier; rather, it can influence metal dispersion, active-site accessibility, interfacial charge transfer, and catalyst durability.

From a mineral processing and applied mineralogy perspective, clay minerals should therefore be considered mineral-derived functional supports rather than passive fillers. Their physicochemical properties can be tailored through purification, particle size control, surface activation, ion exchange, and metal immobilization. These operations modify surface area, cation exchange capacity, hydroxyl distribution, surface charge, interlayer accessibility, and surface defect sites (Bergaya & Lagaly, 2013; Murray, 2007), while also promoting metal anchoring sites and nanoparticle dispersion in clay-supported catalytic systems (Fatimah et al., 2022; Ochirkhuyag et al., 2024). Such processing-induced modifications are highly important for understanding catalyst support performance in NaBH_4 -based hydrogen generation, where surface accessibility, reactant diffusion, metal-support interactions, and interfacial electron-transfer behavior strongly influence catalytic activity.

Clay minerals such as kaolinite, halloysite, and montmorillonite differ significantly in layer structure, morphology, and surface chemistry. Kaolinite has a 1:1 plate-like structure with limited interlayer accessibility, halloysite exhibits a 1:1 tubular morphology with inner and outer surface heterogeneity, and montmorillonite has a 2:1 swelling structure with high cation exchange capacity. These structural and morphological differences influence metal nanoparticle dispersion, reactant accessibility, charge distribution, surface hydroxyl availability, and catalytic behavior. Therefore, a mechanistic understanding of how clay mineral architecture affects hydrogen generation performance is essential for the rational design of clay-supported catalysts.

Although clay-supported catalysts have been widely reported for NaBH_4 -based hydrogen generation, the influence of intrinsic phyllosilicate layer structure, morphology, cation exchange capacity, surface chemistry, and preparation-induced surface transformations is often discussed descriptively rather than mechanistically. Moreover, the electrochemical aspects of these systems, including interfacial charge transfer, surface redox behavior, ion transport, and catalyst/electrolyte interactions, are rarely integrated with mineralogical and physicochemical interpretations. This lack of a unified framework limits the rational design of mineral-derived catalyst supports.

Accordingly, this review aims to establish a physicochemical and electrochemical framework for understanding clay mineral supports in NaBH_4 -based hydrogen generation. Unlike general catalyst reviews, this work evaluates clay minerals as tunable mineral-derived functional supports and links their layer structure, morphology, surface chemistry, cation exchange behavior, metal dispersion

capacity, and interfacial electrochemical characteristics to hydrogen generation performance. By integrating concepts from applied mineralogy, surface chemistry, catalysis, and electrochemical performance analysis, this review highlights how mineral processing-related operations can improve catalyst support design for sustainable hydrogen generation technologies.

2. Hydrogen production pathways and role of catalyst supports

Hydrogen can be produced through multiple technological pathways, including thermochemical, electrochemical, photochemical, and chemical hydrogen release routes, each associated with distinct energy inputs, carbon footprints, and catalytic requirements. In the broader context of carbon neutrality, hydrogen production routes are commonly classified as green, blue, and gray hydrogen depending on the energy source and carbon management strategy. Fig. 1 provides a conceptual representation of these hydrogen pathways and their relationship to the carbon-neutral energy transition.

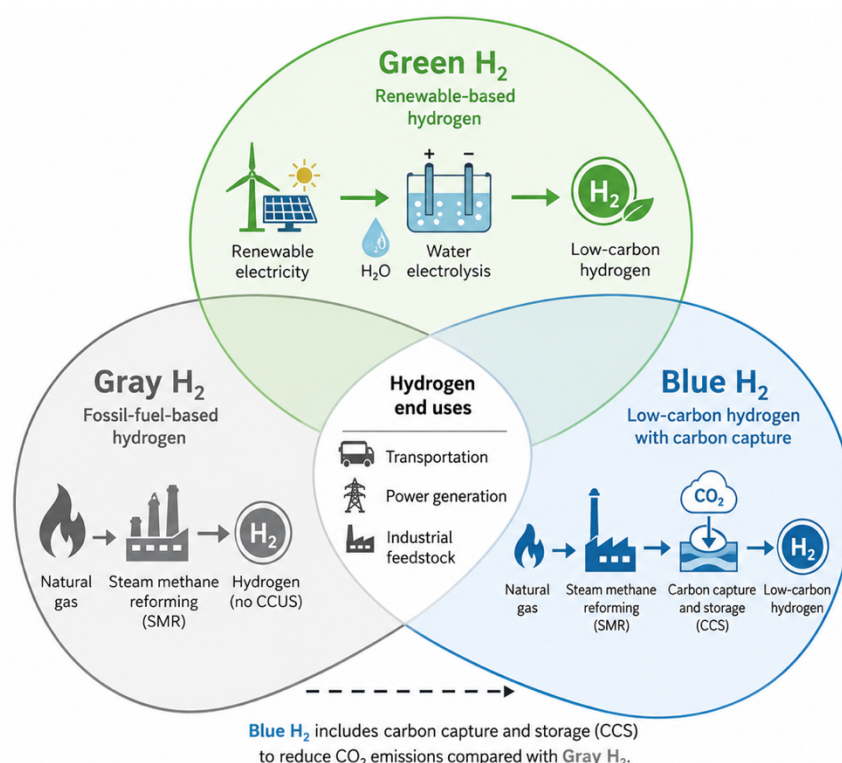


Fig. 1. Green, blue, and gray hydrogen pathways toward carbon neutrality

Among these approaches, photocatalytic hydrogen production has emerged as a promising strategy within green hydrogen technologies, enabling solar-driven water splitting without direct fossil fuel consumption (Kumar et al., 2024). In photocatalytic systems, semiconductor materials absorb light to generate electron-hole pairs that drive oxidation and reduction reactions, including the hydrogen evolution reaction (HER). Despite significant progress, major challenges remain, particularly charge-carrier recombination, limited surface stability, insufficient visible-light response, and long-term catalytic efficiency. Fig. 2 schematically illustrates the sequential steps involved in photocatalytic water splitting.

In addition to water electrolysis and photocatalytic water splitting, chemical hydrogen storage materials such as sodium borohydride (NaBH₄) have attracted attention as complementary hydrogen generation systems because they enable controllable hydrogen release under relatively mild conditions (Dragan, 2022; Chin et al., 2025). In NaBH₄-based systems, catalyst design is particularly important because the hydrogen generation rate, activation energy, conversion efficiency, and operational stability are strongly governed by the nature of the active phase and the support material. Therefore, support architecture, surface chemistry, and interfacial reaction behavior are central factors in the development of efficient hydrogen generation platforms.

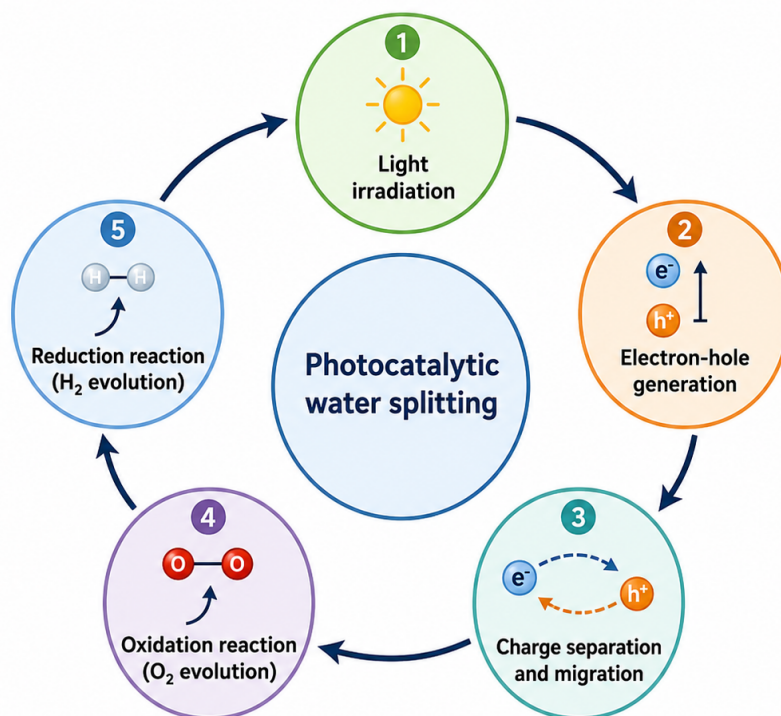


Fig. 2. Sequential steps involved in photocatalytic water splitting

Clay minerals possess nanoscale layered architectures and tunable physicochemical properties, including high specific surface area, cation exchange capacity, swelling behavior, surface reactivity, and structural stability, which make them suitable platforms for functional material design (Yang, 2025). In aqueous NaBH_4 -based systems, swelling can modify the interlayer spacing and accessibility of reactive sites, thereby influencing mass transfer, dispersion of catalytic species, and catalyst-reactant interactions. However, excessive swelling may compromise structural stability and catalyst reusability. Mineral-derived supports and silicate-based materials have also been shown to enhance photocatalytic performance by improving surface area, light-harvesting efficiency, structural stability, and charge separation (Li et al., 2022). Their colloidal and surface properties are particularly important in clay mineral-derived photocatalysts, where clay supports can host semiconductor nanoparticles and influence light-driven catalytic behavior (Freitas et al., 2022). In hybrid photocatalytic systems, the surface charge and hydroxyl-rich surfaces of clay minerals can facilitate the immobilization of TiO_2 , ZnO , and other semiconductor nanoparticles, thereby improving nanoparticle anchoring and structural stability during photocatalytic reactions (Ruiz-Hitzky et al., 2019). Building on these structure-function relationships, Fig. 3 illustrates how mineral processing operations, clay mineral architecture, surface chemistry, metal anchoring, and catalyst dispersion collectively control NaBH_4 -based hydrogen generation performance.

In addition, clay-supported metal and metal oxide nanoparticles benefit from the low cost, mechanical and chemical stability, and environmentally benign character of clay supports, which can help suppress agglomeration and improve catalyst dispersion in catalytic and photocatalytic processes (Fatimah et al., 2022). Recent critical reviews further indicate that clay mineral-based photocatalysts can be improved through activation, metal or non-metal doping, metal deposition, and heterojunction design strategies, which enhance surface area, adsorption capacity, ion-exchange behavior, and photogenerated charge-carrier separation (Qi et al., 2024). Halloysite nanotubes are especially relevant in this context because their tubular morphology, high surface accessibility, and stability make them promising supports for catalytic and photocatalytic applications (Massaro et al., 2022; Abid et al., 2023). Therefore, layered and tubular clay minerals may play a transferable role in photocatalytic, photo-assisted, and chemically driven hydrogen generation platforms by linking mineral-derived surface chemistry with nanoparticle stabilization, interfacial charge separation, and catalytic performance.

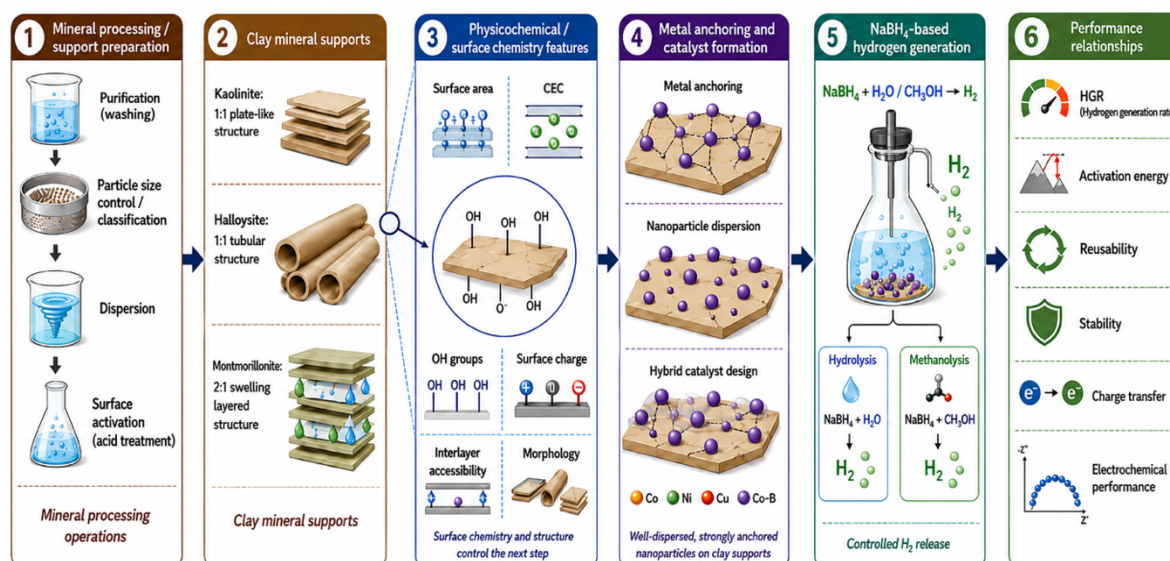


Fig. 3. Clay mineral supports from surface chemistry to NaBH_4 -based hydrogen generation performance

From a mineral processing perspective, operations such as purification, dispersion, particle size classification, and surface activation directly influence surface accessibility, defect density, particle-particle interactions, and active-site exposure. These parameters are critical not only for photocatalytic water splitting but also for NaBH_4 -based catalytic hydrogen generation, where reactant diffusion, metal dispersion, and interfacial reaction kinetics strongly depend on support properties. Therefore, integrating mineralogical structure with catalytic functionality provides a broader framework for evaluating clay-based materials across different hydrogen generation systems.

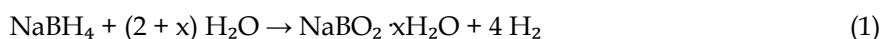
Therefore, integrating mineralogical structure with catalytic functionality provides a broader framework for evaluating clay-based materials across different hydrogen generation systems. Unlike direct water electrolysis or photocatalytic water splitting, NaBH_4 systems rely strongly on catalyst design, support architecture, and interfacial reaction kinetics. Therefore, understanding the role of clay mineral supports in NaBH_4 hydrolysis and methanolysis provides a useful basis for linking mineral-derived surface chemistry with hydrogen generation performance and supports with improved physicochemical and electrochemical performance, particularly in NaBH_4 -based hydrogen generation.

3. Hydrogen generation from sodium borohydride (NaBH_4)

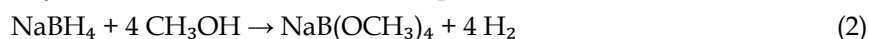
3.1. Hydrolysis and methanolysis pathways

Sodium borohydride (NaBH_4) is widely recognized as an efficient chemical hydrogen storage material due to its high theoretical hydrogen capacity of 10.8 wt% and relative stability under ambient and alkaline conditions (Nguyen-Dinh et al., 2026). In liquid media, NaBH_4 releases hydrogen mainly through hydrolysis in water and alcoholysis in lower alcohols, including methanolysis in methanol (Eqs. 1 and 2).

Hydrolysis produces hydrated sodium metaborate ($\text{NaBO}_2 \cdot x\text{H}_2\text{O}$), which may precipitate during operation and cause surface passivation, active-site blockage, or reactor fouling. Although hydrolysis offers high hydrogen yield and relatively simple reaction chemistry, by-product accumulation and catalyst deactivation remain important challenges for long-term and portable hydrogen generation systems.



Methanolysis produces soluble sodium tetramethoxyborate, which can reduce clogging problems and improve operational stability compared with aqueous hydrolysis systems. In addition, methanolysis can proceed under near-ambient conditions with simplified system design, although solvent selection, catalyst stability, and reaction control remain important considerations.



3.2. Catalytic performance parameters and kinetic evaluation

Catalytic performance is commonly evaluated using the hydrogen generation rate (HGR), generally expressed as the volume of hydrogen produced per unit time divided by catalyst mass. Additional parameters, including activation energy, induction time, conversion efficiency, catalyst reusability, and stability under repeated cycles, are also important. Additional parameters, including activation energy, induction time, conversion efficiency, catalyst reusability, and stability under repeated cycles, are also important for assessing practical performance.

The reaction kinetics of NaBH_4 hydrolysis and methanolysis are strongly affected by catalyst composition, active-site accessibility, reactant concentration, temperature, medium composition, and mass-transfer conditions (Demirci & Miele, 2014; Hoşgün, 2024; Ates et al., 2026). In methanol media, interfacial kinetic models, including Eley–Rideal-type pathways, can be used to interpret the interaction of solvated BH_4^- species with alcohol-derived species activated on the catalyst surface (Demirci & Miele, 2014; Nguyen-Dinh et al., 2026; Ates et al., 2026). Activation energy measurements provide further insight into catalytic efficiency and mechanistic pathways, while reusability tests are essential for evaluating catalyst durability under practical operating conditions (Hoşgün, 2024; Mirshafiee et al., 2024; Ates et al., 2026).

Considerable efforts have focused on enhancing NaBH_4 decomposition kinetics through catalytic activation. Transition-metal catalysts, including Ru, Co, Ni, Cu, and their bimetallic or boride-based derivatives, have been widely investigated because of their ability to activate BH_4^- species and accelerate hydrogen release. However, challenges related to catalyst cost, metal leaching, long-term durability, by-product accumulation, and resource sustainability remain critical, particularly for portable and on-demand hydrogen generation systems.

3.3. Interfacial and electrochemical aspects of NaBH_4 -based hydrogen generation

Although NaBH_4 -based hydrogen generation is generally discussed in terms of hydrolysis or methanolysis kinetics, the reaction also involves interfacial processes that are closely related to surface charge, adsorption behavior, electron transfer, and catalyst/electrolyte interactions. The activation of BH_4^- species on metal or metal-boride active sites depends strongly on the accessibility and electronic environment of the catalyst surface. Therefore, electrochemical and interfacial characterization can provide useful insight into the surface processes governing hydrogen release.

Electrochemical methods such as cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), and open-circuit potential measurements can evaluate charge-transfer resistance, surface redox behavior, ion transport, and interfacial stability. In supported catalyst systems, these parameters are influenced not only by the active metal phase but also by the physicochemical properties of the support, including surface charge, hydroxyl groups, porosity, conductivity, and metal anchoring ability.

In this context, structured mineral supports such as layered, tubular, and swelling clay minerals offer an alternative pathway by enabling controlled metal anchoring, nanoparticle dispersion, enhanced surface accessibility, and improved structural stability. Therefore, integrating electrochemical analysis with mineralogical and physicochemical characterization provides a more comprehensive framework for understanding how clay mineral supports influence NaBH_4 -based hydrogen generation performance.

4. Catalyst types for NaBH_4 decomposition

The decomposition of NaBH_4 is kinetically slow in the absence of catalytic activation. Therefore, extensive research has focused on developing catalysts capable of enhancing hydrogen generation rates (HGR) under mild conditions. Catalyst design is particularly important because hydrogen release performance is governed not only by the intrinsic activity of the active phase but also by active-site accessibility, metal dispersion, support interactions, and mass-transfer characteristics.

4.1. Transition-metal catalysts

Transition metals such as Co, Ni, Cu, and Ru, as well as their bimetallic counterparts, have demonstrated high catalytic activity in NaBH_4 hydrolysis and methanolysis systems (Sun et al., 2018).

These catalysts typically operate by facilitating BH_4^- activation on the metal surface, promoting rapid hydrogen release. Reported hydrogen generation rates and apparent activation energies vary considerably depending on catalyst composition, support type, reaction medium, temperature, catalyst dosage, and the reporting basis used for normalization. Therefore, quantitative comparison is more appropriately discussed on a study-specific basis, as summarized for clay-supported systems in Table 1.

Nanostructured, supported, and electrospun transition-metal catalysts have shown improved efficiencies due to increased active surface area, enhanced metal dispersion, and improved mass-transfer characteristics. Despite their effectiveness, metal-based catalysts still face challenges related to cost, metal leaching, long-term durability, by-product accumulation, and resource sustainability, especially in portable or on-demand hydrogen generation systems. These limitations have encouraged the development of supported, hybrid, and mineral-derived catalyst systems that can stabilize active phases while improving accessibility and reusability.

4.2. Metal-free catalysts

In response to these limitations, metal-free catalysts, particularly heteroatom-doped carbon materials, have emerged as promising alternatives. Nitrogen-doped carbons (NCs) have been widely investigated because nitrogen functionalities can act as active sites that facilitate interactions between methanol and borohydride species (Nguyen-Dinh et al., 2026). Catalytic activity depends not only on the total nitrogen content but also on the specific configuration of nitrogen species (e.g., pyridinic, pyrrolic, graphitic nitrogen).

Although encouraging hydrogen generation performances have been reported, the mechanistic interpretation of metal-free systems often remains empirical, relying primarily on correlations with surface area, defect density, or bulk heteroatom content. These trends highlight the importance of support architecture, surface chemistry, and structural control in catalyst design. Mineral-based supports, particularly clay minerals, provide an alternative platform for connecting support structure, surface functionality, catalyst dispersion, and hydrogen generation performance.

5. Clay composites and structural comparison of layered clay minerals

Layered clay minerals have gained considerable attention in catalysis and composite materials due to their structural diversity, surface reactivity, and tunable physicochemical properties. Clay minerals can be broadly classified according to their layer arrangement as 1:1 type, i.e., T-O, and 2:1 type, i.e., T-O-T, where T represents tetrahedral silica sheets, and O represents octahedral alumina or magnesia sheets. These structural differences strongly influence cation exchange capacity, interlayer accessibility, swelling behavior, surface hydroxyl distribution, and the ability to immobilize catalytic species.

5.1. Kaolinite: 1:1 plate-like clay mineral

Kaolinite is a type of 1:1 layered aluminosilicate that consists of one octahedral alumina sheet and one tetrahedral silica sheet. Its chemical composition is $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. The layers are strongly held together by hydrogen bonding, which limits interlayer expansion and results in a relatively low cation exchange capacity compared with 2:1 type clay minerals.

Kaolinite has been widely used as a reinforcement material in clay-polymer composites and as a support or component in heterogeneous catalytic systems. However, its compact layer structure limits interlayer ion exchange and restricts access to internal surfaces. From a catalytic perspective, kaolinite-supported systems demonstrate that even low-swelling 1:1 clay mineral can contribute to catalytic performance when their surface chemistry and support architecture are appropriately engineered. For example, the reported hydrogen generation rate and activation energy of kaolin-supported Co-Cr catalysts indicate that kaolin-supported systems can achieve competitive catalytic performance in NaBH_4 hydrolysis, highlighting the relevance of support architecture in hydrogen generation reactions (Onat & Ekinici, 2024). These findings reinforce the broader principle that catalyst morphology, surface accessibility, and support structure critically influence hydrogen generation efficiency in clay-based systems.

5.2. Montmorillonite (MMT) (2:1 type clay)

Montmorillonite (MMT), which belongs to the smectite group, has a 2:1 layer structure consisting of one octahedral sheet sandwiched between two tetrahedral silica sheets. Isomorphous substitution within the layers generates a net negative charge, which is compensated by the interlayer exchangeable cations such as Na^+ or Ca^{2+} (Bergaya & Lagaly, 2013).

Unlike kaolinite, montmorillonite exhibits high swelling capacity and much higher CEC values. The presence of weak van der Waals interactions and exchangeable cations in the interlayer spaces enables intercalation and exfoliation, making montmorillonite highly suitable for nanocomposite preparation and catalyst immobilization (Murray, 2007). These characteristics are beneficial in catalytic applications because high surface area, interlayer accessibility, and ion-exchange capacity can enhance nanoparticle dispersion and reduce catalyst agglomeration.

5.3. Halloysite (1:1 Type, tubular morphology)

Halloysite has a chemical composition similar to kaolinite and also belongs to the 1:1 clay mineral group. However, unlike plate-like kaolinite, halloysite commonly occurs as naturally formed nanotubes, known as halloysite nanotubes (HNTs). This tubular morphology results from the rolling of 1:1 aluminosilicate layers due to lattice mismatch between the tetrahedral and octahedral sheets (Bergaya & Lagaly, 2013). Although halloysite is less swellable than montmorillonite, its tubular structure provides distinct inner and outer surfaces, accessible lumen spaces, and confinement effects that are useful for hosting ions, molecules, nanoparticles, and catalytic species. These features make halloysite advantageous as a carrier or support in catalytic reactions, adsorption systems, and controlled-release applications. In clay-supported hydrogen generation systems, the tubular morphology of halloysite may facilitate nanoparticle dispersion, reactant diffusion, and catalyst reusability.

Catalyst morphology and particle size are decisive parameters governing hydrogen generation performance. Reduced particle size increases active surface exposure, while hierarchical porosity can improve reactant diffusion and gas release. However, in clay-supported systems, morphology is not limited to metal nanoparticles; it also includes the intrinsic architecture of the support material itself. Plate-like kaolinite, tubular halloysite, and swelling montmorillonite provide fundamentally different structural environments for metal bonding, reactant accessibility, and interfacial reaction behavior. While tubular morphologies may enhance confinement and diffusion pathways, thermal treatments such as calcination can modify interlayer structure, surface hydroxyl distribution, and surface chemistry, potentially diminishing morphology-driven advantages. Therefore, catalytic performance should be interpreted as the combined outcome of clay layer structure, surface chemistry, metal dispersion, particle size distribution, and post-treatment effects. Recent experimental studies provide valuable insight into how clay layer structure, cation exchange capacity, morphology, and preparation route affect hydrogen generation performance. A comparative review of studies published between 2020 and 2025 enables the assessment of whether tubular, layered, or swelling clay structures consistently lead to superior catalytic outcomes, as summarized in Table 1.

Table 1. Representative clay mineral-supported catalytic systems for NaBH_4 -based hydrogen generation, including recent advances up to 2026

Study	Catalyst / Clay Support	Clay architecture	Reaction / Performance	Structure-Performance Relevance
Tian et al. (2010)	Co-B/attapulgite	Attapulgite; fibrous clay	Alkaline NaBH_4 hydrolysis	Early example showing that fibrous clay-supported Co-B catalysts can be used for portable hydrogen generation applications.
Sahiner et al. (2017)	Amine-functionalized HNT	Halloysite; 1:1 tubular	NaBH_4 methanolysis; HGR: $2218 \text{ cm}^3 \text{ min}^{-1} \text{ g}^{-1}$	Chemically modified halloysite acted as a functional metal-free catalytic platform.

Meşe et al. (2018)	Co-B@thermal-activated sepiolite	Sepiolite; fibrous clay	NaBH ₄ hydrolysis / hydrogen delivery	Demonstrates the potential of thermally activated fibrous clay minerals as mineral-derived supports for Co-B catalysts.
Selvitepe et al. (2019)	Co-B / phosphoric-acid-treated sepiolite	Sepiolite; fibrous clay	NaBH ₄ hydrolysis; HGR: 1486 and 5025 cm ³ min ⁻¹ gcat ⁻¹ at 30 and 60 °C, respectively; Ea: 21.4 kJ mol ⁻¹	Phosphoric acid treatment modified the sepiolite surface and improved its effectiveness as a Co-B support, leading to an approximately five-fold increase in maximum hydrogen production rate.
Saka et al. (2021)	CoB / organic-acid-modified kaolin	Kaolinite; 1:1 plate-like	NaBH ₄ hydrolysis; HGR up to 3400 cm ³ min ⁻¹ gcat ⁻¹ ; Ea: 49.41 kJ mol ⁻¹	Organic acid modification of kaolin improved catalytic performance by changing surface properties and enhancing CoB-support interactions.
Hoşgün et al. (2021)	Co-B/Hly	Halloysite; 1:1 tubular	NaBH ₄ hydrolysis; HGR: 33,854 cm ³ min ⁻¹ gCo ⁻¹	Tubular halloysite improved Co-B dispersion and helped reduce aggregation and reusability limitations of unsupported Co-B particles.
Balbay et al. (2021)	Fe-doped CoB / acid-activated MMT	Acid-activated montmorillonite; 2:1 swelling	NaBH ₄ hydrolysis	Acid activation of MMT can increase surface area, acidity, and anchoring sites, linking mineral surface modification with catalytic performance.
Hoşgün and Hoşgün (2024)	Co/MMT	Montmorillonite; 2:1 swelling	NaBH ₄ hydrolysis; HGR: 2328 cm ³ min ⁻¹ gcat ⁻¹	Pillared MMT provided interlayer accessibility and high CEC, supporting Co anchoring and catalyst accessibility.
Onat and Ekinici (2024)	Co-Cr@Kaolin	Kaolin; 1:1 plate-like	NaBH ₄ hydrolysis; HGR: 5007 cm ³ g ⁻¹ min ⁻¹ ; Ea: 19.36 kJ mol ⁻¹	Kaolin support enhanced catalytic efficiency compared with unsupported Co-Cr catalyst, highlighting the role of mineral support architecture.
Rabiei Chamgordani et al. (2026)	Cu-Mo-B / acid-treated MMT	Acid-treated montmorillonite; 2:1 swelling	NaBH ₄ hydrolysis; kinetic and thermodynamic analysis	Acid treatment tailored MMT surface chemistry and anchoring/acidic sites; Cu-Mo-B composition and support ratio influenced dispersion, mass transfer, and catalytic performance.
Selvitepe et al. (2019)	Co-B / phosphoric-acid-treated sepiolite			

The representative studies compiled in Table 1 provide a comparative basis for evaluating the role of clay mineral supports in NaBH_4 -based hydrogen generation. Rather than functioning merely as inert substrates, clay minerals contribute to catalytic performance through their intrinsic structural, morphological, and physicochemical characteristics. The comparison indicates that tubular, fibrous, plate-like, and swelling clay architectures offer different surface environments for active-phase immobilization, nanoparticle dispersion, reactant transport, and catalyst stabilization. Moreover, support modification strategies such as acid activation, phosphoric acid treatment, thermal activation, pillaring, and organic functionalization can substantially alter surface area, acidity, hydroxyl distribution, interlayer accessibility, and metal-support interactions. These support-related parameters are therefore central to understanding the observed differences in hydrogen generation rate, activation energy, and catalyst durability.

The reported catalytic performances cannot be compared solely based on numerical HGR values because reaction temperature, NaBH_4 concentration, alkaline medium, catalyst loading, active metal content, and normalization basis differ markedly among studies. Accordingly, Table 1 should be interpreted as a structure-performance comparison rather than a direct activity ranking. This perspective is particularly important for clay-supported systems, where the catalytic response reflects the combined influence of active metal chemistry, clay mineral architecture, surface modification route, and preparation-induced structural transformations.

6. Conclusions

This review has evaluated how the structural, morphological, physicochemical, and interfacial properties of clay minerals influence hydrogen generation behavior, particularly in NaBH_4 -based systems. Representative studies on clay-supported catalysts indicate that catalytic performance is not determined solely by the inherent activity of the metal phase. Instead, hydrogen generation efficiency depends on the combined effects of metal anchoring, nanoparticle dispersion, particle size, surface accessibility, and the structural environment provided by the clay support.

The comparison of 1:1 and 2:1 phyllosilicates highlights that layer configuration directly affects metal anchoring capacity, cation exchange behavior, surface hydroxyl distribution, interlayer accessibility, and operational stability. Kaolinite, halloysite, montmorillonite, sepiolite, and attapulgite provide distinct catalytic environments due to differences in interlayer bonding, swelling behavior, tubular or fibrous morphology, and surface reactivity. Although tubular, fibrous, or expandable structures may facilitate confinement, reactant diffusion, and improved dispersion, preparation methods such as acid activation, pillaring, impregnation, chemical reduction, and thermal treatment can significantly modify surface chemistry and support functionality. Therefore, catalytic outcomes must be interpreted as the combined result of intrinsic clay architecture and preparation-induced physicochemical transformations.

From an electrochemical and interfacial perspective, clay mineral supports can influence NaBH_4 -based hydrogen generation by modifying charge distribution, active-site accessibility, ion transport, charge-transfer resistance, and metal-support interactions at the catalyst/electrolyte interface. Therefore, electrochemical tools such as cyclic voltammetry and electrochemical impedance spectroscopy can complement mineralogical and physicochemical characterization by clarifying whether improved hydrogen generation performance originates from enhanced metal dispersion, lower interfacial resistance, improved electron-transfer behavior, or greater catalyst stability.

Taken together, these insights underscore the importance of aligning mineralogical characteristics with catalytic engineering strategies. Advancing clay-based systems for green hydrogen applications will require careful control of support structure, surface chemistry, metal-support interaction, interfacial charge-transfer behavior, and durability under practical operating conditions. This integrated perspective can support the rational design of sustainable, mineral-derived catalyst supports for next-generation NaBH_4 -based hydrogen generation systems.

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