

Article

Study on the Promotion of Methane Hydrate Formation by Surface Modification of Quartz Sand

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Abstract

Natural gas hydrates, with their vast reserves and high gas storage density, have emerged as a highly promising alternative energy source and technology for gas storage and transportation. Wettability, as a core surface property of porous media, directly influences hydrate nucleation, growth, occurrence morphology, and flow behavior. In this study, quartz sand with varying surface properties was prepared with the octyltrimethoxysilane (OTMS) silane coupling agent via surface chemical reactions. The methane hydrate (MH) equilibrium conditions as well as the formation kinetics in silica sand were measured, and the mechanism and potential of the surface modification for enhancing methane hydrate storage capacity were analyzed. The experimental results indicate that surface modification of quartz sand has no significant effect on the MH equilibrium condition. Hydrophobic modification of quartz sand provides more gas–liquid interfaces, increases the contact area, and thereby significantly enhances mass transfer under high-water-saturation conditions and accelerates the MH formation rate. However, excessively high surface hydrophobicity may reduce the effective gas–liquid interfacial area and limit the overall hydrate formation rate. Due to the influences of the hydrate distribution and aggregation, as well as gas diffusion on hydrate formation, the effect of the initial formation pressure on MH formation is only observed during the early stages of MH formation, while the temperature effect is less pronounced than that of formation pressure. It is suggested to further consider combining stirring with continuous gas injection to enhance gas–liquid flow and improve gas–liquid contact, thereby increasing the formation rate of hydrates.



Academic Editor: Marcin Dębowski

Received: 24 June 2026

Revised: 23 July 2026

Accepted: 1 August 2026

Published: 5 August 2026

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Keywords: methane hydrate; porous media; surface modification; wettability; formation behavior

1. Introduction

Natural gas hydrates (NGHs) are considered a promising alternative energy source due to their vast reserves in marine sediments and permafrost regions. Gas hydrates also possess exceptionally high gas storage densities; for example, one unit volume of MHs can typically store approximately 160 volumes of methane (CH₄) gas at standard temperature

and pressure (STP). These properties make hydrate-based technologies for gas storage, transportation, and separation highly attractive.

Porous media have larger specific surface areas and high thermal conductivity, enhancing gas–liquid contact and heat/mass transfer, thereby accelerating hydrate formation and increasing overall storage capacity [1]. Compared to physical disturbances such as mechanical stirring and the addition of chemical accelerators, porous media have the advantages of non-pollution, recyclability, and low cost. However, the use of porous media reduces the effective formation volume of hydrates, increases the weight of the system, and increases the cost of hydrate storage and transportation. Therefore, current research on enhancing hydrate formation technology through porous media mainly focuses on improving hydrate nucleation and formation rate, increasing final gas storage density, and designing and synthesizing low-cost and lightweight porous media materials [2].

Various media, including quartz sand, activated carbon, metal–organic frameworks (MOFs), and metal foams, have been explored to optimize storage density and heat dissipation [2,3]. In porous media, the formation and decomposition of hydrates are influenced by many factors, including sediment grain size, pore structure, mineral composition, etc., [4–7]. In addition to these properties, the surface characteristics of sediment particles play a critical role in modifying the gas–liquid interfacial microenvironment. In particular, particle wettability, together with surface roughness and electrochemical properties, strongly regulates hydrate nucleation, growth behavior, and the resulting multiphase flow patterns and hydrate morphologies at the pore scale [7,8]. From a theoretical perspective, classical heterogeneous nucleation theory suggests that the Gibbs free energy barrier for nucleation is strongly dependent on the three-phase contact angle. Wettability affects the manner in which liquid water adheres to particle surfaces, thereby directly influencing local water and gas distribution, and hydrate formation and dissociation behaviors [9–11]. Moreover, recent studies have demonstrated that the evolution of wettability is one of the important factors affecting the permeability of hydrate-bearing sediments, exerting a significant impact on gas production efficiency during NGH exploitation [8]. Therefore, an investigation of the effects of sediment wettability on MH formation kinetics is essential for understanding and regulating MH growth behavior in porous media.

Esmail and Beltra [12] conducted MH formation experiments on glass, sapphire, and polyvinyl chloride surfaces with progressively decreasing wettability, and reported that MHs form faster on more hydrophilic surfaces. Guo et al. [13] investigated the effects of calcium carbonate nanoparticles with different wettability on MH formation kinetics, demonstrating that, under specific hydrophilic modification conditions, nanoparticles can significantly accelerate MH formation, highlighting the high sensitivity of hydrate kinetics to surface wettability. Kou [14] systematically investigated xenon hydrate formation morphology and spatial distribution in porous media with different particle sizes under various formation conditions using X-ray computed tomography (CT) scanning and found that wettability differences lead to pronounced variations in hydrate distribution patterns and morphological evolution. Chaouachi et al. [15] employed CT imaging to study xenon hydrate formation in quartz sand, revealing that hydrophilic quartz grains tend to develop a continuous water film, causing hydrates to preferentially form at the water–gas interface during the early stage of formation. In contrast, hydrophobic quartz grains exhibit stronger gas adsorption, resulting in gas bubbles trapped between the grain surface and the hydrate phase. Fuji et al. [16] numerically investigated hydrate growth in sand pores with contact angles of 20°, 90°, and 120°, finding that the wetting condition dictates the growth pattern: under strongly water-wet condition (20°), hydrates coat sand grains, whereas under intermediate (90°) or non-wet (120°) conditions, they form as discrete particles in pore spaces.

Overall, variations in particle surface wettability directly alter the adsorption and distribution states of water and CH₄ molecules on grain surfaces. On the one hand, enhanced local continuity and ordering of water molecules increase the gas molecule density near the interface, thereby reducing the nucleation energy barrier and promoting gas hydrate nucleation [17]. On the other hand, differences in gas–water contact configurations induce local interfacial energy heterogeneity [18], significantly enhancing mass transfer efficiency and ultimately governing hydrate nucleation modes, growth pathways, and final morphologies in porous media [14,19].

Recently, it has been demonstrated that modifying the surface properties of porous media can enhance gas–liquid interfacial contact, thereby promoting or inhibiting hydrate nucleation and growth without adding thermodynamic or kinetic additives [20–22]. Kim et al. [20] achieved faster carbon dioxide (CO₂) hydrate formation rates and higher CO₂ consumption in modified silica sand systems through simple surface modification, without adding any thermodynamic or kinetic additives. Compared with literature records, the CO₂ formation rate and total storage capacity were improved by 55.3% and 21.6%, respectively. Li and Wang [21] surface-treated glass particles using the silane coupling agents octadecyltrichlorosilane (OTS) and N-dimethyl-N-octadecyl-3-aminopropyl trimethoxysilyl chloride (DMOAP). The study found that in all tested hydrate systems, strongly hydrophobic OTS-coated particles significantly increase nucleation rates and shorten the induction time for hydrate formation. Rothmund et al. [22] employed molecular dynamics (MD) simulations to investigate how the surface wettability of porous activated carbon ranging from strongly hydrophilic to strongly hydrophobic influences the formation, stability, and gas storage capacity of hydrogen (H₂) and CH₄ clathrate hydrates under confined conditions. The study revealed that when the surface exhibits moderate hydrophilicity (water contact angle $\approx 43^\circ$), the hydrate formation rate, stability, and gas storage capacity reach their maximum values. Strongly hydrophilic surfaces hinder the tetrahedral coordination structure required for hydrate formation and increase the thickness of the interfacial “pre-melt layer”. Strongly hydrophobic surfaces promote gas–water phase separation, generating numerous empty cages at the interface and leading to structural instability.

Although a substantial amount of research has been conducted on hydrate formation in various porous media, gas–liquid contact and mass transfer remain important limiting factors that restrict the formation rate and gas storage capacity of hydrates. For example, the hydrate films at gas–liquid interfaces act as mass transfer barriers due to the rapid formation of hydrates hinder further gas diffusion, resulting in the “encrustation effect” and reducing the hydrate formation rate [23,24]. As the primary reservoir medium for natural gas hydrates, the characteristics of hydrate formation in quartz sand have been extensively studied. The investigation on the impact of surface modification of quartz sand on hydrate formation is helpful to understand the influence of interfacial interactions on the hydrate formation rate, gas storage capacity, and hydrate distribution behavior, which is of great significance for the development of hydrate gas storage technology, phase control in hydrate exploitation, and carbon dioxide sequestration technology. Currently, although preliminary studies indicate that surface modification of porous media also holds promise for improving hydrate formation rates and enhancing hydrate gas storage capacity, the research remains limited regarding the effects of different surface properties on MH formation behavior in porous media. In particular, the coupled interaction mechanisms between modified surfaces and hydrate formation conditions, such as formation temperature and pressure across different stages of hydrate formation, require further in-depth investigation. This gap in mechanistic understanding constrains the engineering implementation of surface modification techniques in applications related to hydrates.

In this study, to investigate the influence of surface properties on MH formation in porous media, OTMS was selected as the silane coupling agent to modify the surface wettability of silica sand and conduct hydrate formation experiments. Through controlled specific surface chemical reactions, hydrophobic functional groups were grafted onto the quartz sand surface to shield or replace the inherent hydrophilic silanol groups, thereby producing silica sand with tunable surface wettability. Building upon this, by systematically varying experimental temperature and pressure, the equilibrium (formation and dissociation) behavior and hydrate formation kinetics of MH under different surface wettability conditions were measured. The resulting trends and underlying mechanisms were analyzed and compared with those of unmodified silica sand across a range of water saturations.

2. Experimental Sections

2.1. Apparatus

A schematic diagram of the experimental apparatus for MH formation and dissociation in sandy sediments is shown in Figure 1 [25]. The core of the system is a high-pressure reactor (labeled as CR) constructed from 316 L stainless steel, with a total effective volume of approximately 56.91 mL and a maximum operating pressure of 20 MPa. In addition to the main reactor, a high-pressure gas supply vessel (labeled as SV) is also submerged within the same water bath. This gas supply vessel is designed to pre-cool the injected methane gas to the target experimental temperature, thereby preventing thermal fluctuations during gas injection. The temperature of the reactor was controlled by a water bath (XT5204-BS30, Xutemp Temptech Co., Ltd., Hangzhou China), which maintained temperature within the range of 243.15–363.15 K. The temperature and pressure inside the reactor were monitored using a Pt100 resistance thermometer (Hasteco Technology Co., Ltd., Dongguan, China; standard uncertainty: ± 0.10 K) and a BD pressure transducer (Hante Machinery Co., Ltd., Shanghai, China; standard uncertainty: 0.1% FS, range 0–25 MPa), respectively. A data acquisition system recorded pressure and temperature data at 8 s intervals.

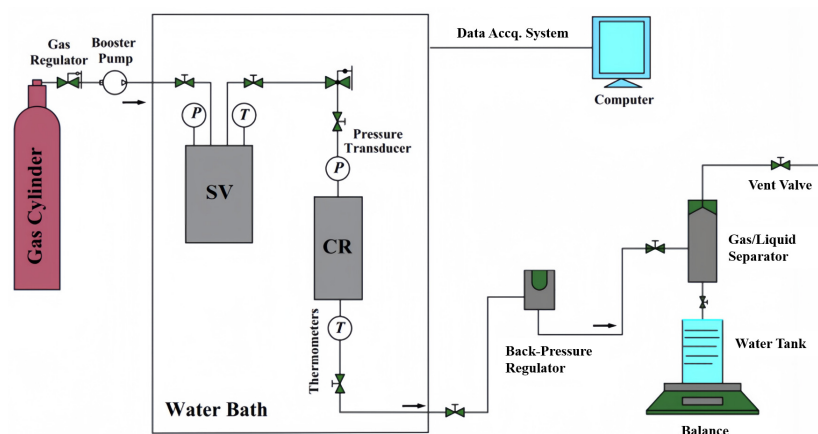


Figure 1. Schematic of the experimental apparatus.

2.2. Materials

The experimental materials used in this study are listed in Table 1. Methane gas (>99.95% purity) employed in the experiments was supplied by Guangzhou Junduo Gas Co., Ltd. (Guangzhou, China). Deionized water was prepared using an ultrapure water system (Nanjing Ultrapure Water Technology Co., Ltd., Nanjing China) with a resistivity of $18.25 \text{ M}\Omega \cdot \text{cm}^{-1}$. Quartz sand was supplied by Shanghai Macklin Biochemical Technology Co., Ltd. (Shanghai, China), with an average particle size of $224.76 \mu\text{m}$. OTMS ($\geq 97\%$ purity), used for quartz sand surface modification, was provided by Shanghai

Macklin Biochemical Technology Co., Ltd. Ethanol (99.5%) was supplied by Shanghai Aladdin Biochemical Technology Co., Ltd. (Shanghai, China).

Table 1. Properties of materials used in the experiments.

Materials	Specifications	Suppliers
Deionized water	18.25 MΩ·cm ^{−1}	Self-made by deionized water machine
CH ₄ gas	Purity of 99.95%	Guangzhou Junduo Gas Co., Ltd.
Quartz sand	Median particle size of 224.76 μm	Shanghai Macklin Biochemical Technology Co., Ltd.
OTMS	Purity of 97%	Shanghai Macklin Biochemical Technology Co., Ltd.
Ethanol	Purity of 99.5%	Shanghai Aladdin Biochemical Technology Co., Ltd.

2.3. Surface Modification Methods for Quartz Sand

In this work, OTMS was employed as a silane coupling agent for surface modification of quartz sand, with the reaction mechanism illustrated in Figure 2. The modification process involves two key steps. First, OTMS undergoes hydrolysis in the presence of water, converting its methoxy groups into reactive silanol groups. Next, these silanols react with the surface silanol groups of quartz sand via a dehydration condensation reaction, forming stable siloxane (Si–O–Si) bonds. As a result, the originally hydrophilic Si–OH groups are replaced by hydrophobic long-chain alkyl groups, forming a molecular hydrophobic coating that prevents direct contact between water molecules and the quartz sand surface, thereby transforming the surface properties from hydrophilic to hydrophobic [26].

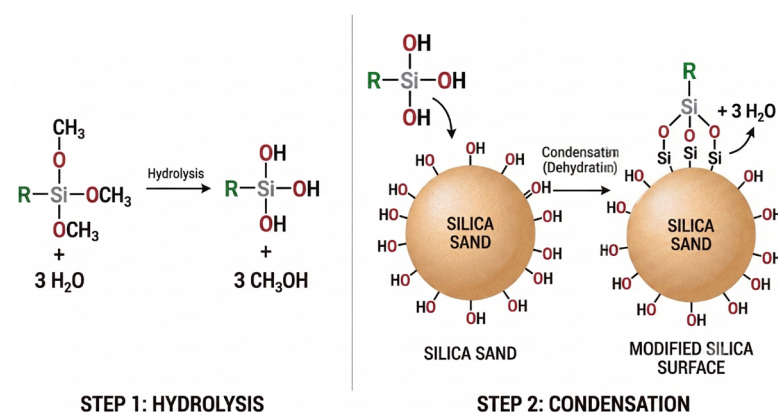


Figure 2. Schematic diagram of the reaction mechanism for surface modification of quartz sand using coupling agents.

The quartz sand surface was modified using OTMS following these procedures: (1) The sand was thoroughly rinsed with deionized water and ethanol, then dried at 373.15 K for 24 h. A total of 150 g of quartz sand was placed in a beaker and mixed with 150 mL of a solution containing 75% ethanol and 25% deionized water. Here, ethanol serves as an essential co-solvent; because the long hydrophobic alkyl chains make OTMS immiscible with pure water, the ethanol–water mixture ensures that OTMS is uniformly dissolved and adequately hydrolyzed before reacting with the sand surface; (2) OTMS was added at concentrations of 0.7 wt% and 1.4 wt% to achieve surface modification; (3) The mixture was mechanically stirred at 600 rpm for 10 h at 293.15 K to ensure uniform modification; (4) After the reaction, the solvent was removed by vacuum filtration, and the modified sand was rinsed ten times with ethanol and deionized water. Finally, the surface-modified quartz sand was dried at 373.15 K for 8 h [27].

To comprehensively validate the surface modification, X-ray photoelectron spectroscopy (XPS) measurements were conducted on a Thermo Scientific K-Alpha+ spectrom-

ter (Thermo Fisher Scientific, Waltham, MA, USA) using Al K α radiation ($h\nu = 1486.6$ eV). Binding energies were calibrated using the adventitious carbon C 1s peak at 284.8 eV. Fourier transform infrared (FT-IR) characterization was performed using a Micro FT-IR spectrometer (Thermo Fisher Scientific, Waltham, MA, USA) over the wavenumber range of 4000 to 400 cm^{-1} . The surface morphology of the quartz sand samples was examined using a Hitachi S-4800 scanning electron microscope (SEM) (Hitachi, Ltd., Tokyo, Japan). This instrument operates with a nominal maximum resolution of approximately 1.0 nm. Given that the theoretical length of a single OTMS molecule is roughly 1.0–1.5 nm, individual molecules cannot be distinctly resolved on the bulk quartz substrate. Therefore, the SEM was exclusively utilized to observe the larger-scale morphological evolution, specifically the formation of cross-linked silane polymeric aggregates on the particle surfaces. Furthermore, the specific surface area and pore structure of the samples were evaluated using the nitrogen adsorption–desorption method (BET method) on an automated surface area and pore size analyzer. To determine wettability, the static contact angle of each sample was measured three times using a Chengde Dingsheng JY-82C video contact angle measuring instrument (Chengde Dingsheng Testing Machine Co., Ltd., Chengde, China) to obtain the average contact angle (θ).

The XPS survey spectra (Figure 3) provide direct quantitative evidence for the successful grafting and controllability of the modification process. All samples exhibit characteristic peaks for O 1s (at 532 eV), Si 2p (at 103 eV), and C 1s (at 284.8 eV). Compared to the pristine sand, the intensity of the C 1s peak increases significantly and scales positively with the OTMS concentration (from 0.7 wt% to 1.4 wt%). Conversely, the relative intensities of the O 1s and Si 2p peaks decrease as the thickness of the organic OTMS layer increases, confirming that the modification is both effective and highly controllable.

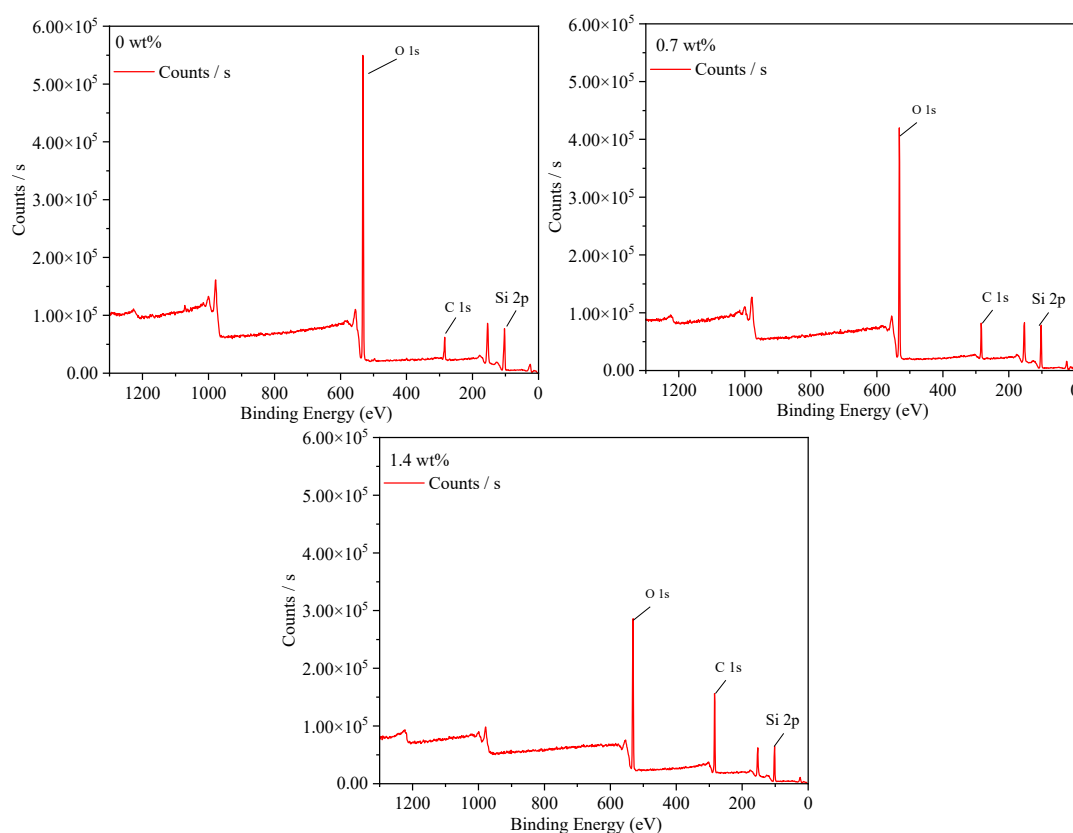


Figure 3. X-ray photoelectron spectroscopy (XPS) survey spectra of quartz sand samples. The x-axis is binding energy (eV), and the y-axis is count rate (Counts/s). Characteristic core-level peaks of O 1s, C 1s, and Si 2p are labeled in each spectrum.

Complementing the XPS data, the FT-IR results presented in Figure 4 elucidate the chemical bonding mechanism. Distinct absorption peaks at 2920 cm^{-1} (asymmetric $-\text{CH}_2-$ stretching) and 2850 cm^{-1} (symmetric $-\text{CH}_2-$ stretching) appear exclusively for the modified samples, along with the CH_2 scissoring vibration at 1460 cm^{-1} , confirming the presence of long-chain alkyl groups. Furthermore, the broad bands around 3400 cm^{-1} (Si-OH stretching) and 1630 cm^{-1} (adsorbed water bending) decrease markedly after modification. This indicates that the surface silanol groups (Si-OH) act as primary reactive sites, consumed via dehydration condensation with the modifier to form stable siloxane bridges. The retention of core SiO_2 peaks at 1100 , 800 , and 470 cm^{-1} demonstrates that the modification occurred exclusively on the surface without altering the bulk crystal structure.

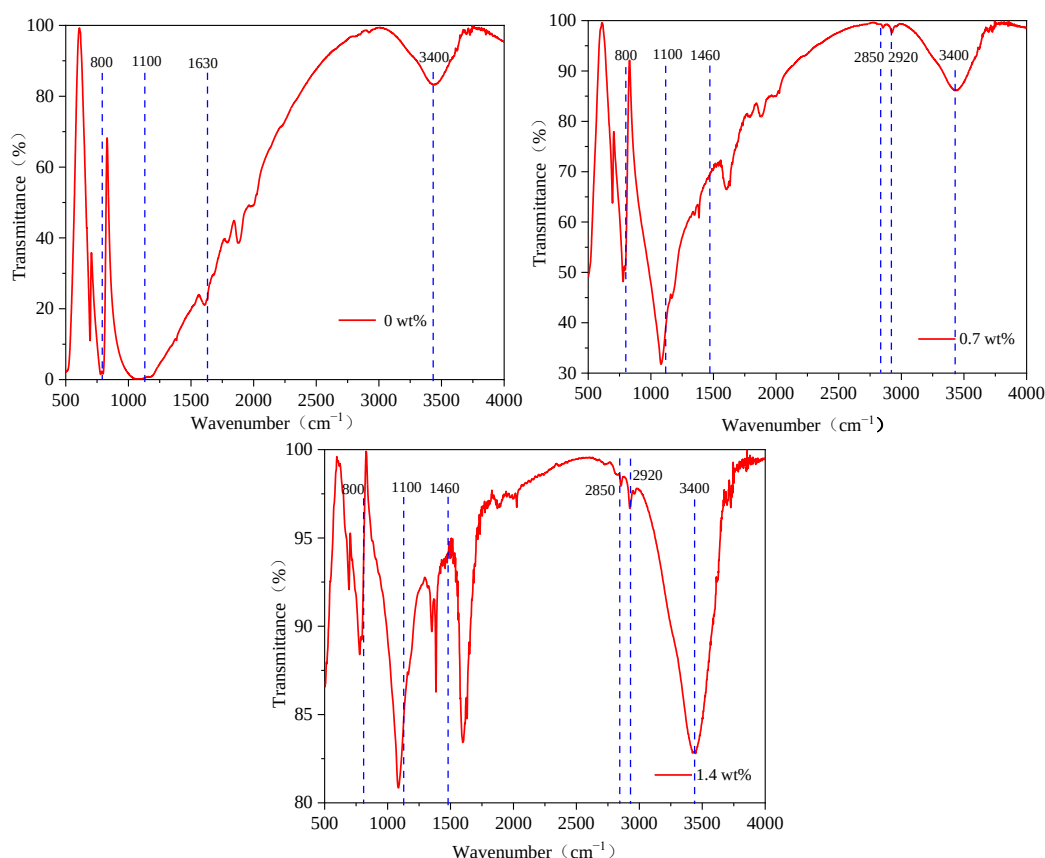


Figure 4. Fourier Transform Infrared (FT-IR) spectra of the quartz sand. All spectra were acquired in transmission mode over the wavenumber range of 4000 to 400 cm^{-1} ; the y-axis represents the transmittance (%).

The SEM images in Figure 5 further reveal distinct morphological changes induced by OTMS modification. The pristine quartz sand exhibits relatively smooth surfaces with typical conchoidal fractures and minor fine debris. It is crucial to note that the Hitachi S-4800 SEM (Hitachi, Ltd., Tokyo, Japan) used herein operates with a nominal maximum resolution of approximately 1.0 nm . Since a single OTMS molecule has a theoretical length of roughly 1.0 – 1.5 nm , individual physically adsorbed molecules cannot be resolved on the bulk non-conductive quartz substrate. In contrast, the modified sand (particularly the $1.4\text{ wt\%}$ sample) is uniformly covered by a coating of submicron-to-nanoscale granular aggregates. Rather than simple single-molecule adsorption, these distinct structures are macroscopic modifications induced by the chemical treatment procedure—specifically, the extensive cross-linking and condensation polymerization of multiple OTMS molecules.

This polymerization forms a rough, worm-like nano-protrusion network without evidence of large-scale delamination or uneven accumulation.

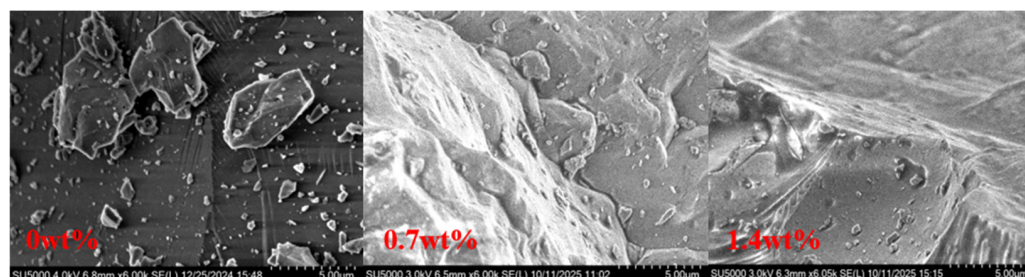


Figure 5. Scanning electron microscope (SEM) image of quartz sand.

Nitrogen adsorption–desorption analysis further confirms that the modification alters surface polarity significantly without disrupting the fundamental pore structure (Figure 6). As detailed in Table 2, the pristine quartz sand exhibits an extremely low specific surface area (SBET) of $0.195 \text{ m}^2/\text{g}$. Following modification, (SBET) slightly increases (up to $0.681 \text{ m}^2/\text{g}$ for the 1.4 wt% sample), with total pore volume (V_p) and average pore diameter (D_p) showing only negligible fluctuations. Crucially, the BET C-constant (a direct indicator of surface polarity) drops precipitously from 7.787 in the pristine sand to 1.507 in the 1.4 wt% modified sample. Because methane hydrate predominantly forms within macroscopic interstitial spaces rather than within mesopores, these subtle structural variations exert a minimal influence on formation kinetics. Instead, it is this chemically induced hydrophobicity that decisively regulates water distribution and facilitates optimal gas–water–solid contact.

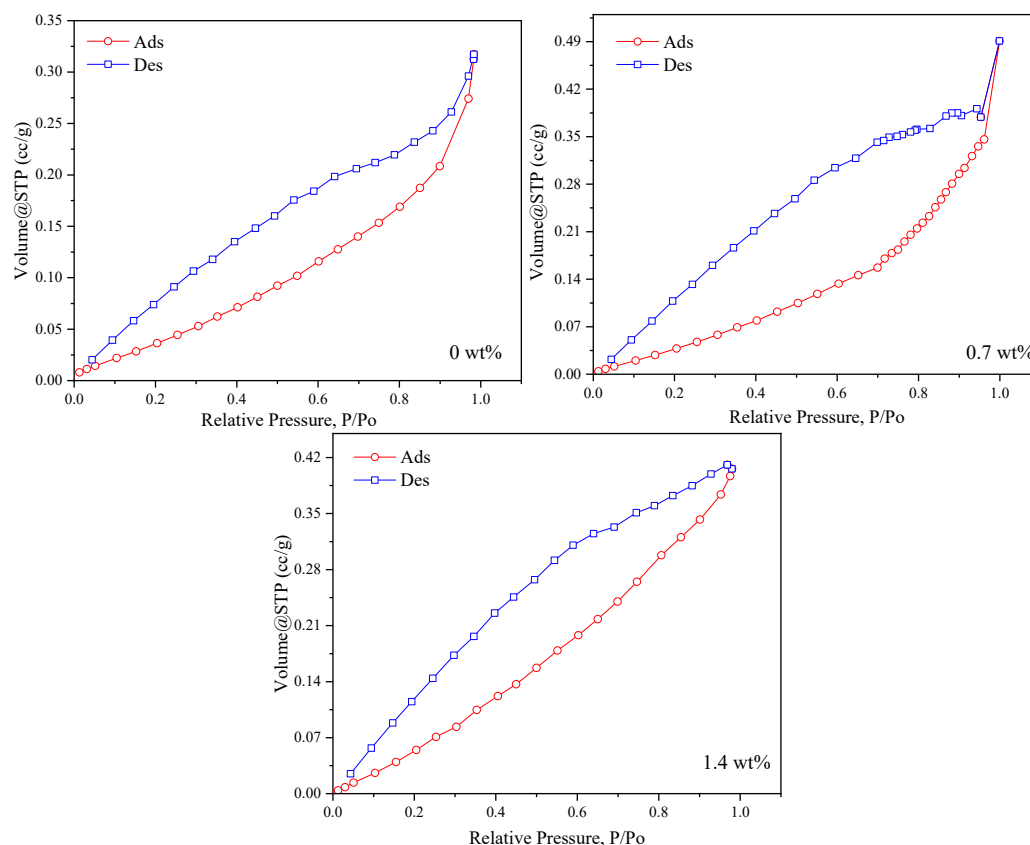
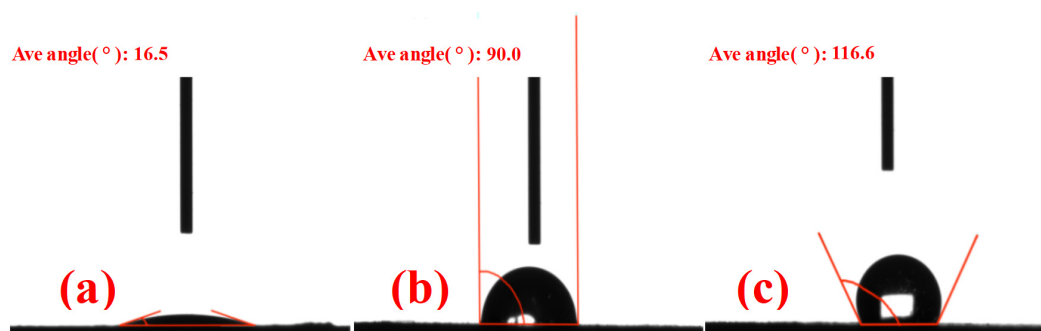


Figure 6. Nitrogen adsorption–desorption isotherms of the quartz sand. Blue squares and red dots denote the adsorption and desorption branches, respectively.

Table 2. Textural properties and pore structure parameters of the pristine and modified quartz sand.

Key Parameters	Quartz Sand	0.7 wt% Modified Sand	1.4 wt% Modified Sand
BET Specific Surface Area (m ² /g)	0.195	0.302	0.681
BET C-constant	7.787	3.002	1.507
Total Pore Volume (cc/g) × 10 ^{−4}	4.919	7.613	6.294
Average Pore Diameter (nm)	10.114	10.093	7.400

As shown in Figure 7, the average θ of the samples are 16.5° (unmodified, denoted as 0 wt% OTMS), 90.0° (modified with 0.7 wt% OTMS), and 116.6° (modified with 1.4 wt% OTMS). The selection of contact angles at 16.5°, 90.0°, and 116.6° (corresponding to unmodified, moderate-concentration, and high-concentration OTMS modification, respectively) was strategically determined based on macroscopic multiphase flow mechanics. While previous molecular dynamics simulations suggest an optimal hydrophilic angle (e.g., ~43°) for nanoscale confined pores due to molecular entropic barriers [22], mass transfer in macroscopic sandy sediments (median size ~224.7 μm) is fundamentally governed by macroscopic capillary pressure (P_c). According to the Young–Laplace equation, the transition of P_c from positive (spontaneous imbibition) to negative (drainage) hinges strictly on the 90° threshold [28].

**Figure 7.** Contact angle measurement images of quartz sand at different modification concentrations: (a) 0 wt%; (b) 0.7 wt%; and (c) 1.4 wt%.

Therefore, these three specific points were deliberately chosen to bracket distinct macroscopic fluid distribution regimes: the 16.5° pristine sand serves as the strongly hydrophilic baseline where positive capillary forces form continuous, diffusion-blocking water films; the 90.0° state represents the critical neutral wettability point where minimized capillary forces yield finely dispersed droplets, theoretically maximizing the gas–liquid interfacial area; and the 116.6° state represents the strongly hydrophobic regime, serving to test the limits of water repulsion and identify potential droplet agglomeration (the “over-modification” effect). These three representative parameters effectively capture the complete transition interval necessary for systematically studying the macroscopic wettability effect on hydrate mass transfer kinetics.

For practical applications, the durability of the silane coating was assessed over five consecutive hydrate formation/dissociation cycles using the S3 sample ($\theta \approx 90^\circ$). After five cycles, the contact angle was maintained at $90 \pm 1.5^\circ$, and the gas consumption rate remained within 95% of the initial run (Figure 8). This high stability is attributed to the robust Si–O–Si covalent bonding of the OTMS layer, which resists leaching and hydrolysis

under repeated hydrate cycling, in contrast to physically adsorbed kinetic promoters such as SDS. The absence of degradation confirms that the kinetic promotion effect is a persistent interfacial phenomenon, highlighting the potential of OTMS-modified quartz sand for reusable hydrate-based applications.

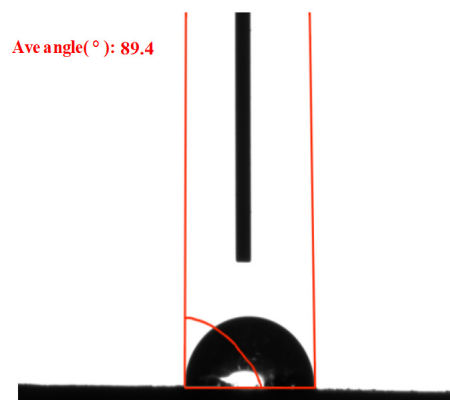


Figure 8. Contact angle measurement images of sample S3 after five hydrate formation/dissociation cycles.

These multi-scale characterizations (XPS, FT-IR, and SEM) collectively confirm that the replacement of hydrophilic silanol groups with hydrophobic alkyl chains creates an ideal microenvironment for accelerating hydrate kinetics by optimizing gas–water–solid contact.

2.4. Hydrate Formation Process

In this study, the mass of the modifier on the quartz sand surface after modification was negligible and thus considered to have no effect on the true density of the sand. Table 3 gives the masses of the quartz sand and water in the reactor for different experimental systems. During the filling process, to avoid cavitation within the reactor and ensure a completely homogeneous macroscopic distribution, the quartz sand and water were divided into three equal portions and alternately layered and gently compacted into the reactor [29]. This specific packing procedure ensures that the quartz sand forms a uniform, horizontal cylindrical packed bed rather than an irregular pile. Furthermore, this method guarantees that the water is uniformly distributed throughout the interstitial pore spaces of the sand matrix, effectively preventing gravity-driven drainage and ensuring that no bulk liquid layer forms at the bottom of the reactor. For each system, the reactor was filled with 37.50 g of quartz sand, assuming an apparent quartz sand density of $1.4 \text{ g}\cdot\text{cm}^{-3}$ and a porosity of 38.6%, as summarized in Table 3. The water saturation was calculated using the following formula:

$$S_w = \frac{V_w}{V_{\text{pore}}} = \frac{m_w}{\rho_w V_{\text{pore}}} \quad (1)$$

where m_w and ρ_w denote the mass and density of water, respectively, and V_{pore} represents the total pore volume.

Table 3. Summary of all systems used for MH formation.

System	OTMS Mass Fraction (wt%)	Sand Mass (g)	Water Quality (g)	Gas Volume (ml)	Water Saturation (%)
S1	0	37.50	17.80	24.70	144
S2	0	37.50	9.45	33.10	70
S3	0.70	37.50	17.80	24.70	144
S4	1.40	37.50	17.80	24.70	144

After the reactor was filled, it was flushed with CH₄ gas at least twice to remove residual air. The water bath temperature was then set to 20 °C, and CH₄ gas was injected into the reactor to the preset pressure. In order to avoid the influence of methane dissolution on the calculation of gas consumption for hydrate formation, the reactor was kept stationary for sufficient time after gas injection to ensure that the temperature and pressure inside the reactor reached stability. Once the temperature and pressure inside the reactor stabilized, the water bath temperature was adjusted to the target MH formation temperature, and the MH formation experiment was initiated. In general, MH formation is considered complete when the reactor pressure remains constant for 5 h. However, in this study, MH formation proceeded at a relatively slow rate, resulting in an excessively long completion time. Therefore, each MH formation experiment was terminated after 72 h. This 72 h duration was selected based on preliminary observations showing that hydrate growth in modified systems (S3 and S4) primarily concentrated within the first 20–30 h, followed by a diffusion-controlled stage with a gas consumption plateau. Extending the observation to 72 h ensures that all systems, including the pristine sand (S1), sufficiently reach a representative reaction endpoint where growth nearly ceases, capturing the full kinetic trajectory from nucleation to mass transfer limitation [30,31].

The CH₄ gas consumption during MH formation was calculated using the Soave–Redlich–Kwong (SRK) equation of state based on pressure and temperature variations in the reactor [32]. To guarantee strict comparability across systems with varying wettability, all trials were performed under standardized, synchronized experimental protocols: Mass Consistency: 1. The quartz sand and water masses were weighed using a high-precision digital balance (± 0.01 g) to ensure identical water saturation (S_w) in every system. 2. Standardized Packing: As described, the sand and water were divided into three equal portions and alternately layered and gently compacted to fill the specific volume of the reactor, maintaining a uniform bed density and an identical initial porosity of 38.6%. 3. Atmosphere Control: After assembly, the reactor was flushed with CH₄ gas at 0.5 MPa for at least two cycles to remove residual air, ensuring uniform gas-phase purity across all systems. 4. Thermal Equilibrium: Before gas injection, the system was stabilized in the water bath for 60 min to ensure that the sediment bed reached the initial thermal equilibrium. These protocols ensured that any observed kinetic variations could be exclusively ascribed to the differences in surface wettability rather than experimental artifacts. Consequently, the observed kinetic variations and 72 h terminal metrics can be exclusively ascribed to the reconfiguration of pore-scale water distribution and mass transfer pathways driven by surface modification. The CH₄ gas consumption within the sediment at any given time was calculated using the following equation:

$$\Delta n_{\text{CH}_4,t} = n_0 - n_t = \frac{1}{R} \left[\left(\frac{V_g P_0}{Z_0 T_0} \right) - \left(\frac{V_g P_t}{Z_t T_t} \right) \right] \quad (2)$$

where P_0 , T_0 , and P_t , T_t are the pressures (MPa) and temperatures (K) in the reactor at the initial time and at any given time t , respectively; Z_0 and Z_t represent the compressibility factor at the initial time and at any given time t , respectively; V_g is the gas volume (cm³) of gas; n_0 and n_t are the amounts of gas (mol) at the initial time and at any given time t , respectively. Assuming a hydration number of 5.75, the water conversion rate was calculated based on methane gas consumption.

2.5. Measurement of Phase Equilibrium Conditions

In the experiment for measuring phase equilibrium conditions, the water bath temperature was initially set to 293.15 K, and CH₄ gas was injected into the reactor to a predetermined pressure of 8 MPa. After the system temperature stabilized, the reactor was

cooled to 277.15 K to form MHs. When the reactor pressure remained constant for 5 h, hydrate formation was considered complete. Subsequently, the temperature was gradually raised to 293.15 K to induce MH decomposition. During the initial stepwise heating phase, the system was heated at a rate of 1 K/h to the target temperature. Upon approaching the phase equilibrium point, the heating rate was reduced to 0.1 K/h until the initial temperature was reached. This study defines the intersection point of the P-T curves from rapid cooling and multi-step heating as the MH phase equilibrium point, indicating complete decomposition [33].

3. Results and Discussion

3.1. Effect of Surface Wettability of Quartz Sand on MH Equilibrium Conditions

Factors influencing hydrate formation kinetics in porous media include hydrate equilibrium conditions, gas–liquid contact area, and heat and mass transfer processes. Phase equilibrium condition for hydrate formation determines the spontaneous direction of the reaction and the magnitude of its driving force. Porous media alter hydrate phase equilibrium boundaries through capillary effects, pore structure constraints, and interfacial interactions, thereby regulating nucleation and growth kinetics [34,35]. Extensive research indicates that capillary effects within pores, changes in the chemical potential of water, and the properties of the solid–liquid interface (i.e., wettability), significantly alter local phase equilibrium conditions. This leads to actual hydrate formation conditions deviating from macroscopically predicted ones. Simultaneously, wettability, as the fundamental property determining the contact morphology and interfacial energy among the gas, liquid, and solid phases, which is not only regulates the spatial distribution and contact efficiency between gas and water but also directly influences the nucleation site selection, growth patterns, and adhesion strength of hydrate crystals to sediment particles [36,37].

In this study, to evaluate the effect of hydrophobic modification of quartz sand surfaces via OTMS on MH formation and decomposition, the hydrate equilibrium conditions of MHs in the modified quartz sand were measured. Figure 9 presents the P-T variation curve from the experiments, alongside the phase equilibrium curve of MHs in a pure water system [38].

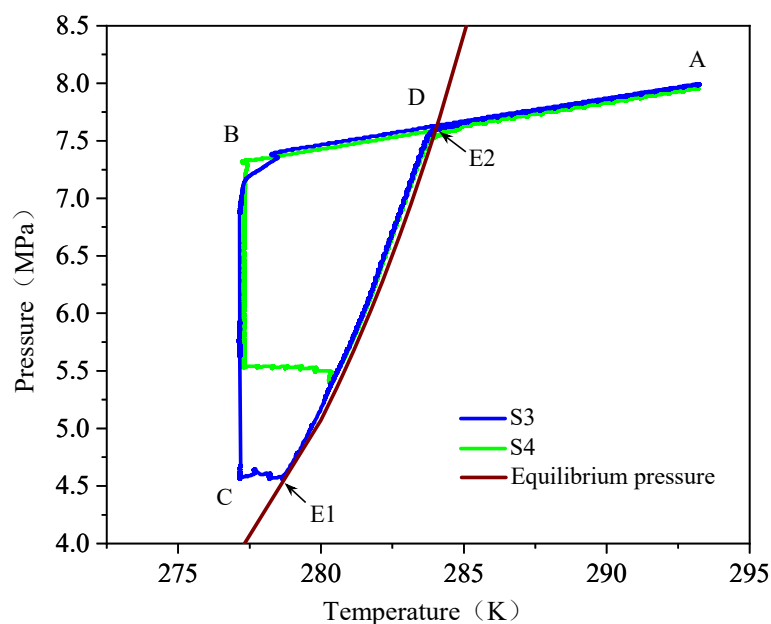


Figure 9. Phase equilibrium behaviors of MHs in system S3 ($\theta = 90.0^\circ$) and system S4 ($\theta = 116.6^\circ$).

As shown in Figure 9, taking system S3 as an example, at Point C, with the formation of a large number of hydrates, the pressure in the reactor is basically stable, and the temperature begins to rise to decompose the hydrates. It should be pointed out that at this time, the hydrate in the reactor has not reached a stable state, but the formation rate of the hydrate becomes extremely slow due to mass transfer. Between points C and E1, the pressure within the reactor does not increase significantly despite the rising temperature, likely due to fluctuations caused by ongoing hydrate formation and temperature changes. After point E1, as the temperature continues to rise, the hydrates within the quartz sand gradually decompose, achieving complete decomposition at point E2. Between points E1 and E2, the pressure in the reactor closely follows the phase equilibrium pressure curve of MHs in pure water. It is worth noting that while the slow continuous heating method (0.1 K/h) fundamentally relies on dissociation kinetics and typically yields quasi-equilibrium conditions, the excellent agreement between our measured curves and the theoretical pure water baseline [38] serves as robust validation. This alignment confirms that hydrate dissociation in these highly permeable quartz sand systems is sufficiently fast, meaning that the 0.1 K/h heating rate did not introduce significant kinetic hysteresis. The hydrate decomposition curve for S4 exhibits identical patterns, indicating that hydrophobic modification of quartz sand surfaces using OTMS has no significant effect on the equilibrium conditions of MHs. Specifically, the experimentally determined complete dissociation points (corresponding to the intersection point E2 in Figure 9) for both the S3 and S4 validation systems were recorded at approximately 283.97 K and 7.60 MPa, which perfectly aligns with the theoretical phase boundary. This macroscopic observation is well-supported by microscale insights from molecular dynamics (MD) simulations. Although variations in surface wettability profoundly regulate local gas enrichment, molecular adsorption, and pore-scale fluid dynamics during the kinetic growth phase [39], the intrinsic thermodynamic stability of the crystalline hydrate cages remains essentially unaffected by the solid substrate's surface properties [40]. Consequently, the fundamental phase equilibrium boundaries of MHs are not significantly shifted by the chemical modification, further confirming that the promotional effect of OTMS modification is exclusively kinetically driven.

3.2. Effect of Surface Properties on MH Formation

In this study, hydrate formation experiments were conducted using two types of quartz sand with varying degrees of surface modification, as well as unmodified quartz sand. Table 4 provides detailed information on the experiments performed, including the initial pressure for hydrate formation, the formation temperature, the induction time, final gas consumption and water conversion rate. To comprehensively evaluate the kinetic performance of the surface-modified sand, a multi-tier experimental design was implemented involving two distinct water saturation regimes. The 70% water saturation series (System S2) served as an unsaturated, gas-preferential baseline, representing the optimal kinetic performance achievable by pristine sand due to the presence of interconnected gas channels. Conversely, the 144% water saturation series (Systems S1, S3, and S4) represented a diffusion-limited, flooded state. By comparing the hydrophobically modified systems (S3 and S4) against the S2 baseline, we aimed to determine whether surface modification could effectively reconfigure the internal fluid distribution to overcome mass transfer limitations and achieve formation rates comparable to those of the unsaturated state, despite the macroscopic excess of water.

Table 4. Experimental conditions and results for all experiments.

Experiment Number	System	Initial Pressure (MPa)	Formation Temperature (°C)	Induction Time (h)	Final Gas Consumption (mol)	Water Conversion Rate (%)
1	S1	10	2	5.00	0.0058	3.39
2		10	4	5.00	0.0043	2.48
3		10	6	7.50	0.0029	1.71
4	S2	10	2	6.30	0.0664	72.76
5		10	4	7.20	0.0688	75.34
6		10	6	6.00	0.0708	77.57
7	S3	8	2	5.47	0.0486	28.26
8		8	4	5.05	0.0493	28.69
9		8	6	3.45	0.0388	22.56
10		8	8	9.40	0.0242	14.05
11		10	2	3.60	0.0506	29.46
12		10	4	3.68	0.0511	29.74
13		10	6	3.73	0.0516	30.02
14		12	2	2.66	0.0514	29.92
15		12	4	3.24	0.0649	37.75
16		12	6	3.07	0.0551	32.05
17	S4	8	2	3.90	0.0369	21.49
18		8	4	4.47	0.0388	22.58
19		8	6	4.60	0.0393	22.88
20		8	8	58.90	0.0145	8.43
21		10	2	10.37	0.0489	28.47
22		10	4	13.60	0.0350	20.37
23		10	6	3.69	0.0498	28.96
24		12	2	6.25	0.0579	33.69
25		12	4	13.08	0.0415	24.16
26		12	6	4.44	0.0516	30.04

Figure 10 compares the kinetic processes of MH formation in quartz sand under varying water saturation and surface wettability conditions. It includes the curves showing pressure, gas consumption, driving force changes, and gas consumption rates over time. The initial system temperature in the experiment was 20 °C, the hydrate formation temperature was 2 °C, and the initial formation pressure was 10 MPa, as shown in Table 4. The driving force for hydrate formation is defined as follows:

$$\Delta P_{\text{driving}}(t) = P_{\text{gas}}(t) - P_{\text{eq}}(t) \quad (3)$$

Among these, $\Delta P_{\text{driving}}(t)$, $P_{\text{gas}}(t)$ and $P_{\text{eq}}(t)$ denote the driving force (MPa), pressure (MPa) and phase equilibrium pressure (MPa) at time t , respectively.

The gas consumption rate can be calculated using the following formula:

$$\left(\frac{dn}{dt}\right)_t = \frac{n_{t+\Delta t} - n_t}{\Delta t}, \Delta t = 2 \text{ h} \quad (4)$$

where t represents time (h). Using the equation, the average gas consumption rate per 2 h is calculated.

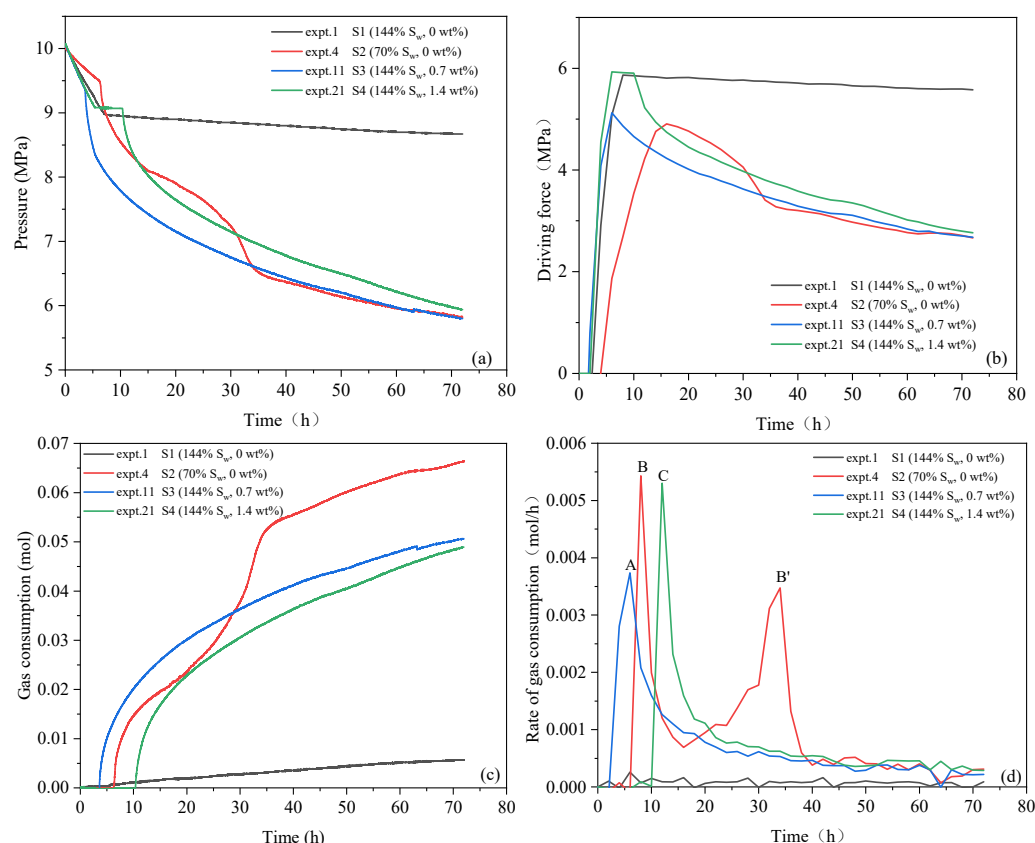


Figure 10. Evolution of (a) pressure; (b) driving force; (c) gas consumption; and (d) gas consumption rate during MH formation in systems S1–S4 (Initial pressure = 10 MPa, Temperature = 2 °C).

As shown in Figure 10a, during the initial stage of the experiment, the pressure in each experiment decreases as the system temperature drops. As shown in Figure 10b, the driving force for MH formation gradually increases when the system temperature reaches the MH formation temperature and then gradually decreases as hydrates form and the pressure in the reactor decreases. Water saturation in porous media significantly influences gas diffusion and the gas–liquid contact area during MH formation, thereby affecting formation rates. This study compared hydrate formation in two pure quartz sand systems with water saturations of 144% (S1) and 70% (S2). As shown in Figure 10a, the pressure curve of the high-water-saturation pure quartz sand system (S1) exhibits a “flat and delayed” characteristic: it remains nearly horizontal or shows only a slight slope during the initial hours before gradually decreasing, with no abrupt pressure drop occurring throughout the entire process. In contrast, the pure quartz sand system with low water saturation (S2) exhibits a more pronounced pressure decline trend. This correlates with the gas consumption and reaction rates depicted in Figure 10c,d. For instance, the high-water-saturation system (S1) consumes only 0.006 mol of gas, with a reaction rate approaching zero far lower than that of the low-water-saturation pure quartz sand system (S2). This indicates that, in unmodified hydrophilic quartz sand systems (S1 and S2), water saturation significantly influences MH formation kinetics. As shown in Figure 10b, after reaching its peak, the driving force for hydrate formation in system S1 maintains an extremely high level for an extended period with only a very gradual decline, suggesting minimal pressure drop and negligible MH formation. In the experiment of system S2, there is a distinct induction period followed by a pronounced inflection point around 10–20 h, where the driving force begins a sustained, substantial decline. Two significant formation peaks (Point B at about the 8 h and Point B' at about the 34 h) represent the rapid hydrate formation periods. At high water saturation (S1), excessive water fills the pores, drastically reducing the

gas–liquid contact area and causing severe mass transfer resistance. In contrast, low water saturation (S2) provides more gas-phase pathways, significantly enhancing mass transfer at the reaction interface. This phenomenon is attributed to the fact that, at high water saturation, water occupies the majority of pore channels and forms a thick film covering the sand particle surfaces, greatly limiting the gas–liquid contact area and hindering CH₄ gas diffusion into deeper pores [4,41]. Consequently, MH formation primarily occurs at gas–liquid contact surfaces, and the porous media fails to promote nucleation, MH growth, and gas diffusion. Gas must dissolve and diffuse through the aqueous phase to reach the growth front, potentially shifting the reaction from “interface-controlled reaction” to “diffusion-controlled reaction”. Excessively high water saturation may then inhibit the overall formation rate due to mass transfer limitations [42]. Conversely, in the low-water-saturation system (S2), despite a prolonged induction period for MH formation, the highest endpoint gas consumption (>0.06 mol) was observed. This is because low water saturation keeps pore channels open, facilitating thorough gas contact and ultimately achieving a high conversion rate of water to MHs. Porous media increase gas–liquid contact area, promote MH nucleation, and enhance heat and mass transfer, significantly facilitating MH formation. This further demonstrates that mass transfer process is a critical determinant of MH formation. Linga et al. [43] also confirmed that maintaining moderate porosity in static sand beds is crucial for improving gas–liquid contact and ultimately water conversion rates.

Although directly measuring the in situ diffusion rate of methane within the pore water is experimentally challenging, the specific kinetic contribution of the impregnating agent can be clearly isolated through our comparative macroscopic design. Compared to the unmodified quartz sand system (S1), under identical sand and water quality conditions (maintaining the same porosity, P-T conditions, and 144% water saturation), the MH formation rate in the hydrophobic-modified quartz sand system at identical water saturation significantly increases and exhibits a MH formation rate similar to that of system S2 during the initial period. Because the bulk aqueous diffusion barrier is the primary rate-limiting factor in S1, the order-of-magnitude enhancement in gas consumption observed in the modified systems effectively isolates the contribution of the impregnating agent: it reconfigures the continuous water film into dispersed droplets, drastically reducing the diffusion path length. As shown in Figure 10d, in both systems S3 and S4, the MH formation rates rapidly increase after initiation, and then gradually decrease after reaching their maximum values. The formation rate maintains a relatively stable level over an extended period, with a slower rate of decline. As shown in Figure 10, despite the 144% water saturation, the modified system S3/S4 exhibits a kinetic profile strikingly similar to that of the unsaturated S2 baseline, confirming the successful ‘kinetic rescue’ driven by wettability modification. Comparing Figure 10c,d, although the quartz sand (S3) with a smaller contact angle exhibits a peak formation rate of only 0.0037 mol/h, it drastically shortens the induction period, enabling rapid hydrate formation within the first 3 h of the experiment. In contrast, the quartz sand (S4) with a larger contact angle exhibits an induction period lasting up to 10 h, and its final gas consumption is lower than that of system S3.

The hydrate formation is a complex crystallization process involving gas, liquid, and solid phases. Porous media not only provide physical support, but their surface properties also directly determine the distribution state of fluids at the pore scale. Hydrate formation in porous media is governed by factors such as reaction driving force, sediment grain size, pore size, and surface properties. These factors determine the hydrate formation rate by regulating the gas–liquid contact area as well as heat and mass transfer rates. Notably, the surface properties, surface energy, and pore size of quartz sand particles play a decisive role in determining the states and distribution of pore water, which in turn affects the kinetics of

hydrate growth. Specifically, the capillary pressure (P_c) at the curved gas–liquid interface within the pore throats can be quantified by the Young–Laplace equation:

$$P_c = P_g - P_w = \frac{2\gamma \cos \theta}{r_c} \quad (5)$$

where P_g and P_w are the gas and water phase pressures, γ is the interfacial tension, θ is the contact angle, and r_c is the radius of curvature. According to the Young–Laplace equation, the θ determines the direction and magnitude of capillary forces, thereby controlling whether the aqueous phase spreads over the particle surface (S1, hydrophilic, $\theta < 90^\circ$) or contracts into clusters suspended at the pore center (S4, hydrophobic, $\theta > 90^\circ$) [36]. This difference in fluid distribution provides distinctly different “templates” for MH nucleation and growth. In hydrophilic systems, water layers envelop quartz sand particles. MHs tend to grow at particle contact points (pore-filling). Initial MH crystals form within water bridges at grain contact points. As water wets the particle surfaces, the growing MHs effectively act as a “cement”, binding loose sediment particles together [44–46]. Specifically, in the unmodified hydrophilic sand system ($\theta = 16.5^\circ$), $\cos \theta$ is positive, generating a positive capillary pressure. This force acts to draw water into the narrowest pore throats and distribute it across the particle surfaces. In this state, the capillary pressure manifests as a strong driving force for spontaneous imbibition, causing the aqueous phase to spontaneously infiltrate and occupy the micro-pores and pore throat regions. Macroscopically, the water exists in the form of continuous capillary water and wetting water films adhering to the particle surfaces, constituting a highly interconnected liquid-phase network. Conversely, methane gas, as the non-wetting phase, is excluded into the central channels of the larger pores [8]. This limits gas access to the internal pore spaces and promotes a ‘pore-filling’ morphology, wherein hydrates grow outward from the particle contact points. This leads to the premature formation of a hydrate shell that encapsulates the unreacted water—a phenomenon termed the ‘encrustation effect.’ Conversely, in hydrophobic systems, water exists as dispersed droplets while the gas phase fills the pores as a continuous phase. Hydrate nucleation occurs at the droplet surface (gas–liquid interface) and grows inward toward the droplet core [47,48]. Hydrates preferentially grow at pore centers or in a suspended state (floating or pore-rimming). The gas phase, being the continuous phase (the wetting phase) in hydrophobic media, occupies channels near pore walls. The liquid phase “floats” as dispersed droplets within the gas stream or is supported by hydrophobic particles at the pore center, creating reaction interfaces with extremely high specific surface areas that enhance mass transfer efficiency [49,50]. Specifically, in the hydrophobic system ($\theta > 90^\circ$), $\cos \theta$ is negative, causing the capillary pressure to become negative. In this state, the gas phase preferentially wets the particle surfaces, causing water to be ‘expelled’ from the pore throats into the centers of the larger pore bodies [51]. This prevents the water from spreading into stable liquid films on the grain surfaces; instead, the water phase undergoes contraction and isolation, ultimately accumulating in the central regions of the pores as discontinuous droplets or alternating gas–liquid slug flows. It should be noted that because the quartz sand used in this study has a relatively large median particle size (224.76 μm), the capillary pressure is inherently small compared to the macroscopic operating pressure (~ 10 MPa). Consequently, capillary effects do not significantly alter the overall thermodynamic phase equilibrium boundaries. As water exists in the form of dispersed droplets, hydrate nucleation initiates at the gas–liquid interface of these droplets and propagates toward the interior [52]. Since the gas phase remains the continuous phase (the wetting phase), pore connectivity is maintained for a longer duration during the formation process, allowing methane to penetrate deep into the sand layer and contact unreacted water droplets. The intermediate wettability system ($\theta \approx 90^\circ$) minimizes the capillary force (P_c),

thereby facilitating the most uniform and fine dispersion of water droplets throughout the pore space. This maximizes the reaction surface area and achieves the highest formation rate observed in the S3 system.

Furthermore, the magnitude of the capillary force under the current experimental conditions was quantified. Due to the large grain size of the quartz sand used in this study, the capillary pressure calculated according to the Young–Laplace equation is relatively small, indicating that capillary forces have a limited impact on water distribution. Hydrates preferentially form on the particle surfaces and at gas–liquid interfaces rather than within the narrow pore throats. This finding suggests that under our experimental conditions, the gas–liquid contact on the particle surfaces, rather than capillary imbibition or displacement, is the primary factor controlling the hydrate formation rate. The observed differences are mainly attributed to the change in particle surface wettability and the consequent optimization of the local interfacial environment. Although the quartz sand is globally submerged, the wettability determines the microscopic water–solid interaction. On the hydrophilic surface, water forms a tenacious, continuous film that acts as a physical barrier shielding the high-energy nucleation sites on the quartz. In contrast, the hydrophobic modification lowers the surface adhesion energy, facilitating the formation of Triple-Phase Contact Lines (TPCLs) at the solid surface [53]. This effectively ‘unmasks’ the active quartz sites, allowing for enhanced gas–solid–liquid interaction despite the macroscopic water-saturated environment.

Figure 11 compares the final gas consumption and induction time for MH formation in different systems. Specifically, the induction time in this study is defined as the elapsed time from the point the system reaches the preset experimental conditions to the intersection point on the time axis where the onsets of sudden pressure drop and temperature rise coincide. This definition is consistent with the time when the gas consumption first becomes greater than zero. As shown in Figure 11, in the unmodified quartz sand system, the final gas consumption is significantly lower at the higher water saturation. In this system, the water volume exceeds the quartz sand’s original pore volume. Consequently, MH formation begins primarily at the interface between methane gas and water, with the porous media showing no significant promotion effect on MH formation. In contrast, MH formation accelerates markedly in the S2 system, with final gas consumption increasing substantially within 72 h compared to the S1 system. While induction times are inherently stochastic and present natural fluctuations, the macroscopic growth phase clearly demonstrates that MH formation accelerates markedly in the S2 system, with final gas consumption increasing substantially within 72 h compared to the S1 system.

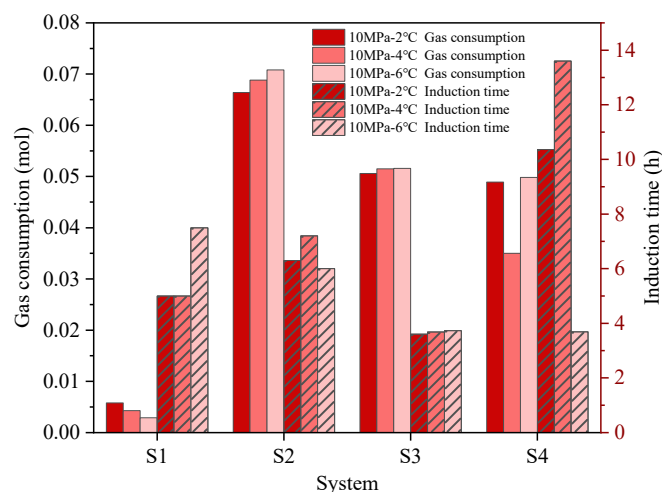


Figure 11. Final gas consumption and induction time for MH formation in different systems.

Figure 11 also demonstrates that hydrophobic modification of quartz sand significantly enhances the formation kinetics of MHs. In system S1, MH growth is severely inhibited, with extremely low gas consumption. This indicates that, under the experimental conditions, the strong surface hydrophilicity of unmodified quartz sand drives water to form continuous films adhering to the particles. This surface-wetting behavior leads to unfavorable water distribution that hinders gas–liquid contact and results in extremely slow reaction kinetics. By contrast, while the absolute contribution of capillary pressure to the thermodynamic driving force is negligible, its role in controlling the pore-scale fluid distribution (topology) is dominant. As established, this capillary-driven redistribution of water is the fundamental mechanism causing the observed differences in formation kinetics. In contrast, the modified system demonstrates a dramatic increase in both formation rate and final gas consumption. As shown in Table 4, the final gas consumption for the experiments in system S1 at the initial pressure of 10 MPa and the formation temperatures of 2, 4, and 6 °C is 0.0058, 0.0043, and 0.0029 mol, respectively. At the same formation conditions, the final gas consumption for the experiments in system S3 is 0.0506, 0.0511, and 0.0516 mol, with an average increase of 11.8 times. It must be emphatically noted that these significant discrepancies in final gas consumption under identical P-T conditions do not imply a shift in thermodynamic equilibrium. As conclusively demonstrated in Section 3.1, the inherent thermodynamic equilibrium boundaries remain unaffected by surface modification. Instead, the varying gas consumptions reflect a kinetic plateau dictated by severe mass transfer limitations within the 72 h experimental window. In systems with unfavorable pore-scale fluid configurations (such as the continuous water films in S1), extreme mass transfer resistance heavily restricts gas diffusion, causing the hydrate growth to kinetically stall prematurely. Compared with the system of S2 with a low water saturation of 70%, the final gas consumption of the experiments in system S3 is slightly lower than that in system S2 with a low water saturation of 70%. However, in system S2, the lower water content results in a significantly higher water conversion rate under similar gas consumption, which may limit the gas consumption rate in the later stage and the total gas storage capacity.

It is worth noting that while the total water volume exceeds the pore capacity in systems S1, S3, and S4—leading to the visual appearance of total immersion—this does not imply uniform water coverage. The hydrate formation kinetics are governed not by the bulk water volume, but by the microscopic fluid topology dictated by surface wettability. In the hydrophilic S1 system, strong positive capillary forces promote the formation of continuous, thick water films that encapsulate the sand grains, acting as a profound diffusion barrier that ‘shields’ the surface from gas access. In contrast, in the hydrophobically modified S3 and S4 systems, the negative capillary pressure drives the water to retract from the grain surfaces, forming discontinuous clusters even under excess water conditions. This surface-driven redistribution exposes a substantially larger gas–liquid–solid interfacial area and creates reactive pathways for methane, thereby overcoming the macroscopic diffusion limitations encountered in the hydrophilic system. Thus, the performance enhancement is definitively attributed to the surface-effect-driven reconfiguration of fluid phases at the pore scale, rather than the macroscopic bulk water content.

In addition, the total gas consumption of system S3 is slightly higher than that of system S4. Rather than stochastic nucleation variations, this performance degradation under strong hydrophobicity (S4) can be fundamentally interpreted through the Young–Laplace framework and its impact on the active growth phase. When θ significantly exceeds 90°, the negative capillary pressure intensifies, driving water droplets to coalesce into larger, isolated clusters to minimize surface energy. This agglomeration severely reduces the specific gas–liquid interfacial area available for continuous hydrate growth compared to the

finely dispersed droplet state achieved at intermediate wettability ($\theta \approx 90^\circ$ in S3), thereby inhibiting the overall mass transfer efficiency and reducing the final gas storage capacity.

This performance degradation under strong hydrophobicity can be interpreted through the Young–Laplace framework. When θ significantly exceeds 90° , the negative capillary pressure intensifies, driving water droplets to coalesce into larger, isolated clusters to minimize surface energy. This reduces the specific gas–liquid interfacial area available for hydrate nucleation compared to the finely dispersed droplet state at intermediate wettability ($\theta \approx 90^\circ$), thereby inhibiting the overall reaction efficiency. Molecular dynamics (MD) simulations revealed that hydrophobic surface energy induces tetradic ordered arrangements of adjacent water molecules resembling clathrate structures. This pre-ordered water structure lowers the entropic barrier for nucleation [54]. This optimized interfacial configuration stems from diminished adhesion forces between water and sand particle surfaces, facilitating the formation of abundant active nucleation sites and thereby promoting a more rapid transition into the mass-transfer-dominated growth phase. This acceleration stems from diminished adhesion forces between water and sand particle surfaces, facilitating the formation of active nucleation sites. The performance degradation in the “over-modified” effect (S4) likely stems from excessive water aggregation. Under highly hydrophobic conditions, water droplets tend to coalesce into larger, isolated clusters to minimize surface energy. This suggests that excessively high surface hydrophobicity may cause droplet coalescence or agglomeration of modified particles, thereby blocking local gas channels. In addition, the specific surface area available for hydrate nucleation is reduced compared to that in the finely dispersed system of S3, thereby inhibiting reaction efficiency [55].

3.3. Effects of Pressure and Temperature on MH Formation

To further elucidate the influence of the MH formation driving force on the formation rate, Figure 12 presents the evolution of pressure, gas consumption, MH formation driving force, and gas consumption rate during MH formation in system S3. All experiments were conducted at an MH formation temperature of 2°C , with initial formation pressures ranging from 8 to 12 MPa. As shown in Figure 12a, due to differences in initial pressure, the experiment with higher initial pressure reaches the MH formation condition earlier as the temperature decreases. Correspondingly, the onset time of MH formation decreases with increasing initial pressure. However, a clear lag is exhibited before MH formation commences. For instance, at 12 MPa, the driving force first exceeds zero at 1.07 h, while MH formation commences at 2.66 h. As the reactor temperature gradually decreases to the experimental formation temperature, the MH formation driving force rises rapidly. Subsequently, with the onset of MH formation and the gradual decrease in reactor pressure, the driving force begins to decline. Throughout the formation process, the driving force for MH formation increases with rising initial formation pressure. As shown in Figure 12b, the MH formation rate initially exhibits a rapid rise followed by a gradual decline, with the peak gas consumption rate increasing with higher initial pressure. However, as MH formation progresses, the formation rates across different experiments converge. Scientifically, this kinetic behavior reflects a distinct transition in the rate-limiting mechanism. During the initial stage, a higher initial pressure significantly elevates the chemical potential gradient across the gas–liquid interface, thereby accelerating methane dissolution and intrinsic nucleation rates (an interface-controlled regime). However, as the initial hydrate layer rapidly forms at the gas–liquid boundary, the reaction undergoes a fundamental shift to a diffusion-controlled regime. In this later stage, the formation rate is heavily bottlenecked by the diffusion of methane molecules through the dense, newly formed hydrate shells to reach the unreacted water. Because this structural diffusion resistance is dictated by the pore geometry and the morphology of the hydrate shell rather than the macroscopic

pressure, the formation rates across different initial pressures inevitably converge. As shown in Figure 13, the total gas consumption over 72 h generally increases with higher initial pressure. However, the overall increase does not match the magnitude of the initial pressure increase, and the rate of increase also varies at different temperatures.

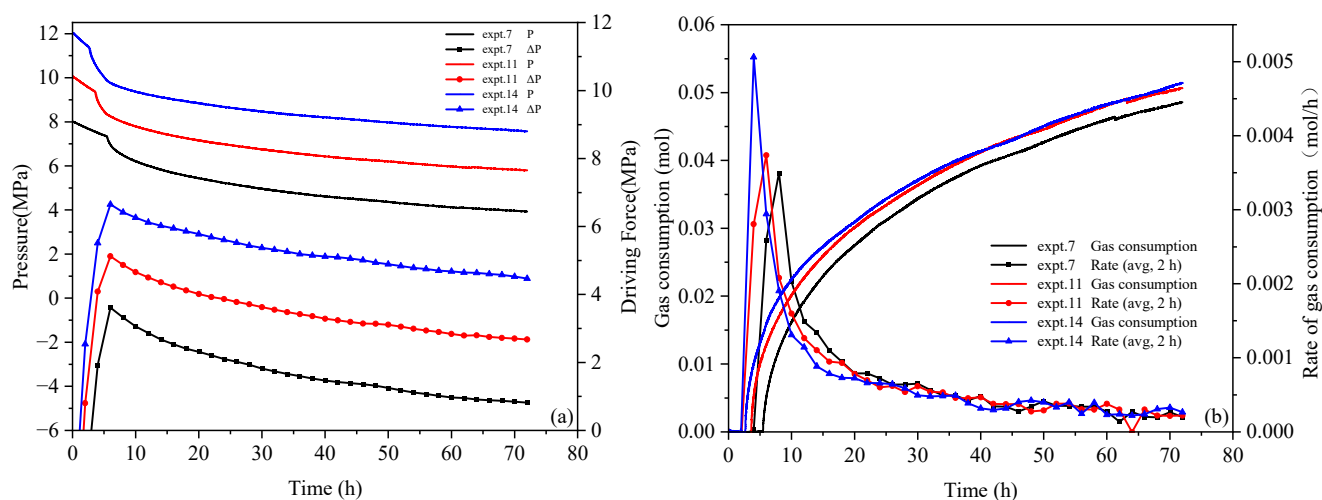


Figure 12. Evolution of (a) pressure (P) and driving force (ΔP); and (b) gas consumption and gas consumption rate during MH formation in system S3.

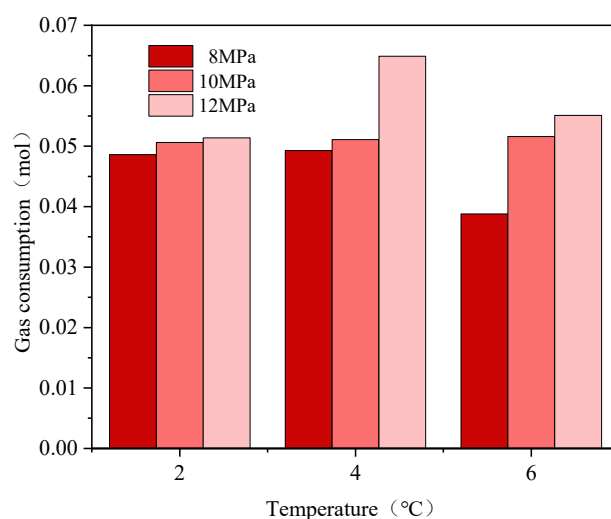


Figure 13. Comparison of final gas consumption at different pressures in system S3.

Figure 14 presents the time-dependent curves for pressure, gas consumption, formation driving force, and gas consumption rate during MH formation in system S4. The MH formation temperature in the experiment was 2 °C, with formation pressures ranging from 8 to 12 MPa. As shown in Figure 14, compared to system S3, the MH formation process, gas consumption, and formation rate exhibit similar patterns influenced by initial pressure. However, the induction time exhibits a relatively larger variation in system S4, as shown in Figure 14b. This variation also impacts the total gas consumption (as shown in Figure 15). At 4 °C and 10 MPa, the induction time is 13.60 h (as shown in Table 4), while the gas consumption was significantly lower than that observed at 8 and 12 MPa.

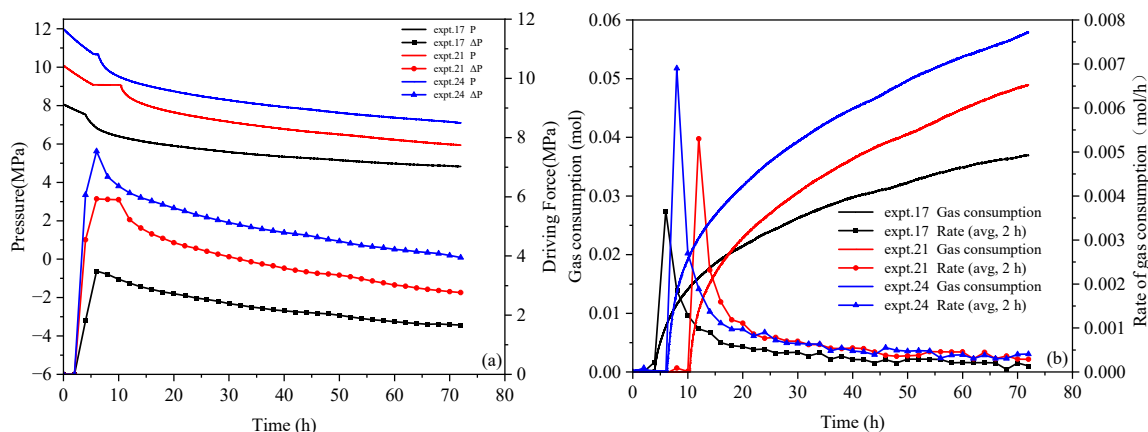


Figure 14. Evolution of (a) pressure and driving force; and (b) gas consumption and gas consumption rate during the MH formation in system S4.

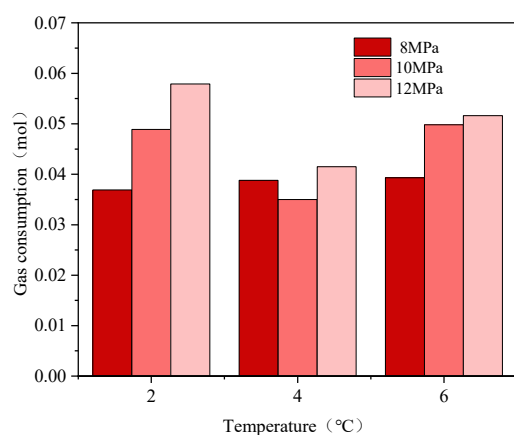


Figure 15. Comparison of final gas consumption at different pressures in system S4.

It is important to highlight that the hydrate formation kinetics exhibit non-monotonic behavior with respect to temperature and pressure, particularly at 4 °C and 10–12 MPa. These phenomena reflect the complex competition between the thermodynamic driving forces of hydrate formation, hydrate nucleation and growth, and pore scale mass transfer processes. Normally, the formation rate of hydrates increases with the increase in formation driving force. However, the formation rate of hydrates in porous media is also closely related to their morphological and distribution characteristics, as well as gas diffusion rate. Specifically, we attribute these phenomena to the interaction between the “crust” effect of hydrate shells and gas diffusion. The nucleation and growth of hydrates are inherently random. In hydrophobic modified systems, water is distributed in many discontinuous droplets. The precise spatial location and time of initial nucleation events on these isolated droplets are highly random. As mentioned earlier, the formation of a dense hydrate shell at the gas–liquid interface hinders gas diffusion, and the formation of hydrates is usually self-limiting. Under intermediate conditions (such as 4 °C and 10 MPa), supercooling and pressure are sufficient to trigger rapid shell formation. If random nucleation occurs randomly at spatial locations that block critical pore throats or promote rapid coalescence of these shells, it will prematurely cut off methane diffusion pathways, thereby reducing overall gas consumption. When the driving force of the reaction is further increased, the gas consumption is further increased, but overall it is smaller than the increase in driving force.

Compared to the influence of initial pressure on MH formation, formation temperature is also a key parameter affecting the hydrate formation driving force and the formation rate of MHs. Figure 16 shows the total gas consumption over 72 h for experiments of

systems S3 and S4. As illustrated, the final gas consumption at different temperatures does not exhibit a clear pattern relative to the initial formation pressure. As depicted in Figure 16a, the gas consumption over 72 h exhibits a certain positive correlation at different formation temperatures under the same pressure. The influence of formation temperature on final gas consumption exhibits complexity and non-monotonicity. In system S3, the final gas consumption does not show linear decay or growth with increasing temperature. Furthermore, as shown in Figure 14b, the final gas consumption occurs at the formation temperature of 4 °C when the formation pressures are 10 and 12 MPa, respectively. By calculation, the equilibrium MH formation pressures at 2 °C, 4 °C, and 6 °C are 3.18 MPa, 3.85 MPa, and 4.67 MPa, respectively, with a maximum driving force difference of 1.49 MPa. In actual formation processes, MH formation is not only affected by thermodynamic driving forces but is also strongly influenced by kinetic factors such as induction time, interfacial mass transfer resistance, and the state of water occurrence.

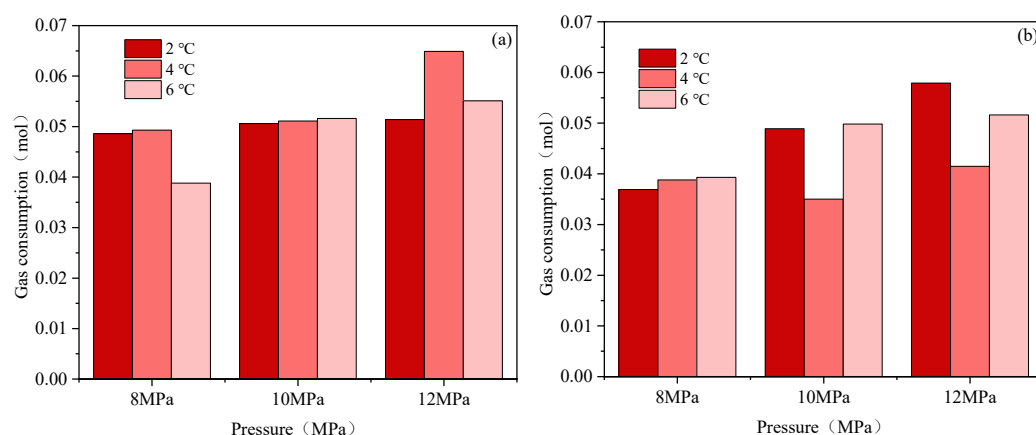


Figure 16. Comparison of final gas consumption at different temperatures in (a) system S3; and (b) system S4.

The difference in total gas consumption between systems S3 and S4 should not be interpreted as a shift in thermodynamic equilibrium, as the P-T conditions were identical. Instead, this reflects the extent of reaction before the system enters a diffusion-limited kinetic plateau. As the reaction progresses, the formation of hydrate shells at the gas–liquid interfaces creates a structural barrier that impedes further methane diffusion [56]. In System S4, the strong hydrophobic repulsion forces water into larger, isolated agglomerates with a lower surface-to-volume ratio compared to System S3. This fluid configuration leads to a more rapid formation of “encrustation” layers that seal off the unreacted water within the droplets. Consequently, the reaction stalls at an earlier stage (lower total conversion) in S4 compared to S3, where the more finely dispersed water allows for a higher degree of water-to-hydrate conversion before the mass transfer pathways are fully obstructed.

In this study, factors such as pore scale fluid distribution and local mass transfer resistance have a greater impact on hydrate formation due to relatively small differences in driving forces caused by temperature changes. Although lower temperatures typically provide higher undercooling, this advantage is easily masked by the randomness of hydrate growth and changes in mass transfer resistance in hydrophobic modified systems (especially S4). The strong negative capillary force promotes the random coalescence of discontinuous water droplets to minimize surface energy. Once hydrate shells form on the surface of these aggregated water droplets, severe local “crust formation” occurs, preventing further inward gas diffusion pathways. Therefore, in porous media, particularly chemically modified systems, relying solely on adjusting temperature and pressure parameters to optimize MH formation efficiency has inherent limitations. It is recommended to further

consider combining agitation with continuous gas injection to enhance gas–liquid flow and improve gas–liquid contact, thereby increasing the hydrate formation rate and gas storage capacity. Subsequent research should focus on elucidating how surface properties influence gas–liquid distribution patterns, nucleation mechanisms at multiphase interfaces, gas diffusion during growth, and gas–liquid contact efficiency. This will reveal the underlying kinetic mechanisms by which modified media enhance MH conversion rates.

4. Conclusions

This study treated quartz sand with the silane coupling agent OTMS for surface hydrophobic modification and investigated the effects of the quartz sand surface wettability on MH equilibrium conditions as well as formation kinetics through a series of experiments. The main conclusions are as follows:

- (1) Surface modification of quartz sand has no significant effect on the equilibrium conditions of MHs, indicating its negligible influence on the MH formation driving force.
- (2) Under identical sand and water quality conditions, hydrophobic modification of quartz sand enhances the reaction rate of MH formation. Quartz sand with hydrophilic surfaces exhibits extremely slow hydrate formation kinetics due to strong capillary force constraints that hinder water distribution and gas–liquid contact. In contrast, the modified system exhibits dramatic increases in both formation rate and final gas consumption. The hydrophobic surface reduces water adhesion to sand particles, causing water to occupy larger pore spaces. This exposes more gas–liquid interfaces, increasing the contact area and further significantly enhancing mass transfer under high-water-saturation conditions.
- (3) The system with the lower modification level (contact angle of 90.0°) exhibits higher gas consumption and a more rapid mass-transfer-driven growth phase than that with the higher modification level (contact angle of 116.6°). Under highly hydrophobic conditions, water droplets tend to coalesce into larger, isolated clusters to minimize surface energy. This reduces the specific gas–liquid interfacial area available for sustained hydrate growth. The system with the lower modification degree (contact angle of 90.0°) maintains good pore connectivity while increasing the gas–water interface area, preventing premature reaction termination caused by the shell effect commonly observed in static hydrophobic systems.
- (4) The influence of initial formation pressure on the MH formation rate is primarily evident during the initial stages of MH formation. As the amount of MHs formed increases, the formation rate becomes increasingly influenced by gas diffusion and gas–liquid contact capability. Due to the relatively small driving force difference caused by formation temperature in the experiments, factors such as the pore-scale fluid distribution, MH distribution and aggregation, and gas diffusion rate exert a stronger influence on the MH formation rate. Consequently, the effect of temperature is less pronounced than that of formation pressure.

Author Contributions: D.W.: Investigation, Writing—original draft. Y.C.: Investigation. C.C.: Validation. X.L.: Conceptualization, Supervision. Y.Z.: Methodology, Writing—review & editing. Z.C.: Writing—review & editing. All authors have read and agreed to the published version of the manuscript.

Funding: The authors are very grateful for the support of the Special Project for Marine Economy Development of Guangdong Province (GDNRC[2024]33), which is gratefully acknowledged.

Data Availability Statement: The original contributions presented in this study are included in the article. Further inquiries can be directed to the corresponding author(s).

Conflicts of Interest: The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Abbreviations

The following abbreviations are used in this manuscript:

OTMS	Octyltrimethoxysilane
MH	Methane hydrate
NGHs	Natural gas hydrates
STP	Standard temperature and pressure
CH ₄	Methane
MOFs	Metal–organic frameworks
CT	X-ray computed tomography
CO ₂	Carbon dioxide
OTS	Octadecyltrichlorosilane
DMOAP	N-dimethyl-N-octadecyl-3-aminopropyl trimethoxysilyl chloride
MD	Molecular dynamics
H ₂	Hydrogen
XPS	X-ray photoelectron spectroscopy
FT-IR	Fourier transform infrared
SEM	Scanning electron microscope
BET	Nitrogen adsorption–desorption method
SiO ₂	Silicon dioxide

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