

# Review Hydrogen Adsorption in Porous Geological Materials: A Review

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Abstract: The paper adopts an interdisciplinary approach to comprehensively review the current knowledge in the field of porous geological materials for hydrogen adsorption. It focuses on detailed analyses of the adsorption characteristics of hydrogen in clay minerals, shale, and coal, considering the effect of factors such as pore structure and competitive adsorption with multiple gases. The fundamental principles underlying physically controlled hydrogen storage mechanisms in these porous matrices are explored. The findings show that the adsorption of hydrogen in clay minerals, shale, and coal is predominantly governed by physical adsorption that follows the Langmuir adsorption equation. The adsorption capacity decreases with increasing temperature and increases with increasing pressure. The presence of carbon dioxide and methane affects the adsorption of hydrogen. Pore characteristics—including specific surface area, micropore volume, and pore size—in clay minerals, shale, and coal are crucial factors that influence the adsorption capacity of hydrogen. Micropores play a significant role, allowing hydrogen molecules to interact with multiple pore walls, leading to increased adsorption enthalpy. This comprehensive review provides insights into the hydrogen storage potential of porous geological materials, laying the groundwork for further research and the development of efficient and sustainable hydrogen storage solutions.

**Keywords:** porous geological materials; large-scale hydrogen storage; physical adsorption hydrogen; coal; sustainability

# 1. Introduction

The current global energy supply heavily relies on fossil fuels, including coal, oil, and natural gas, raising concerns about the effects of their consumption on global climate change [1–3]. There is a need to transform existing fossil fuels into alternative, clean, and renewable energy sources for short- and long-term sustainability [1–5]. Among various potential clean energy sources, hydrogen (H<sub>2</sub>) stands out as an ideal option because it is carbon-free, non-polluting, and produces only water upon combustion [6–8].

Hydrogen is one of the most abundant elements in the universe, constituting approximately 75% of the mass of the universe and providing an abundant source for the generation of H<sub>2</sub> [9–11]. Additionally, hydrogen has a higher energy density than gasoline and coal [12]. Recognizing these advantages, research communities and governments worldwide have acknowledged the imminence of the era of hydrogen [13–15]. However, key technological challenges, such as hydrogen storage and transportation, must be addressed before a hydrogen-based economy can be realized [16]. Hydrogen can be stored as a liquid or in a solid form, such as in the form of synthetic chemical hydrides or adsorbed into porous materials [17]. Porous materials, which are known for their rapid kinetics, excellent recyclability, and high adsorption capacity, have thus garnered widespread attention [18,19]. Various porous materials—including porous carbon, zeolites, metal–organic frameworks (MOFs), and porous polymers—have been extensively studied [20–24]. Moreover, large-scale hydrogen storage has become a subject of broad interest [25–27].



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Hydrogen can be stored underground for several months or even years, providing a backup during periods when renewable energy sources cannot meet energy production demands [28]. This stored hydrogen can be extracted from underground structures and released into the energy grid, leading to grid stability and stable electricity pricing [29]. Several countries, including the United States, Poland, the United Kingdom, Spain, and Turkey, have conducted studies on the potential and feasibility of underground hydrogen storage [30-33]. Various sites, such as salt caverns, abandoned mines, depleted oil and gas reservoirs, and aquifers, offer potential storage solutions [32]. The feasibility of hydrogen storage in salt caverns has been proven, but research on depleted oil and gas reservoirs, aquifers, and mines is still ongoing [34]. The dense structure of rock salt is instrumental in preventing the leakage of gases such as hydrogen [35]. The strong plasticity and deformability of rock salt allow it to adapt to the volumetric changes induced by hydrogen storage, mitigating stress concentration in the geological layers and contributing to the stability of underground hydrogen storage facilities [36]. Furthermore, rock salt exhibits a remarkable self-healing capability. Under specific conditions, the structure of rock salt can rearrange itself, facilitating the repair of deformations [37]. Additionally, hydrogen reactions are hindered under high-salt-concentration conditions, which suppress microbial hydrogen consumption. These properties make rock salt an ideal material for hydrogen storage [35–37]. Aquifers, with extensive gas storage potential and widespread global distribution, serve as an alternative for underground hydrogen storage in areas lacking depleted oil and gas reservoirs or salt formations [38]. Aquifers comprise porous and permeable rock layers containing fresh or saline water, with an impermeable caprock sealing the top [39]. The storage of hydrogen in such reservoirs may be affected by factors such as hydrogen migration, chemical reactions, and leakage along undetected faults [40]. Therefore, comprehensive geological research is imperative to assess caprock tightness and mineral composition in aquifers. In cases where knowledge about the geological structure and rock-sealing properties of aquifers is limited, the drilling of new wells may be required to enhance geological understanding and assess the sealing properties [38]. Storage in depleted oil and gas reservoirs is prevalent both globally and in China [41,42]. Abundant resources and low construction costs make depleted oil and gas reservoirs attractive for this purpose [43]. However, when using depleted oil and gas reservoirs for large-scale hydrogen storage, attention must be paid to issues such as reduced hydrogen purity and quality loss during storage [41]. Residual oil in the reservoir may lead to decreased hydrogen purity, with hydrogen reacting chemically with it to form gases such as methane, resulting in irreversible hydrogen loss [42]. Therefore, assessing the content and distribution characteristics of residual oil in reservoirs and clarifying the reaction conditions and rates between residual crude oil and hydrogen are crucial when using depleted oil and gas reservoirs for large-scale hydrogen storage [43]. In addition, reactions may occur between stored hydrogen, rocks, formation water, and unexhausted hydrocarbons. Despite its higher economic costs, salt-cavern storage offers advantages in terms of reduced leakage risk, biogeochemical reactions with surrounding media, cushion gas volume, injection and extraction flexibility, and environmental protection. However, many regions lack welldeveloped salt deposits, which presents a challenge to the use of high-quality salt mines for hydrogen storage. Therefore, the search for new materials for large-scale hydrogen storage remains crucial.

In nature, numerous porous materials—such as clay minerals, zeolites, organic-rich shales, and coal beds—possess structural nanopores that can be one-, two-, or even threedimensional [44–55]. Because of their structural nanopores, porous minerals typically exhibit large surface areas, which provide a significant number of adsorption sites for hydrogen. The theoretical principles of hydrogen storage in porous minerals, which are similar to those in other porous solid materials, primarily involve physical adsorption, in which the binding forces between hydrogen molecules and the mineral surfaces are predominantly van der Waals forces [44]. With their considerably large surface areas, these porous materials offer excellent adsorption capacity for hydrogen and are widely distributed in nature, making them cost-effective. This review explores the extensive literature and summarizes recent research progress on hydrogen storage in natural porous geological materials. It analyzes and summarizes the characteristics of hydrogen storage as well as the factors influencing hydrogen storage to provide insights into large-scale hydrogen storage. Therefore, it contributes to promoting the sustainability of clean energy.

# 2. Adsorption of Hydrogen in Clay Minerals

Clay minerals are abundant globally, widely distributed in the Earth's crust, and constitute a fundamental component of soils. They are also found in marine sediments and atmospheric aerosols [56–58]. Clay minerals have diverse applications in ceramics, pottery, paper coating, cosmetics preparation, pharmaceuticals, decorations, and art [56–58]. The crystal structure of clay minerals consists of two fundamental structural units: silicon-oxygen tetrahedron and aluminum–oxygen octahedron (Figure 1) [59]. Based on their different types of crystal structures, layered silicate minerals are mainly categorized as 2:1 layered structures, such as the montmorillonite (MMT) group (e.g., MMT) and layered-chain structures such as the illite group (e.g., illite), and 1:1 layered structures such as the kaolinite group (e.g., kaolinite) [59]. The layer thicknesses and interlayer spacings of clay minerals are approximately 1 nm, with interlayer spaces occupied by water molecules or cations [59]. Because of their unique molecular structures and large surface areas, clay minerals exhibit excellent adsorption capacity.



**Figure 1.** Structural illustration of clay minerals: (**a**) silicon–oxygen tetrahedron; (**b**) aluminum–oxygen octahedron; (**c**) octahedral layer; (**d**) tetrahedral layer; (**e**) alternating occurrence of octahedral aluminum–oxygen layers and tetrahedral silicon–oxygen layers (adopted and redrawn from [46]).

The typical structure of a 2:1 clay mineral interlayer is shown in Figure 2, demonstrating that hydrogen molecules have sufficient space to penetrate between layers and access dispersed cation binding sites. The thickness of the clay layer is ~9 Å, which results in an interlayer distance of ~12 Å if the material is completely dry [49]. Within the interlayer, hydrogen molecules are confined to nanopores, and the influence of the potential field from the two clay surfaces enhances the strength of the adsorbent–hydrogen interactions.



**Figure 2.** Schematic illustration of the interlayer structure of an ideal clay mineral. The diameter of the exposed cation is greater than the diameter of the hydrogen molecule, and the spacing of the clay mineral layers is sufficient to accommodate the diameter of the hydrogen molecule (adopted and redrawn from [46]).

Rocks rich in clay minerals in the Cigar Lake uranium deposit (northern Saskatchewan, Canada) are primarily composed of illite, smectite, and kaolinite [60–62]. Thermal desorption measurements showed hydrogen enrichment of up to 500 ppm (i.e., 0.25 mol kg $^{-1}$  of rock), surpassing the methane adsorption capacity reported for pure clay minerals or shales elsewhere [60]. These investigators suggested that hydrogen produced by the radiolysis of water in the Cigar Lake uranium deposit was trapped in the surrounding clay rocks [63]. Sudoite (Al-Mg dioctahedral smectite) may be responsible for the hydrogen adsorption [60]. Montmorillonite (MMT) was exposed to pure hydrogen gas at temperatures of 77, 195, and 303 K, gradually increasing the gas pressure to 50 bar over time [64]. At all temperatures, hydrogen adsorption increased non-linearly with pressure, eventually reaching a saturation plateau. These researchers found that both the Langmuir and Freundlich isotherm models provided good fits to the experimental data, producing similar International Union of Pure and Applied Chemistry (IUPAC) Type I isotherms [64]. The Langmuir model provided a better fit with a smaller least-squares error, indicating that a uniform adsorption mechanism ultimately leads to monolayer surface saturation, where all sites are equivalent and there is no interaction between adsorbed molecules [62]. The hydrogen adsorption capacity on six pure clay minerals (MMT, illite, kaolinite, smectite, sepiolite, and chlorite) was tested at different temperatures (0 °C, 25 °C, 45 °C, and 75 °C) and pressures (up to 18 MPa) [44]. Among the six pure clay minerals, sepiolite and smectite exhibited significantly higher excess adsorption than did MMT or illite, whereas kaolinite and chlorite exhibited low or negligible excess adsorption. The differences in hydrogen adsorption capacity (HAC) among different clay minerals were attributed to variations in their pore structures, including their specific surface areas and micro-/mesopore volumes [44]. More complex pore structures and larger specific surface areas provide more adsorption sites for hydrogen molecules [65,66]. Regardless of the type of clay mineral, HAC increased with increasing pressure and decreased with increasing temperature [44,67].

From the perspective of mineral structure, among these clay minerals, kaolinite and talc lack layer charges cannot attract interlayer cations and have no binding sites for H<sub>2</sub> adsorption. In illite, potassium ions are the main interlayer cations, and the interlayer space is too small for hydrogen gas, limiting its adsorption [68,69]. Mica exhibits a similar behavior. Natural one-dimensional porous phyllosilicate minerals—such as sepiolite and palygorskite, both of which have a 2:1 chain-like structure—share similarities in size, shape, and structure with artificially synthesized nano-materials (carbon nano-tubes) [70–72]. As fibrous clay minerals, they possess high specific surface areas, relatively high porosity, and multiple surface charges, which result in excellent adsorption performance and significant hydrogen storage capacity [69–72]. MMT has a high specific surface area and a tunable interlayer region that can be controlled by exchanging large ions or adjusting the water-vapour pressure [47]. By further adjusting the binding potential between the layers through ion exchange with ions such as  $Ca^{2+}$  and  $Mg^{2+}$ , a suitable binding energy can be provided for H<sub>2</sub> adsorption, which enters the thermodynamically favorable strong physical adsorption region for hydrogen storage. Scanning electron microscope (SEM) images of MMT show particles that often appear cellular, enveloped by filamentous or wavy protrusions, and that are interconnected with each other (Figure 3). The edges of the pores exhibit leaf-like and petal-like layered structures, forming wide and narrow fissure-like connections deep inside [44–47]. Additionally, honeycomb-shaped pores develop, with pore diameters of <50 nm, providing favorable conditions for hydrogen adsorption [44].



**Figure 3.** SEM microstructure of MMT: (**a**) micron-scale image of MMT aggregates; (**b**) numerous large and mesopores in MMT aggregates; (**c**) wavy edges of MMT; (**d**) honeycomb-like MMT with numerous nanopores.

Sepiolite and palygorskite belong to the hydrated, chain-layered magnesium silicate mineral family, also known as phyllosilicate minerals, with a 2:1 chain-like structure [50]. Sepiolite exhibits a fibrous morphology, with needle-like or belt-like crystals approximately  $1-10 \mu m$  in length and 0.01  $\mu m$  in width. They share certain characteristics with zeolites,

such as high specific surface areas, well-developed pores, and polar surface features, making them widely applicable for adsorption and catalysis. Owing to the periodic inversion of the tetrahedral active oxygen, the octahedral sheets become discontinuous, forming unique one-dimensional channels that extend along the C-axis [51]. The resulting channels are highly regular, equal in size and parallel; however, they are non-interacting and present a "honeycomb" appearance in the cross-section (Figure 4). The cross-sectional area of individual channels in palygorskite and sepiolite minerals is larger than the kinetic diameter of a hydrogen molecule [51]. Owing to the regular nature of their channels, palygorskite and sepiolite exhibit some selectivity in the adsorption or exchange of molecules or ions, allowing only molecules (such as  $H_2$ ) or ions smaller than their diameter to enter, whereas larger molecules can only be adsorbed onto the surfaces outside the channels. Numerous fibrous palygorskite aggregates with sheet-like structures and irregular spheres, which display fibrous edges wrapped in thorn-like or irregularly shaped protrusions, are presented in Figure 4. The diameters of the irregular spheres range from 2 to 8  $\mu$ m. In high-ratio



**Figure 4.** Microscopic morphology of palygorskite: (**a**) fibrous crystals of palygorskite; (**b**) aggregation of palygorskite crystals forming plate-like structures with spiky edges; (**c**) aggregation of palygorskite crystals forming irregular spherical shapes; (**d**) palygorskite aggregates in irregular spherical shapes with abundant nanoscale pores.

In addition to well-known properties such as specific surface area  $(m^2/g)$  and pore structure, another factor that affects adsorption by a porous solid is the surface adsorption potential [64–66]. Surface functional groups typically constitute centers of residual charges, which make them active sites for the adsorption of polar adsorbate molecules or easily polarizable molecules (such as H<sub>2</sub>) [73]. Palygorskite and sepiolite have five types of surface functional groups: tetrahedral siloxane holes on tetrahedral sheets, magnesium alcohols on octahedral sheets, silicon and magnesium alcohols on sheet edges, and Lewis-acid sites on edges [68,69,74]. Therefore, palygorskite and sepiolite are highly polar adsorbents with a relatively high surface functional group density, strongly adsorbing cations, polar molecules, or easily polarizable molecules.

Clay minerals reflect the physical and chemical conditions in the weathering process, in which physical weathering mainly produces inherited clay minerals such as illite and chlorite, and kaolinite and montmorillonite are mainly produced by transformation [45]. In addition to quartz, other silicate minerals can produce clay minerals through weathering. Montmorillonite can be produced by the conversion of olivine, pyroxene, and hornblende and the conversion of potassium feldspar, mica, and chlorite under alkaline conditions [46]. The hydrogen adsorption capacity of montmorillonite at 25 °C and 18 MPa is ~2 cm<sup>3</sup>/g [44]. The transition from illite to montmorillonite is a simple degradation process. Illite–montmorillonite [47]. Illite does not adsorb hydrogen, and the adsorption capacity will be increased when it is transformed into clay minerals. Illite is usually derived from weathering of feldspar, Muscovite, and biotite, and is widely present in metamorphic rocks with limited weathering and in felsic to neutral magmatic rocks [48]. Illite, feldspar, biotite, and Muscovite may be directly or indirectly converted to kaolinite under strong weathering conditions [45]. Kaolinite basically does not adsorb hydrogen [44].

Clay minerals possess many other characteristics that render them suitable candidates for hydrogen storage, such as low cost, global abundance, simplicity and scalability of synthesis, and environmental safety [47–49]. Furthermore, because of the structural integrity of clay, contamination of H<sub>2</sub> is less likely when used under low-temperature conditions [44–47]. The physical adsorption mechanism of clay minerals has the advantages of fast charge–discharge kinetics and long-term reversible cycling [44].

However, there is a significant difference in the adsorption capacity of clay minerals for hydrogen; for example, at 25 °C and 18 MPa, the adsorption capacity of hydrogen in sepiolite is 18.5  $\text{cm}^3/\text{g}$ , while under the same conditions, the adsorption capacity of montmorillonite, which is more widely present in the Earth's crust, is only 2.0  $\text{cm}^3/\text{g}$ , much lower than that of sepiolite [44]. In the future, the adsorption capacity for hydrogen can be improved through the modification of clay minerals. Currently, it has been discovered that clay minerals can be enhanced through physical or chemical modification [75–77]. For instance, the melt-blending method can incorporate organic cations into the interlayer space of clay minerals, making the hydrophilic clay mineral surface hydrophobic. The substitution of organic cations for exchangeable inorganic cations in clay increases the interlayer distance and greatly enhances the adsorption capacity of clay minerals [78]. Additionally, combination techniques, such as using organic materials and biopolymers, metal-pillared clay minerals, combinations with biochar or two different clay minerals, and thermal activation, can synthesize new clay-based nanocomposite materials [79,80]. These modifications help increase the specific surface area, adjust the pore size of clay minerals, and obtain different surface functional groups [81]. Furthermore, acid activation can also modify clay minerals, with the dissolution of cationic components leading to increased porous structure and specific surface area, thereby improving adsorption capacity [82–84].

# 3. Adsorption of Hydrogen in Shale

The composition of shale includes common clay minerals such as montmorillonite and illite, with the addition of organic matter, similar to the organic modification of clay minerals. Shale is a type of fine-grained clastic sedimentary rock characterized by its heterogeneous composition, typically consisting of organic (kerogen) and inorganic minerals (such as clay and quartz), which influence its microscopic structure [85–87]. Shale exhibits a high total organic carbon (TOC) content. Kerogen is classified into four types based on its source and thermal maturity [85]. Unlike conventional reservoirs, shale reservoirs contain numerous nanoscale pores, providing abundant adsorption space for gas storage. Gases can exist within the large pores in shale in both free and adsorbed forms. It has been reported that 20–85% of the gases in shale gas reservoirs can be stored through adsorption [86].

The adsorption capacity of shale depends on the type and maturity of the organic matter, geological conditions, and inorganic components [86]. Understanding gas adsorption is crucial for the extraction of shale gas, and numerous studies have investigated the adsorption characteristics of methane and other gases in shale. For example, the adsorption of  $CH_4$ ,  $C_2H_4$ , and  $CO_2$  as single components and binary and ternary mixtures were studied within representative kerogen nanostructures [87].

With increasing attention to hydrogen, researchers have explored the adsorption of hydrogen in shale and its competitive adsorption with  $CH_4$  and  $CO_2$ . For instance, the adsorption isotherms of hydrogen, methane, ethylene, and their binary and ternary mixtures were studied [88]. The diffusion rates of hydrogen, methane, and carbon dioxide in organic kerogen nanopores were investigated [89]. The adsorption of pure  $H_2$ ,  $H_2$  mixed with  $CH_4$ , and  $H_2$  mixed with  $CO_2$  in representative kerogen and MMT were studied using grand canonical Monte Carlo (GCMC) [90]. The adsorption behaviors of hydrogen in representative organic kerogen nanopores of various pore sizes, considering different gas components, including hydrogen ( $H_2$ ), carbon dioxide ( $CO_2$ ), methane ( $CH_4$ ), ethane ( $C_2H_6$ ), and propane ( $C_3H_8$ ), were investigated [91]. The adsorption behaviors of  $H_2$ ,  $CO_2$ , and  $CH_4$  on organic-rich source rocks at 60 °C were tested [92]. The impacts of the presence of humic acid in Eagle Ford shale on the adsorption capacities of  $H_2$  and  $CH_4$  were studied, respectively [93].

Comparison of the adsorption of hydrogen and methane in shale showed that the adsorption of both gases increased with increasing pressure [88–93]. The adsorption rate gradually decreased with increasing pressure, and the adsorption behavior of methane and hydrogen was Type I Kerogen (organic matter rich in algae and fungal remnants) [88–90]. This manifests that methane and hydrogen are adsorbed as monolayers on the shale surface. Under isobaric conditions, the adsorption of hydrogen decreased with increasing temperature; this was because of the enhanced kinetic energy of the hydrogen molecules at higher temperatures, leading to the desorption of the adsorbed hydrogen gas [90–93]. The adsorption of hydrogen was lower than that of methane (~80% of the amount of methane adsorption) [94]. This occurred because both methane and hydrogen are nonpolar, resulting in weak interactions with shale. However, shale is a complex heterogeneous material, as discussed above, and methane exhibits stronger van der Waals interactions than hydrogen, suggesting that methane binds more strongly to kerogen than does hydrogen. This may be due to interactions between the carbon in methane and the organic carbon in shale, leading to the relatively strong adsorption tendency in shale [90–93]. In addition, shale contains abundant oxygen-containing groups, including alcohols and carbonyls, which further increase the affinity of methane and shale. Four isotherm models (the Langmuir, BET, Freundlich, and Dubibin-Astakhov (D-A) models) were used to fit the adsorption, and it was found that the Freundlich model provided the better description of the hydrogen adsorption behavior [94].

Kerogen and clay minerals are the two main components contributing to hydrogen adsorption in shale samples. To study the individual effects of kerogen and clay minerals to the HAC, Wang et al. prepared inorganic shale samples and shale samples containing kerogen for hydrogen adsorption testing at 30 °C. The adsorption capacities of samples without kerogen were significantly lower than those of samples with kerogen. This indicates that kerogen contributes significantly to the HAC of shale. In addition, the adsorption capacities of samples with kerogen, indicating that the inorganic content of shale contributes to more than 60% to the total HAC. The adsorption of hydrogen in kerogen and MMT nanopores were simulated using the GCMC method [90]. It was found that excess hydrogen adsorption occurred in both the kerogen and MMT nanopores, increasing with pressure [90]. The amount of hydrogen adsorbed in the kerogen nanopores was almost twice that in the MMT nanopores, demonstrating greater adsorption capacity in the kerogen nanopores. The pore sizes in the MMT and kerogen also influenced the hydrogen adsorption capacity. Kerogen and MMT with a 5 nm

pore size (Figure 5) [68]. These experiments collectively confirm the significant roles of clay minerals and kerogen in hydrogen adsorption in shale.



**Figure 5.** Adsorption of hydrogen in kerogen and MMT nanopores with different pore sizes. Purple represents pure hydrogen, pink represents a mixed gas with 50% methane, and gray represents a mixed gas with 50% carbon dioxide (adapted with permission from Ref [90]). 2023, Elsevier Ltd.

Researchers have studied the adsorption characteristics of hydrogen-containing gas mixtures [90–95]. The adsorption of  $C_3H_8$ ,  $C_2H_6$ ,  $CO_2$ ,  $CH_4$ , and  $H_2$  in kerogen were simulated using GCMC [95]. They found that regardless of the pressure,  $CO_2$  exhibited the highest adsorbed mass among the gases at a 1 nm pore size, with  $H_2$  having the lowest adsorption. At 2 nm, the sequence was different. At pressures below 5 MPa, the adsorption followed the trend  $C_3H_8 > C_2H_6 > CO_2 > CH_4 > H_2$ . Beyond 5 MPa, however, the sequence shifted to  $CO_2 > C_2H_6 > C_3H_8 > CH_4 > H_2$ . Except for the case of  $C_3H_8$ , the adsorption generally increased with increasing pressure. In kerogen with a 2 nm pore size, the adsorption of all gases was higher than that at 1 nm. The impact of the nanopore size was evident, with a 2 nm kerogen pore size being more favorable for hydrogen adsorption. It is noteworthy that each of the Langmuir, Toth, and Langmuir–Freundlich models accurately described the overall adsorption trends for single components. However, for multicomponent mixtures ( $H_2/CO_2/CH_4/C_2H_6/C_3H_8$ ), the Langmuir ratio correlation model was found to be more reasonable and effective for describing the adsorption.

GCMC simulations were performed to study the HAC of pure hydrogen and mixtures (hydrogen mixed with  $CH_4$  or  $CO_2$ ) at 333.15 K and up to 18 MPa in the narrow nanopores of kerogen and MMT [90]. In the absence of  $CH_4$  or  $CO_2$ , hydrogen formed an adsorbed layer on the surface of both kerogen and MMT. Excess adsorption increased with increasing pressure, and the adsorption capacity for  $H_2$  in kerogen nanopores was nearly twice that in MMT [90]. As the pressure increased, hydrogen molecules were increasingly desorbed from the kerogen, being replaced by  $CH_4$  in the presence of  $CH_4$ . In contrast,  $H_2$  and  $CH_4$  were co-adsorbed on the MMT surface, forming a relatively weak adsorbed layer, resulting in lower  $CH_4/H_2$  adsorption selectivity. In kerogen and MMT nanopores, the  $CH_4/H_2$  adsorption selectivity was greater than unity, illustrating that the adsorption for  $CH_4$  is greater. In  $H_2/CO_2$  mixtures,  $CO_2$  exhibits a stronger adsorption capacity, which completely depletes  $H_2$  from kerogen and MMT, suggesting a stronger interaction between  $CO_2$  and the shale surface than  $CH_4$  [90].

Trace amounts of organic acids in the shale may influence hydrogen adsorption. Abid aged Eagle Ford shale with moderate TOC in humic acid to simulate the effect of organic

acids on shale under actual underground conditions [93]. The adsorption of H<sub>2</sub> on Eagle Ford shale followed a Type I isotherm adsorption curve, indicating monolayer adsorption on mesoporous shale. When the Eagle Ford shale samples were aged in humic acid, the adsorption of hydrogen increased significantly [93]. This is attributed to the modification of the shale surfaces by humic acid, which leads to significant changes in textural properties, increased BET surface areas and pore volumes, and a substantial reduction in pore size [93]. As a result, the shale's adsorption capacity for hydrogen was significantly enhanced. The methane adsorption capacity of Eagle Ford shale was significantly higher; however, ageing the shale in humic acid does not significantly increase the methane adsorption capacity [93].

In summary, both clay minerals and kerogen in shale contribute significantly to hydrogen adsorption [88–93]. Additionally, humic acid plays a positive promoting role in the adsorption of hydrogen in shale [93]. However, the adsorption capacities for  $CO_2$  and  $CH_4$  are stronger than those for hydrogen [88–90]. Therefore, when utilizing shale as a material for large-scale hydrogen storage, it is important to be mindful of displacing  $CO_2$  and  $CH_4$  as much as possible to enhance the adsorption of hydrogen.

# 4. Adsorption of Hydrogen in Coal

Compared to shale, coal has a richer organic content and a more complex and abundant pore structure [94–96]. A coal seam is a reservoir composed of matrix blocks with natural fractures. It exhibits excellent adsorption capacity due to its rich pore structure, which includes micropores (with sizes <2 nm), mesopores (2–50 nm), macropores (>50 nm), and fractures, with most gases adsorbed mainly in the micropores [94,95].

Under similar conditions, the adsorption of  $CO_2$  by coal is approximately 10 times that of hydrogen [96]. This is attributed primarily to the extremely low zeta potential of coal, which results in a high negative surface charge that interacts with  $CO_2$ , through Lewisacid–base reactions, as well as the formation of hydrogen bonds with alcohols or carbonyl groups [97,98]. The complex organic nature of coal, which contains alcohol and carbonyl groups, further enhances the affinity between  $CO_2$  and coal, favoring  $CO_2$  adsorption [97]. Hydrogen, which lacks an external dipole moment and has a small quadrupole moment, undergoes adsorption on coal surfaces due to van der Waals forces only. Consequently, hydrogen adsorption in coal is lower than  $CO_2$  adsorption [98]. Nevertheless, a considerable amount of hydrogen can still be adsorbed in coal, which has an adsorption capacity of 0.23709 mol H<sub>2</sub> kg<sup>-1</sup> under moderate pressure and temperature conditions (303 K and 3.3 MPa) [96]. Thus, coal remains a viable material for underground hydrogen storage, as illustrated in Figure 6.



**Figure 6.** Schematic illustration of hydrogen adsorption in coal seams. Hydrogen is stored in the form of adsorption in the large pores, mesoporous pores, and micropores of the coal seam.

Excess hydrogen adsorption correlates positively with the rank of the coal [99,100]. Under equivalent temperature and pressure conditions, the changes in both the entropy and the Gibbs free energy decrease with increasing coal rank [96,99,100]. Entropy measures the degree of disorder in a thermodynamic system; as hydrogen molecules diffuse to the adsorption layer, their degrees of freedom decrease, resulting in decreased system disorder, which is reflected by the negative entropy change [99,100]. Furthermore, the negative change in the Gibbs free energy indicates that hydrogen adsorption in coal is a thermodynamically spontaneous process [99]. The varying adsorption capacities of different ranks of coal are attributed primarily to the combined effects of surface chemical properties and pore structures [100]. With the increasing degree of thermal metamorphism (coal ranks), organic matter is gradually enriched, and the carbon (C) content increases, while the content of hydrogen (H), sulfur (S), and oxygen (O) decreases. Oxygen-containing functional groups such as hydroxyl and ether in low-rank coal, as well as aliphatic structures, gradually decrease [101]. However, with the increasing coal ranks, aromatic structures of coal increase [102].

In addition to chemical composition, the pore structure varies with the rank of the coal. The characteristics of pore structures (such as total pore volume, specific surface area, and pore size) change with the metamorphism of the coal. Pore structures are critical characteristics that influence the HAC of the coal [102]. The HAC is determined predominantly by the micropores; thus, the specific surface area of these adsorption pores directly determines the gas-adsorption capacity of coal. From a physical adsorption perspective, the adsorption capacity of a material is proportional to the specific surface area of the micropore [103]. The amount of hydrogen adsorbed is positively correlated with the specific surface area of the micropores. The rank of the coal reflects the development of its pore structure, with the number of micropores controlled by the aliphatic content of the coal dominating when the vitrine reflectance is <1.2%. Further, the number of micropores increases with the enrichment of the aromatic carbon content as the vitrine reflectance increases from 1.2% to 4.5% [104]. Thus, lignite (<0.6%) exhibits a high number of macropores and fractures, which decreases gradually with coal compaction. Medium-rank coal has fewer pores, and anthracite (>1.2%) has a significantly increased number of micropores [90–94]. Micropores can provide a substantial number of adsorption sites because of their high specific surface areas.

Unbalanced forces are experienced by surface atoms in the coal pores; the walls of the coal pores possess relatively high surface free energies. Pore walls typically tend to adsorb gases to lower the surface free energy. When hydrogen molecules diffuse from bulk regions to the pore surfaces, their movement is restricted by gas–solid interactions, leading to a decrease in their degrees of freedom. A portion of this kinetic energy is converted into heat and released into the system during the H<sub>2</sub>-adsorption process. Adsorption heat characterizes the strength of the interaction between hydrogen and the coal. The adsorption heat of hydrogen in coal increases with decreasing pore size [105]. Gas-adsorption effects are not prominent in large pores (>50 nm) or some mesopores (2–50 nm); however, in micropores (<2 nm), gas–solid interactions are enhanced, resulting in increased adsorption [105].

In general, compared to clay minerals and shale, coal exhibits stronger adsorption capability for hydrogen. In addition, coal rank has a great influence on hydrogen adsorption, and the adsorption capacity of high-rank coal is stronger than that of low-rank coal [102]. Coal seams can be utilized as large-scale hydrogen storage materials. However, coal seams contain significant amounts of carbon dioxide and methane, which have stronger adsorption capacities compared to hydrogen [97,98]. This hinders the adsorption of hydrogen in coal. Therefore, in industrial applications, displacement of carbon dioxide and methane is necessary to reduce their impact.

#### 5. Mechanism of Hydrogen Adsorption in Porous Geological Materials

Solid-state hydrogen storage materials are generally classified as those based on chemical or physical storage. Chemical storage involves the formation of chemical bonds to store hydrogen, whereas physical storage relies on adsorption. The potential energy diagram illustrates the interaction between an H<sub>2</sub> molecule and a solid material (Figure 7). For H<sub>2</sub>, the potential energy curve near a solid surface typically exhibits two energy minima at different depths; the one closer to the adsorbent represents physical adsorption at an equilibrium distance farther from the adsorbent, whereas the other at a closer distance corresponds to chemical adsorption of H<sub>2</sub> [102]. Chemical adsorption methods use compounds containing H<sub>2</sub>, such as metal hydrides, chemical hydrides, or complex hydrides, and the release of H<sub>2</sub> usually occurs through heating to a high temperature. Therefore, chemical adsorption is essentially an activation process that requires additional energy to break the chemical bonds between H<sub>2</sub> and other elements, leading to H<sub>2</sub> release with low energy efficiency.



**Figure 7.** Relationship between potential energy and distance from the adsorbent surface for the physical and chemical adsorption of hydrogen gas.  $E_c$ , potential energy of chemical adsorption;  $E_p$ , potential energy of physical adsorption.

In contrast, physical adsorption occurs in most porous materials, where  $H_2$  are absorbed as a monolayer at temperatures above their boiling point [103]. The physical adsorption of  $H_2$  molecules on the surface of porous materials is primarily governed by weak intermolecular forces. These forces include long-range attractive forces between the adsorbent and adsorbate molecules, van der Waals interactions, and short-range repulsive interactions [102–105]. The combined effects of these factors form a shallow potential energy curve minimum at one molecular radius from the surface [106]. The second layer adsorption energy is akin to the vaporization enthalpy of the adsorbate. Therefore, at pressures and temperatures above the boiling point of the adsorbent, the adsorption process leads to the formation of a relatively stable adsorption layer, with gas molecules adsorbed in a monolayer on the surface of the solid adsorbent [107]. This process involves interactions between the adsorbed molecules and the surface of the solid adsorbent, with van der Waals forces playing a predominant role [103]. The adsorption enthalpy of  $H_2$  is considerably small, causing bond rupture; hence, the gas is adsorbed in the molecular form.

Furthermore, because physical adsorption does not involve an activation-energy barrier, this process typically occurs at a rapid kinetic rate [65]. To achieve high  $H_2$  absorption rates through physical adsorption, highly desirable porous materials must have high surface areas, large micropore volumes, appropriate pore sizes, and moderate

adsorption enthalpies [66]. Physical adsorption in porous materials offers the advantages of complete reversibility and fast kinetics compared to chemical storage of hydrogen in metal oxides and complex metal oxide compounds [65–67].

Porous materials can adsorb  $H_2$  either by providing a high surface area or by encapsulating or capturing  $H_2$  in microporous media [66]. In addition, increasing the surface area and porosity of a porous material provides additional adsorption sites on the surfaces and within the pores, thereby enhancing capacity for hydrogen storage through physical adsorption [67]. Parameters such as the surface area, micropore surface area, total pore volume, micropore volume, and pore size thus affect the HAC of porous materials [65–68].

The microscopic mechanism of hydrogen adsorption by clay minerals were studied through DFT and GCMC simulations, and the results showed that no hydrogen molecules were adsorbed in the bulk phases of illite, kaolinite, chlorite, and montmorillonite [44]. The adsorption of hydrogen by sepiolite and palygorskite is a typical physical adsorption, and the adsorption energies are -22,125.11 kJ/mol/molecule and -5.02, respectively. From the perspective of physics, the physical adsorption of H<sub>2</sub> involves charge polarization [44]. The charged ions in the substrate generate a local electric field to polarize H<sub>2</sub>, and the generated electric field depends on the charge on the metal ion [108]. Based on density-derived electrostatic and chemical charge analysis [109], the positive charges of Mg and Al in palygorskite are 2.0 and 2.4, respectively, and the positive charges of Mg in sepiolite are 2.0. The hydrogen molecules have a "side-pair" configuration with respect to the metal ion site, and the distance is greater than 5 Å. It is considered that adsorbed hydrogen in palygorskite and sepiolite is on the outer surface and in the bulk phase, while montmorillonite and chlorite is adsorbed only on the outer surface [44]. The possible adsorption sites in palygorskite and sepiolite are shown in Figure 8.



**Figure 8.** Surfaces of accessible volume (light purple surfaces) and possible adsorption sites (dark violet) of  $2 \times 2 \times 2$  supercell: (a) palygorskite and (b) sepiolite (adapted with permission from Ref [44] 2023, Elsevier Ltd.).

GCMC were used to simulate the adsorption of hydrogen in shale, with kerogen representing the organic matter in shale. They investigated the adsorption of hydrogen in the nanopores of kerogen and montmorillonite separately and found the formation of a single adsorption layer [90]. With increasing pressure, the absorption peak gradually increased. Figure 9a shows the adsorption of hydrogen molecules in kerogen, while Figure 9b displays representative snapshots of H<sub>2</sub> molecule distribution on kerogen surfaces at 12 MPa in the presence of methane [90]. It can be seen that the presence of methane weakens the adsorption of hydrogen. The adsorption of hydrogen in the nanopores of kerogen is slightly greater than that in montmorillonite (approximately twice as much), and the narrower the pore width, the greater the adsorption capacity. The adsorption of hydrogen in the 2 nm pores of kerogen or montmorillonite is greater than in the 5 nm pores [90].



**Figure 9.** (a) Molecular structural view of H<sub>2</sub> adsorption in kerogen at 12 MPa. (b) Representative snapshots of H<sub>2</sub> molecule distribution on kerogen. Color scheme in kerogen: blue, N; cyan, C; yellow S; red, O atoms; white, H; green, Al; pink balls, H<sub>2</sub> molecules. Adapted with permission from Ref [90]. 2023, Elsevier Ltd.

The adsorption mechanism of coal was explored by using GCMU to simulate the adsorption of hydrogen in coals with different ranks at 20-60 °C and 0-15 MPa [100]. The results indicate that hydrogen exhibits non-uniform distribution in pores of 5.38 nm due to van der Waals forces between hydrogen molecules and the pore surface, forming two adsorption layers within the pores [100]. Hydrogen molecules near the pore walls are highly ordered. Due to the chemical heterogeneity of the pore surface, the two adsorption layers are asymmetric. The interaction among hydrogen molecules under high pressure displays that the adsorption capacity of hydrogen is positively correlated with pressure [100–103]. The pore size, specific surface area, and pore volume of coal vary with the degree of coalification, which are the main factors affecting the adsorption of hydrogen in coal. In micropores, the potential energy accumulates and the enhanced potential energy of micropores increases the hydrogen storage capacity [102–104]. High-rank coals contain a large number of micropores, leading to stronger hydrogen adsorption capacity. Furthermore, the degree of coalification (coal rank) also affects the adsorption of hydrogen by coal mainly through surface chemical properties [105]. The carbon content in coal increases with the increase in coal rank, while oxygen, hydrogen, nitrogen, and sulfur increase with the degree of coalification. In low-rank coals, hydrogen exhibits weaker affinity towards oxygen-containing functional groups, whereas in high-rank coals, it shows stronger binding to oxygen-containing functional groups [101]. This is mainly due to the potential energy of oxygen-containing functional groups being compounded by the roughness of the pore surface of bituminous coal [100], as shown in Figure 10, which demonstrates the surface characteristics of pores of different coal ranks and the trajectory of hydrogen molecules in bituminous coal.







**Figure 10.** Pore surface configuration of (**a**) brown coal, (**b**) bituminous coal, and (**c**) anthracite coal. The blue curve represents the trajectory of a hydrogen molecule (Adapted with permission from Ref [100]. 2023, Elsevier Ltd.).

Among the clay minerals, coal, and shale, coal exhibits the highest abundance of micropores, the largest micropore surface area, and the highest adsorption capacity for hydrogen [44,90,100]. All three materials show well-developed pore structures dominated by physical adsorption, demonstrating rapid kinetics of adsorption-desorption processes that are almost entirely reversible (Table 1). Adsorption increases with increasing pressure at a given temperature [92–100]. Moreover, the adsorption capacity of porous materials for hydrogen exhibits a positive linear relationship with micropore volume and an approximate linear relationship with surface area [44]. These observations reflect the fact that hydrogen storage through physical adsorption in porous materials is controlled primarily by nanopores [64]. In addition to surface area and pore volume, the pore size of a porous material is a crucial parameter for determining the performance of hydrogen storage systems based on physical adsorption. Pore size determines the relationship between surface area and pore volume, significantly affecting adsorption enthalpy [64–66]. As the pore size decreases, the specific surface area generally increases. This occurs because materials with small pores may allow H<sub>2</sub> molecules to interact with multiple pore walls, leading to increased adsorption enthalpy [90]. In narrow pores, the interaction energy between H<sub>2</sub> molecules and a carbon adsorbent can be enhanced because of the overlap of the potential fields on both sides of the pore wall. Although there is no consensus on the importance of pore size for hydrogen storage, the comprehensive study results discussed in this paper

show that the hydrogen storage capacity of shale kerogen and montmorillonite with a diameter of 2 nm is greater than that of 5 nm [90], and in the coal, the hydrogen adsorption capacity increases when the pore size is reduced from 5.38 nm to 0.5 nm [100].

Table 1. Comparison of hydrogen storage characteristics of clay minerals, shale, and coal.

	Clay Mineral	Shale	Coal
Hydrogen adsorption model	Langmuir	Freundlich	Langmuir
Hydrogen adsorption capacity (cm <sup>3</sup> /g)	0.5–18.5	2–5	5–20
The most important control factor for hydrogen storage	The differences in specific surface area and pore volume of clay minerals are caused by their inherent crystal structure.	The components of shale (clay minerals and organic matter content).	The metamorphic degree of coal (coal rank).
Specific surface area measured by nitrogen adsorption (m <sup>2</sup> /g)	18–230 m <sup>2</sup> /g	0.3–7.1	0.4–10.2
The specific surface area of micropores measured by carbon dioxide adsorption (m <sup>2</sup> /g)	21–301	10–30	33.7–198.0
micropore volume $(10^{-3} \text{ cm}^3/\text{g})$	4.3–100.6	3.9–5.5	12.4–76.55
Mesoporous volume $(10^{-3} \text{ cm}^3/\text{g})$	40–68	0.87-4.69	0.23–23.62
Advantage	A total of 21.5% of clay minerals exist in the Earth's crust, widely distributed, and clay does not contain other gases, so it does not compete with hydrogen for adsorption. Clay minerals have chemical and physical stability, low toxicity, and easy regeneration.	The adsorption capacity Is higher compared to montmorillonite, widely distributed, often occurring in large-scale forms, with thick layers.	The adsorption capacity of coal is greater compared to shale and clay minerals, as even low-rank coal exhibits significant adsorption capability for hydrogen gas.
Disadvantage	Clay minerals exhibit significant differences in hydrogen storage capacity. Kaolinite hardly adsorbs hydrogen, whereas smectite has an adsorption capacity of $0.47 \text{ cm}^3/\text{g}$ , and hydrotalcite of $20.5 \text{ cm}^3/\text{g}$ . However, the abundance of hydrotalcite is not as high as montmorillonite, illite, and kaolinite.	Shale contains methane, and its adsorption capacity for methane is greater than that for hydrogen, which hinders hydrogen adsorption.	Coal contains carbon dioxide, methane, etc., and its adsorption capacity for carbon dioxide and methane is higher than that for hydrogen, which hinders hydrogen adsorption.

# 6. Conclusions

A comprehensive review of the adsorption behavior of hydrogen in porous geological materials—with a focus on clay minerals, coal, and shale—is presented herein. This review delves into the unique properties of these materials in the context of hydrogen adsorption, revealing the fundamental principles of physical hydrogen storage mechanisms within these porous substrates. The following conclusions were drawn:

- 1. In clay minerals, shale, and coal, physical adsorption that follows the Langmuir adsorption equation is the predominant adsorption process. As pressure increases, the adsorption capacity gradually increases; however, the adsorption capacity decreases with increasing temperature.
- 2. The porous structure of a material—particularly including factors such as the specific surface area, micropore volume, and pore size—plays a crucial role in governing its adsorption capacity. The presence of micropores appears to exert a considerable positive effect on enhancing the hydrogen adsorption enthalpy, indicating that small pores facilitate interactions between H<sub>2</sub> molecules and multiple pore walls, thereby increasing the adsorption capacity.

3. The adsorption capacity of shale and coal for hydrogen is notable, although not as high as that for methane or carbon dioxide. Moreover, the presence of organic acids enhances the hydrogen adsorption capacity.

Clay minerals such as sepiolite and palygorskite exhibit a higher adsorption capacity for hydrogen compared to shale. In addition, their properties remain stable; they do not contain gases such as methane and carbon dioxide which hinder hydrogen adsorption. Therefore, the high-quality sepiolite deposit preferentially used as a large-scale hydrogen storage material. The hydrogen storage capacity of coal seam is much greater than that of shale, and the adsorption performance of high-rank coal is better than that of low-rank coal. However, it is important to displace carbon dioxide and methane during use to minimize their effects. Shale has a higher adsorption capacity than common clay minerals such as montmorillonite, chlorite, and kaolinite, making it a viable alternative to sepiolite deposits and coal seams.

However, as the current research on geological porous materials is still in the initial stage, the research on hydrogen's atomic-level interactions with these porous materials is not deep enough, and further research is needed in the future. This will help us to better understand the microscopic mechanism of hydrogen adsorption in clay minerals, shale, and coal. More importantly, little research has been conducted on the real world applications and scalability of these materials for hydrogen storage, which is urgently needed. This will be used to assess whether these porous geological materials can be used for commercial large-scale hydrogen storage.

Overall, this review provides critical insights into the potential of porous geological materials for hydrogen storage. It also offers valuable guidance for exploring new materials suitable for large-scale hydrogen storage, thereby facilitating the storage of surplus energy and achieving the sustainable development of clean energy.

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