

Critical Review on Gas Hydrate Formation at Solid Surfaces and in Confined Spaces—Why and How Does Interfacial Regime Matter?

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ABSTRACT: Gas hydrates are crystalline solids composed of water and gases. They occur abundantly in nature and are potentially significant to industry. Solid surfaces and confined spaces strongly affect the formation of gas hydrates. Research into this particular topic is active, particularly aiming to understand the effects of solid surfaces and confinements on gas hydrate formation and using functional solids for controlling the formation kinetics. Experimental observations appear to vary from one solid to another. The observations demand a knowledge of (1) why the effects vary among the solids and (2) what factors are determining. Here, we critically review experimental observations, discuss the underlying mechanisms, and generalize the literature findings for a better understanding of the mechanism. It is inferred that open hydrophobic solids can promote gas hydrate formation via a tetrahedral ordering of water and an increased density of gases at the solid–water interfaces. Open hydrophilic solids hinder gas hydrate formation via a distorted water structure and a depleted density of gases at the solid–water interfaces. Confining solids have rather complex effects due to the complexity of wetting in confined spaces. Therefore, confined media with moderate wettability and partial water saturation might provide optimum conditions for gas hydrate formation.

1. INTRODUCTION

Gas clathrate hydrates are crystalline solids consisting of water and gases.¹ Water forms a periodic cage-like structure called a host structure via H-bonding. Gas molecules are incorporated intensely in the host structure.¹ Hydrates are similar to ice in terms of the tetrahedral coordination of water. However, they are distinct from ice by incorporating gas molecules into their structures. One water cage within the host structure typically contains one gas molecule. Even so, multiple occupancies are possible for small molecules such as hydrogen.² Experiments have reported mass fractions of 13.3 wt % for methane³ and 4.3 wt % for hydrogen² in the respective hydrates. Hydrates of various gases have been identified, such as CH₄, H₂, N₂, CO₂, C₂H₆, and noble gases.^{4,5} Meanwhile, nongaseous molecules such as cyclopentane and neo-hexane are also found to form hydrates with water.^{4–6}

Hydrates are important for sustainable nature and industry. Vast amounts of natural gases on Earth are trapped in natural gas hydrates (NGHs) in ocean sediments and permafrost regions.^{7–9} NGHs pose potential risks of mass emissions of methane into the atmosphere.^{7,10} Recent studies^{11,12} indicated that such methane emissions are happening at alarming rates in Arctic regions and threatening the Earth's sustainability. However, NGHs also offer an immense source of cleaner fossil fuels, which can be 2-fold larger than total energy borne in conventional fossil fuels (coals and oils).^{7,13} Research into the exploitation of energy from NGHs is currently active.¹⁴

Gas hydrates affect the industry in various ways. Spontaneous formation of gas hydrates in oil and gas pipelines impedes the safety and continuity of drilling operations as the hydrates tend to plug pipelines.^{15,16} Nevertheless, hydrates can open innovative routes to better productions and a cleaner environ-

ment. Intense gas storage in gas hydrates offers novel means for the storage of fuel gases.^{2,3,17,18} Reversible hydrate formation can be used for effective separation of gases^{19–21} and desalination of saline water.^{22,23} CO₂ gas hydrates were observed to form after injection of CO₂ into appropriate geological formations, providing secure and permanent sequestration of carbon dioxide.^{24–26} Because of such significance, studies into gas hydrates have grown rapidly over the past 100 years (Figure 1).

The formation of gas hydrates at solid surfaces or in confined spaces is of central importance. In nature, natural gas hydrates are inherently affected by solid surfaces and confined spaces in geological sediments.²⁷ In laboratories and industries, hydrates always form under the presence of equipment surfaces. Especially, active research is focusing on developing functional solids that can alter the kinetics of hydrate formation in desired manners. Here, we critically review experimental observations on this topic, discuss the underlying fundamentals, and generalize literature findings for a universal understanding.

2. BRIEF DESCRIPTIONS OF GAS HYDRATE FORMATION

Gas hydrates form spontaneously when gases contact water at temperatures (T) of a few degrees Celsius and pressures (P) on

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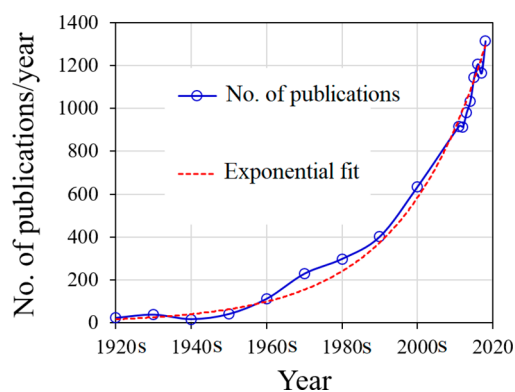


Figure 1. Growing literature in hydrate research over the past 100 years. Data were obtained from Web of Science by searching for articles having “hydrate” in the title. Data point for each decade is an average value for those 10 years. Real numbers can be larger as relevant papers might not include “hydrate” in the titles, but the growing trend would be identical.

the order of MPa, for example, in a high-pressure reactor (Figure 2).^{28,29} In nature, hydrates of natural gases are formed vastly in

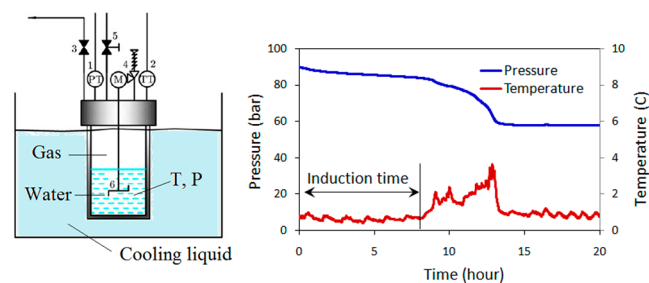


Figure 2. Temperature (T) and pressure (P) profiles of methane hydrate formation in an isochoric reactor. A slight drop of P in the induction period was induced by gas dissolution and hydrate nucleation. A large drop of P and rise of T indicate the onset of exothermic hydrate formation. Constant T and P at the end indicate that hydrate formation completed. The experiment was performed in stirred conditions at an initial pressure of 100 bar and temperature set to 0.5 °C.

the cold seabed or permafrost sediments where T and P reach these conditions.⁸ Hydrate formation involves multiple stages, starting with the dissolution of gases into water and advancing toward the conversion of a gas-saturated solution into a crystalline solid.^{28,30,31} Intermediate stages include the formation of water cages (shells) around individual dissolved gas molecules, agglomeration of gas-bearing cages into clusters (nuclei), and growth of nuclei into big solid masses.^{13,32} The time needed to attain stable hydrate nuclei that can grow steadily into big hydrate crystals is called the *induction time*. In experiments, the induction time is indicated by a period between the point of time when T and P fall into hydrate-forming conditions and the point of time when rapid hydrate growth is observed (Figure 2). The latter is indicated by a rise of T and/or a steep drop of P .

In pure water, gas hydrates nucleate at gas–water interfaces where gas solubility is orders of magnitude higher in the bulk phase.^{13,33} Under quiescent conditions, it leads to the formation of a hydrate film at the interface, which then hinders gas–water contact and stops itself from thickening. Therefore, only micrometer-thick hydrate films are often observed at the gas–

water interfaces.^{34–38} When agitations apply, gas hydrates still nucleate at the gas–water interfaces. However, turbulent conditions break the hydrate films and convey hydrate fragments (nuclei) into the bulk phase where they grow further into big masses.¹³

Not all dissolved molecules can form clathrate structures.¹³ Therefore, the properties of the guests are a crucial factor. Water with intrinsic H-bonding features can adopt small hydrophobic molecules such as methane into its cavities without losing H-bonds,^{39–41} which gives rise to the formation of hydrophobic hydration shells around guest molecules. On hydration shells, OHs of water point tangentially to form H-bonds with their neighbors, thereby forming a cage around the guest. The OHs also point outward from the shells and form H-bonds with external water, thereby linking to neighboring cages.^{40,41} Such an arrangement of water is defined as *hydrophobically ordered* to differentiate with the hydration of ionic solutes.⁴² The latter experiences strong water–ion electrostatic interactions, so that water molecules are bound firmly to ions and water H-bonds are lost (Figure 3b), yielding to an *electrostatically ordered* state of

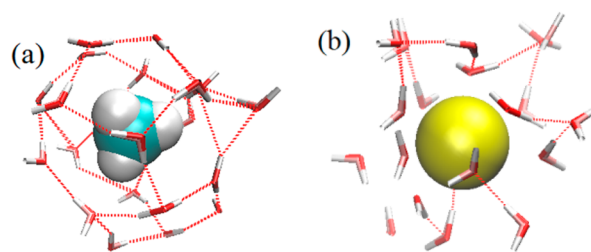


Figure 3. Simulation snapshots of hydration of a methane molecule where water–water H-bonds persist (a) and hydration of a Na^+ ion where water–water H-bonds are lost (b). Details of simulations can be found in our previous work.³⁰

water.⁴² Hydration of polar molecules follows intermediate regimes. Hence, water structures in gas hydrates differ in nature with those in frozen saline solutions.

The ability to form water cages around hydrophobic molecules (hydrophobes) depends on the sizes of hydrophobes.³⁹ Water cannot incorporate large hydrophobes without losing H-bonds.^{39,43} Therefore, hydration shells of large hydrophobes are less structured. Small and large hydrophobes are classified by a crossover length scale, which is around 1 nm as predicted by computer simulations.^{39,43} Arguably, only molecules sized under the crossover length scale can form hydrate structures.

3. SOLID SURFACES AFFECTING GAS HYDRATE FORMATION

3.1. Experimental Observations. Solid surfaces show crucial impacts on gas hydrate formation.^{44–55} The solids may have natural origins such as equipment walls and trace colloidal particles in water. Gas hydrates were observed to form preferentially at the surfaces of reactors.^{47,48} The solids may have artificial origins such as functional solids added to control gas hydrate formation kinetics. In nature, relevant solids arise from minerals, biomass, and geological matters.

Various functional solids have been investigated. Cha et al.⁴⁹ found that additions of clays or hydrophilic polymers alter the kinetics and thermodynamics of methane hydrate formation in a promotive manner. Recently, hydrophobized silica attracted widespread attention. Hydrophobic fumed silica nanoparticles

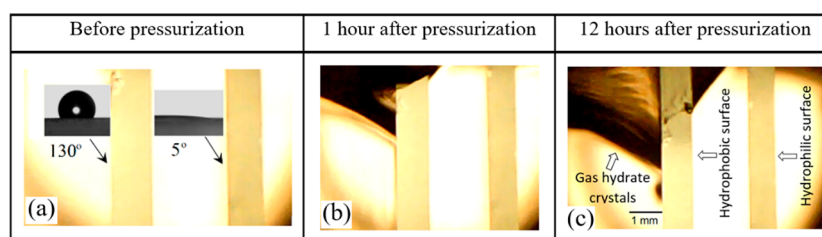


Figure 4. (a) A hydrophobized glass slide (left) and a hydrophilized one (right) were placed in a hydrate formation cell. (b,c) At 6 MPa and 1 °C, CO₂ gas hydrate formed preferentially on the hydrophobized glass surface. Images are reproduced with permission from ref 55. Copyright 2017 American Chemical Society.

Table 1. Experimental Observations on Solid Surfaces Affecting Gas Hydrate Formation

| solid surfaces | key findings ^a |
|---|--|
| hydrophobic fumed silica | gas uptake rose to 175 m ³ methane in 1 m ³ hydrate, equivalent to an increase by a factor of 60; much shorter induction time; ⁵³ no agitation needed ^{51,53} |
| hydrophobized silica sands | induction time decreased from 576 (s) in hydrophilic sand bed to 71 (s) in hydrophobized sand bed; induction time was more reproducible in hydrophobic sand beds ⁵⁴ |
| hydrophobized glass beads | shorter induction time and enhanced hydrate kinetics; no agitation needed ⁵⁷ |
| hydrophobized glass vs hydrophilic glass | preferential formation of CO ₂ gas hydrate on hydrophobized glass surface ⁵⁵ |
| solid surface with various coatings | hydrate nucleation was promoted on hydrophobic surfaces ⁵⁸ |
| hydrophobic glass beads vs hydrophilic glass beads | both strongly hydrophilic beads and strongly hydrophobic beads inhibit methane hydrate formation; slightly hydrophobic beads can promote methane hydrate formation, but capillary pressures have to be considered in packed beds ⁵⁹ |
| hydrophilic nanosilica | hydrophilic silica nanoparticles inhibit methane hydrate formation ⁶⁰ |
| metallic surfaces | shortened induction time and increased final water conversion ⁶¹ |
| hydrophilic silica, hydrophobic silica, graphite surfaces | graphite surface and hydrophobic silica surface promote methane hydrate formation; hydrophilic silica surface inhibits methane hydrate formation ⁶² |
| porous aluminum foams | aluminum (foams) surfaces promote methane hydrate formation by providing nucleation sites and enhancing heat transfer ⁶³ |
| natural and synthetic solid surfaces | methane hydrate formation is insensitive to additions of solid particles ⁵⁶ |

^aIn comparison with hydrate formation in pure water under similar conditions.

showed excellent promoting effects on the formation of carbon dioxide⁵⁰ and methane^{51–53} hydrates. Wang et al. reported a methane uptake at 175 m³ of methane under standard conditions per 1 m³ of methane hydrate formed in a mixture of 95 wt % water and 5 wt % fumed silica, equivalent to a nearly 60-fold increase compared to 3 m³/m³ for methane hydrate formed in pure water under similar *T* and *P*.⁵³ Also, much faster kinetics were observed in the earlier case.⁵³ In another study, Wang et al. showed that hydrophobized sands reduced the induction time of methane hydrate formation by a factor of 8 compared to the untreated (hydrophilic) sands.⁵⁴ The hydrate formation was more reproducible when hydrophobized sands were used.⁵⁴ Nguyen et al. placed a hydrophilized glass slide together with a hydrophobized glass slide in a hydrate formation cell (Figure 4).⁵⁵ They observed a preferential formation of CO₂ gas hydrate at the hydrophobized glass surface in respect to the hydrophilized one.⁵⁵ These studies^{50–54} together with other ones cited in Table 1 indicate that surface hydrophobicity of the solids is a crucial factor impacting gas hydrate formation. Even so, there are also a few studies claiming that methane hydrate formation is insensitive to the presence of solid surfaces.⁵⁶

Significant fundamental studies have been conducted to understand the science behind experimental observations. It is widely agreed that solid surfaces promote gas hydrate formation by providing nucleation sites. Knott et al. indicated that homogeneous nucleation of gas hydrates occurs at extremely low rates, i.e., on orders of 10⁻¹¹¹ (nuclei/cm³·s).⁶⁴ This means that the homogeneous nucleation of gas hydrates is unrealistic in reality.⁶⁴ Instead, gas hydrates would nucleate heterogene-

ously.⁶⁴ However, it is still not clear why solid surfaces do not show comparable effects on gas hydrate formation. A major part of the literature (Table 1) indicates that the surface hydrophobicity of the solids is a governing factor. It is suggested that hydrophobic surfaces can promote gas hydrate formations whereas hydrophilic ones act oppositely. The promoting effects of hydrophobic surfaces might arise from the tetrahedral ordering of water structure^{55,65,66} and the increased gas density^{55,62,65,67,68} at hydrophobic solid–water interfaces. The inhibiting effects of hydrophilic surfaces arise from the distorted water structure^{55,65,66} and the decreased gas density^{55,62,65,67,68} at hydrophilic solid–water interfaces. We discuss these views in the following sections.

3.2. Water Structure near Solid Surfaces. Water molecules coordinate via H-bonds into a tetrahedral network that is best constructed in hexagonal ice.⁶⁹ The melting of ice leads to a breaking of ~10% of the H-bonds and producing liquid water with incomplete tetrahedral structures.^{70,71} More H-bonds are broken as the temperature increases. Therefore, water molecules in the liquid state may have four or fewer H-bonds (Figure 5a). The H-bonded network of water is terminated at water–solid interfaces. The structures of interfacial water are determined by the solid surfaces. Accordingly, interfacial water does not form H-bonds with a hydrophobic surface, which produces free OHs dangling at the interface (Figure 5b). Hence, hydrophobic solid–water interfaces are similar to gas–water interfaces.⁷² In contrast, interfacial water can form H-bonds with a hydrophilic surface (Figure 5c). These interphase H-bonds differ largely from

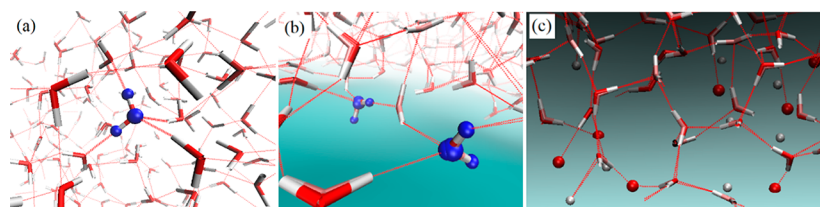


Figure 5. Examples of water structure at 300 K and 1 atm. Tetrahedrality develops partially in the bulk where water molecules have either four or fewer H-bonds (a). Free OHs of water at a hydrophobic solid surface (b). Interphase H-bonds between water and a hydrophilic solid surface (c). Silver and red spheres in c indicate H-bond donors and acceptors on the surface, respectively. Images from our simulations.⁵⁵

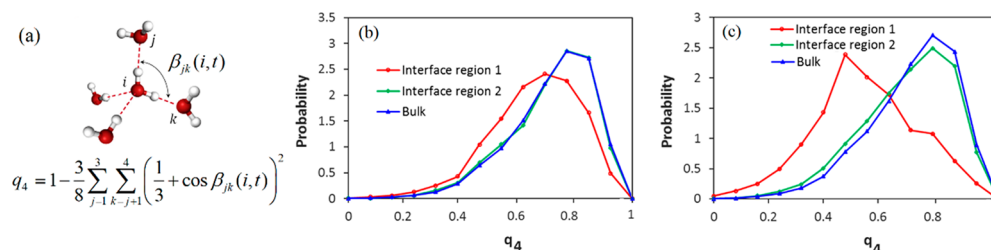


Figure 6. Definition of tetrahedral parameter q_4 (a). q_4 for interfacial water near a hydrophobic solid (b) and near a hydrophilic solid (c). Interface region 1 is the region within 3.2 Å from the instantaneous interface. Interface region 2 is between 3.2 and 5.5 Å. The bulk is beyond a distance of 5.5 Å. These distances were given by density distribution functions. The probability was not normalized. Figure reproduced with permission from ref 55. Copyright 2017 American Chemical Society.

intrinsic water–water H-bonds in terms of strength and orientations.⁷³

A tetrahedral order parameter (q_4) was used to assess the tetrahedral ordering of water.^{55,73} q_4 expresses a summation of deflections between a realistic configuration and an ideal tetrahedral network of water. The deflections are realized by comparing the realistic angle $\beta_{jk}(i, t)$ and the ideal tetrahedral angle of 109.5° (Figure 6a). Summation was iterated spatially following the i variable and temporally following the t variable. These calculations are aided by computer simulations. An ideal water network has no deflection, therefore, $\beta_{jk}(i, t) = 109.5^\circ$, $\cos \beta_{jk}(i, t) = -1/3$, and $q_4 = 1$. Real water experiences certain structural distortions and having $q_4 < 1$. Lower values of q_4 indicate lower degrees of tetrahedrality. Using q_4 , Nguyen et al. observed similar tetrahedral ordering of water near a hydrophobic surface and in the bulk phase (Figure 6b).⁵⁵ Therefore, a hydrophobic solid is not an inhibitor for gas hydrate nucleation in terms of water structure. In contrast, water near a hydrophilic solid experiences a significant loss of the tetrahedral feature (Figure 6c).⁵⁵ Distortions are caused by interphase H-bonds which differ in strength and orientations with intrinsic water–water H-bonds.⁷³ Thus, a hydrophilic solid is an inhibitor for gas hydrate nucleation.^{55,66,73}

3.3. Gas Density at Solid–Water Interfaces. Gas solubility is another principal factor in gas hydrate formation. According to the theory of hydrophobic assembly, dissolved gas molecules tend to populate at hydrophobic solid–water interfaces owing to hydrophobic attractions.^{39,43} Nguyen et al. indicated an interfacial gas-enrichment at an alkylated (hydrophobic) glass surface in contrast to a gas-depletion at a hydroxylated (hydrophilic) glass surface (Figure 7a,b).⁵⁵ The authors used such observed interfacial gas enrichment to explain the preferential formation of CO₂ gas hydrates at the hydrophobic glass (Figure 4).⁵⁵ Other studies consider increased gas densities at hydrophobic surfaces in the form of surface nanobubbles.^{62,67,68} Guo et al. observed a promotive methane hydrate formation in a suspension of hydrophobic graphite particles in contrast to an inhibited methane hydrate

formation in a suspension of hydrophilic mica particles.⁶² On the basis of atomic force microscopy scanning images, they found that nanobubbles exist on graphite surfaces but vanish on mica surfaces (Figure 7c,d).⁶² Therefore, they concluded that surface nanobubbles on hydrophobic solid surfaces serve as nucleation sites for gas hydrate formation.⁶² Maeda et al. assigned a “memory effect” in gas hydrate formation to nanobubbles on equipment surfaces.⁶⁸ “Memory effect” is named for mysterious observations that the reformation of a gas hydrate after the previous dissociation occurs faster than the first formation from fresh water.⁶⁸ According to Maeda et al., although gases released from hydrate dissociation would escape from the solutions due to their low solubilities, trace amounts of gases still persist as nanobubbles on equipment surfaces and facilitate the reformation of the hydrates when the experimental conditions are restored.⁶⁸

In summary, the literature findings infer that open hydrophobic solids can promote gas hydrate formation through the tetrahedral ordering of water and the increased gas density at hydrophobic solid–water interfaces. In contrast, open hydrophilic solids hinder gas hydrate formation due to the distorted water structure and the depleted gas density at hydrophilic solid–water interfaces. These observations for gas hydrate formation are in line with what has been known about ice nucleation for which hydrophobic molecules like steroids and cholesterols promote ice nucleation and hydrophilic surfaces inhibit ice nucleation.^{74–76} However, the situations are more complex for confining solids since water wetting in confined environments is affected by surface chemistry and pore size^{59,77} (discussed below).

4. CONFINED SPACES AFFECTING GAS HYDRATE FORMATION

4.1. Experimental Observations. Confined spaces associate with large interfacial areas, therefore promoting interfacial regimes. Common confined spaces for gas hydrates are pore structures such as activated carbons or metal–organic frame-

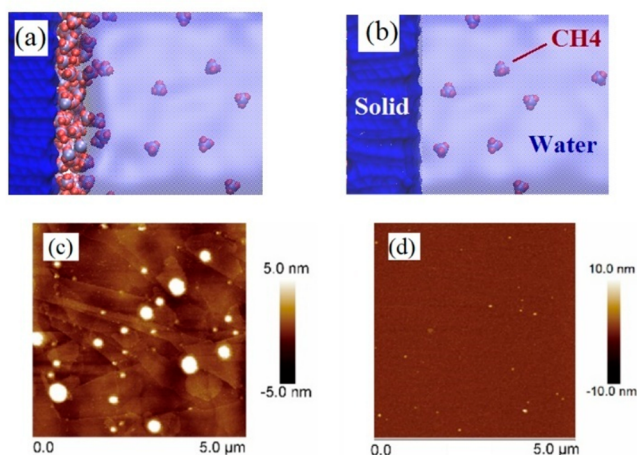


Figure 7. Methane enrichment at a hydrophobic solid surface (a) and depletion at a hydrophilic solid surface (b) from simulations of Nguyen et al.⁵⁵ Methane nanobubbles on a hydrophobic graphite surface (c) and vanishing nanobubbles on a hydrophilic mica surface (d) from atomic force microscopy scanning of Guo et al.⁶²

works (MOFs), layered spaces such as carbon sheets or mica sheets, and porously packed beds.^{18,78–94} Realistic conditions may have combined confinements, for example, individual particles in a packed bed also have pore structures.

Confinements vitally affect gas hydrate formation.^{18,78–94} Casco et al. showed an ultrafast methane hydrate formation in pore structures of activated carbons.¹⁸ A high methane uptake at 24 g of CH₄ per 100 g of activated carbon (dry basic) was achieved under mild conditions (2 °C and 3.5 MPa).¹⁸ Likewise, graphene oxides and multiwalled carbon nanotubes (MWCNTs) were widely shown for promotive effects.^{78–82} Park et al. found that adding MWCNTs to pure water at 40 ppm led to a 3-fold increase in methane uptake and much faster kinetics.⁷⁸ Pasiaka et al. compared the effects of two types of MWCNTs having similar structures but different wettability on methane hydrate dissociations.⁸¹ They found that the dissociation rates increased steadily with the increasing addition of hydrophilic MWCNTs. In contrast, the hydrate dissociated at nominal rates under the presence of hydrophobic MWCNTs, inferring certain stabilizing effects of hydrophobic MWCNTs on methane hydrates.⁸¹ Recently, Casco et al. observed a superior

formation of methane hydrate in prewetted hydrophobic mesopore carbons compared to methane hydrate formation in prewetted hydrophilic mesopore carbons.⁸³ More relevant studies are compiled in Table 2.

Porously packed beds are another type of common confined media for gas hydrate formation. Various packing materials have been used, for example, silica particles, glass beads, sands, minerals, clays, zeolites, etc.^{89–98} Packed beds are of interest primarily because they help to understand the formation of gas hydrates in nature, i.e., in geological structures.²⁷ Also, packed beds are attractive because they can be used for altering hydrate formation kinetics.^{89–98} For hydrophilic beds, most studies indicate that gas hydrates form favorably in the beds that are partially wetted by water (or partial water saturation).^{96–98} Full or nearly full water saturation results in lower hydrate kinetics, lower water-to-hydrate conversion, and lower gas uptake.^{96–98} For example, Fitzgerald et al. studied the kinetics of methane hydrate formation in packed beds of silica beads and found that the fastest hydrate formation was generally attained at 40% water saturation.⁹⁶ Ge et al. reported the highest water-to-hydrate conversion and largest methane uptake in silica beds at water saturation in the range of 50–70%.⁹⁸ Linga et al.⁹⁹ observed a peculiar vertical growth of methane hydrate above the surface of sand beds under 75% water saturation (Figure 8), which might

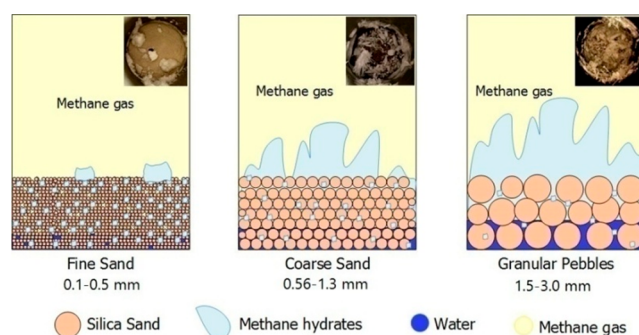


Figure 8. Peculiar growth of methane hydrate above the surfaces of hydrophilic beds under 75% water saturation. Labels are self-explanatory. The figure was reproduced from ref 99. Copyright 2016 American Chemical Society.

Table 2. Experimental Evidence of Confined Spaces Affecting Gas Hydrate Formation

| confined spaces | key findings ^a |
|--|---|
| prewetted activated carbon | ultrafast methane hydrate formation under mild conditions (2 °C and 3.5 MPa), high methane uptake (24 g per 100 g activated carbon in dry basic) ¹⁸ |
| carbon nanotubes | gas uptake increased by 300% and a shorter induction time ⁷⁸ |
| prewetted commercial activated carbons | optimal wetting (mass ratio between absorbed water and carbons = 1) gave maximum methane uptake by hydrate formation in activated carbons ¹⁰⁰ |
| model hydrophilic mesopore carbon vs hydrophobic mesopore carbon | methane hydrate forms favorably inside pores of hydrophobic ordered mesopore carbons with respect to hydrophilic ordered mesopore carbons ⁸³ |
| pores of porous glasses | heat of methane hydrate dissociation tends to be small in pores with diameters ≤ 30 nm ¹⁰¹ |
| silica gels having different pore diameters | dissociation of CO ₂ hydrates in silica gels shifted to lower temperatures; smaller pore diameters give stronger effects; it is inferred that silica gels hinder CO ₂ hydrate formation ⁹³ |
| silica beds with different levels of water saturation | initial rates of methane hydrate formation were highest when the beds were partially water-saturated at 40%; ⁹⁶ highest water-to-hydrate conversion and largest methane uptake attained at water saturation in the range of 50–70% ⁹⁸ |
| porous SiC foam ceramic packed beds | induction time decreased by 88%, methane hydrate growth rate increased by 95%, no agitation was needed ¹⁰² |
| hollow silica packed beds | Increased water-to-hydrate conversion, fast kinetics and increased methane uptake ¹⁰³ |
| hydrophobic vs hydrophilic metal–organic frameworks (MOFs) | hydrophobic MOFs effectively promote methane hydrate formation; hydrate nucleation occurred in interparticle spaces rather than inside the micropores; hydrophilic MOFs did not promote methane hydrate formation ¹⁰⁴ |

^aIn comparison with hydrate formation in purewater under similar conditions.

be an indication of insufficient methane–water contact inside the bed. Filarsky et al. investigated methane hydrate formation in packed beds of untreated, hydrophilically treated, or hydrophobically treated glass beads.⁵⁹ They found that methane hydrate forms favorably in a packed bed of untreated beads.⁵⁹ In contrast, inhibited hydrate formation was observed in the beds of hydrophilic or hydrophobic beads.⁵⁹ The authors concluded that packed beds should be slightly hydrophobic to promote gas hydrate formation.⁵⁹ More relevant studies are presented in Table 2.

4.2. Fundamental Understanding. The formation of gas hydrates in confined spaces appears to be complex since many parameters are involved. Surface chemistry and pore size are determinant factors.^{81,85,105,106} Surface chemistry determines water wettability in pores.^{83,106} Hydrophobic pores might not be wetted by water due to positive capillary pressures (Figure 9a).

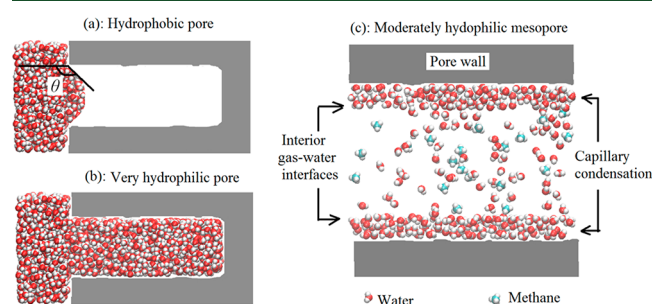


Figure 9. Proposed scenarios of water filling pores as dependent upon surface wettability. Labels are self-explanatory. Drawing scales are instructive but not necessarily precise. Gas hydrate formation in interior pore spaces is not feasible in a and b due to insufficient gas–water contact. System c favors gas–water contact and can promote gas hydrate formation.

In contrast, hydrophilic pores might be fully filled by water, which leads to exclusion of gases (Figure 9b). None of these conditions result in adequate gas–water contact in interior pore spaces. Consequently, hydrate formation is not sustained in these cases. Casco et al. experimentally studied the effects of hydrophobic MOF (ZIF-8) and hydrophilic MOF (MIL-100(Fe)) on methane hydrate formation.¹⁰⁴ At 2 °C and 3–5 MPa, pretreated ZIF-8 showed a double increase in methane uptake compared to unwetted ZIF-8.¹⁰⁴ A neutron scattering study proved that the increase of methane uptake was given by methane hydrate formation.¹⁰⁴ However, the hydrate formed in interparticle spaces rather than within the pores of ZIF-8 as water could not enter the hydrophobic pores.¹⁰⁴ In contrast, hydrophilic MIL-100(Fe) did not show any noticeable methane hydrate formation.¹⁰⁴ Müller et al. theoretically indicated that structural properties of absorbed water in activated carbons rely on the cooperative effects between water–water H-bonding and water–solid interactions.¹⁰⁶ Only pore surfaces having suitable densities and arrangements of active sites can yield to adsorbed water with three-dimensional structures.¹⁰⁶ Capillary condensation only happens in pores having low densities of active sites (moderate surface hydrophilicity).¹⁰⁶ Higher densities (strong hydrophilicity) lead to the continuous filling of pores.¹⁰⁶

Pore size is another essential factor.^{85,105} Pore size determines the specific surface area, thereby determining the weight of the interfacial regimes relative to bulk regimes. Nguyen et al. indicated an interfacial depth of ~0.5 nm at solid–water interfaces, in which structural properties of water are distinguishable from properties of bulk water.⁵⁵ It means that pores with a

diameter $\phi \leq 1$ nm contain only interfacial water. Interfacial water might not be freezable due to the loss of H-bonds.⁵⁵ Likewise, Cuadrado et al. showed that water in micropores ($\phi \leq 0.7$ nm) does not exhibit any phase transition against cooling.¹⁰⁵ Borchardt et al. studied methane adsorption on pretreated model carbons and indicated that mesopore carbons ($\phi \approx 25$ nm) have the highest methane adsorption capacity, at 341 mg per gram of wet carbons at -9 °C and 6 MPa.⁸⁵ Micropore carbons ($\phi \approx 0.8$ nm) and macropore carbons ($\phi \approx 10$ μ m) have lower adsorption capacities under similar conditions, at 163 and 61 (mg/g), respectively.⁸⁵ Complementary synchrotron X-ray diffraction proved that strong methane adsorption in mesopore carbons was given by the formation of methane hydrate with a composition of $1\text{CH}_4 \times 6.3\text{H}_2\text{O}$.⁸⁵

The aforementioned literature indicates that surface chemistry and pore size are equally important for gas hydrate formation in confined spaces. Surface chemistry influences the structure of interfacial water and the wetting of interior spaces.^{83,105} Pore size affects the wetting of water and the feasibility of gas hydrate formation in interior spaces. The diameters of a single gas hydrate cage are 0.79 nm for small cages and 0.86 nm for large cages.¹³ A hydrate nucleus is a cluster of cages.³² Therefore, micropores likely do not provide sufficient interior volume for gas hydrate nucleation. In contrast, mesopores with moderate surface wettability can be optimal media for gas hydrate formation.^{83,85,87,105} Water fills these pores through capillary condensation.¹⁰⁶ Water molecules condensed in these pores maintain their three-dimensional structures.¹⁰⁶ These characteristics favor the occurrence of interior gas–water interface inside the pores (Figure 9c). The nucleation of methane hydrates at such interior methane–water interfaces has been proven by experiments.⁸³ Via this mechanism, mesopores with moderate wettability provide large gas–water interfaces for rapid gas hydrate formation.

Similar discussions are applied to packed beds. Pores in packed beds can be macropores such as interparticle spaces and mesopores/micropores within individual particles. The latter is already discussed in the previous section. Here, we discuss the wetting of interparticle spaces. According to Filarsky et al., a bed of untreated (moderately wettable) glass beads had superior promotive impacts on methane hydrate formation compared to beds of hydrophilized or hydrophobized glass beads.⁵⁹ Studies based on magnetic resonance imaging and X-ray computed tomography have unraveled that gas hydrate formation in packed beds of hydrophilic particles initiates at gas–water interfaces within the interparticle spaces.^{97,107–110} No nucleation was observed at solid–water interfaces.^{97,107–110} These observations agree with our discussions in section 3 that hydrophilic solid surfaces do not sustain gas hydrate nucleation. Hence, gas hydrate formation in hydrophilic beds follows similar mechanisms to those in gas-pure water systems, i.e., happening at water–gas interfaces.^{97,107–110}

Therefore, Figure 10 indicates possible situations happening in packed beds. For a hydrophobic bed, water might not be able to invade interparticle spaces due to positive capillary pressures (Figure 10a). In contrast, water might fully fill the interparticle spaces of strongly hydrophilic beds, resulting in the exclusion of gases (Figure 10b). Both of these cases lead to insufficient water–gas contact inside packed beds, which might give rise to a peculiar hydrate growth in the gas phase in Figure 8. Only beds with moderate hydrophilicity and partial water saturation can provide optimal conditions for gas hydrate formation (Figure 10c). Water films are covering solid particles, and water bridges

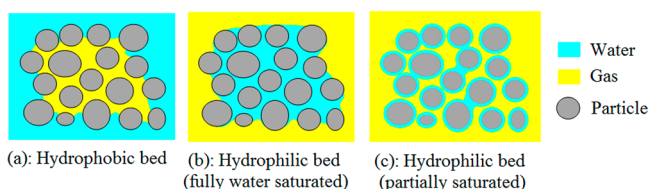


Figure 10. Proposed scenarios of gas–water contact in packed beds as dependent upon surface wettability and water saturation. Labels are self-explanatory. Configurations a and b are not feasible for gas hydrate formation inside the beds due to insufficient gas–water contact. Configuration c can favor rapid gas hydrate formation as it provides a large gas–water contact area within the bed.

form between particles, yet sufficient interparticle spaces are still available for the gas phase. Therefore, large gas–water contact areas can be achieved for rapid gas hydrate formation. In agreement with present concepts, experiments indicated that gas hydrates form most favorably in hydrophilic beds under 40–75% water saturation.^{95–98}

5. CONCLUSIONS AND OUTLOOKS

Gas hydrates are important for sustainable nature and industry. Two principal factors affecting gas hydrate formation are the tetrahedral ordering of water and gas–water contact area. Solid surfaces and confined spaces critically influence gas hydrate formation. The literature infers that open solids affect gas hydrate formation with respect to their surface hydrophobicity. Accordingly, open hydrophobic solids can promote gas hydrate nucleation via a tetrahedral ordering of water and an increased gas density at hydrophobic solid–water interfaces. Open hydrophilic solids can hinder gas hydrate nucleation via a distorted water structure and a depleted gas density at hydrophilic solid–water interfaces. However, confining solids have rather complex effects due to the complexity of wetting in confined spaces where surface chemistry and pore size are equally important. Mesopores with moderate wettability likely are optimal media for gas hydrate formation. In these pores, gas hydrates can form at the interface between adsorbed water and the interior space. Similarly, packed beds having moderate wettability and partial water saturation are optimal media where gas hydrates can nucleate at gas–water interfaces within the interparticle spaces.

This review with insightful discussions has offered a comprehensible and coherent understanding of gas hydrate formation at solid surfaces or in confined spaces. However, there are still many outstanding fundamental issues in this topic that demand further research. One of the unresolved puzzles is the gas hydrate nucleation. The applicability of classical nucleation theory to gas hydrates has been in doubt, as detailed by Maeda et al.¹¹¹ Currently, it remains unclear how the work of heterogeneous gas hydrate nucleation is related to that of homogeneous nucleation. Molecular pictures of gas hydrate formation at solid surfaces or in confinement would not be comprehensive until such an energy landscape has been successfully elucidated. Another puzzle is related to a mysterious phenomenon that gas hydrates often fail to nucleate while a small volume of ice on a solid surface is still melting under a pressurized guest gas but then nucleates steadily as the melted water on the solid surface warms up to higher temperatures (but still within the hydrate formation zone).^{111,112} Conventional perspectives would expect the opposite because the first condition (when ice is still melting) would provide a larger

degree of subcooling. There is currently no plausible explanation for this anomalous behavior of gas hydrate formation. Finally, for future investigations, it would be more meaningful to identify as to whether the nucleation of gas hydrates takes place in the interior or exterior pore spaces. The latter means the interparticle spaces. Correctly identifying the nucleation locations would help to better understand the actual physical mechanisms behind the macroscopic observations, thereby providing hints for designing and fabricating a new generation of structured solids for better functionality.

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Notes

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