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EDITORIAL

Natural gas hydrate, far beyond a vast resource of natural gas

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Natural gas is believed to still act as the premium fuel in the coming decades, which accounts for ~24% of the total primary energy consumption in the context of record-high natural gas prices in Europe and Asia in 2022. Technological progresses have enabled the utilization of the unconventional natural gas resources that were previously untouchable; of particular interest are the significant advances in the extraction of natural gas hydrates (NGHs) widely distributed in the permafrost and oceanic continental shelves. NGHs are a general class of non-stoichiometric clathrates comprising natural gas molecules locked inside a cage-like structure of water molecules at certain pressure and temperature conditions.[1] They arouse wide interest majorly due to the vast energy reserves estimated to be approximately twice the carbon in conventional fossil fuels. This drives a fast-accelerating investment in in-house research as well as field programs worldwide. Besides the great potential as an alternative energy source, gas hydrate itself shows fascinating physicochemical properties and plays a paramount role in nature and various energy and environment-related industrial applications. This encourages us to seek more knowledge on the inherent structure and phase transition behaviors of the NGHs and their interactions with a wide range of chemical additives.

OCEAN-HYDRATE INTERACTION: ROLE OF THE COLD SEEP SYSTEM

The huge quantities of methane stored in the NGHs under the seafloor and its enrichment in the deep ocean make the marine system the largest global methane reservoir. Continuous methane seepage into the seawater occurs ubiquitously (see Figure 1A). Therein anaerobic methane-oxidizing archaea and sulfate-reducing bacteria synergistically participate in the anaerobic oxidation of the escaping and diffusing methane streams; the methane gas plume will also facilitate the formation of hydrate outcrops on the seafloor.

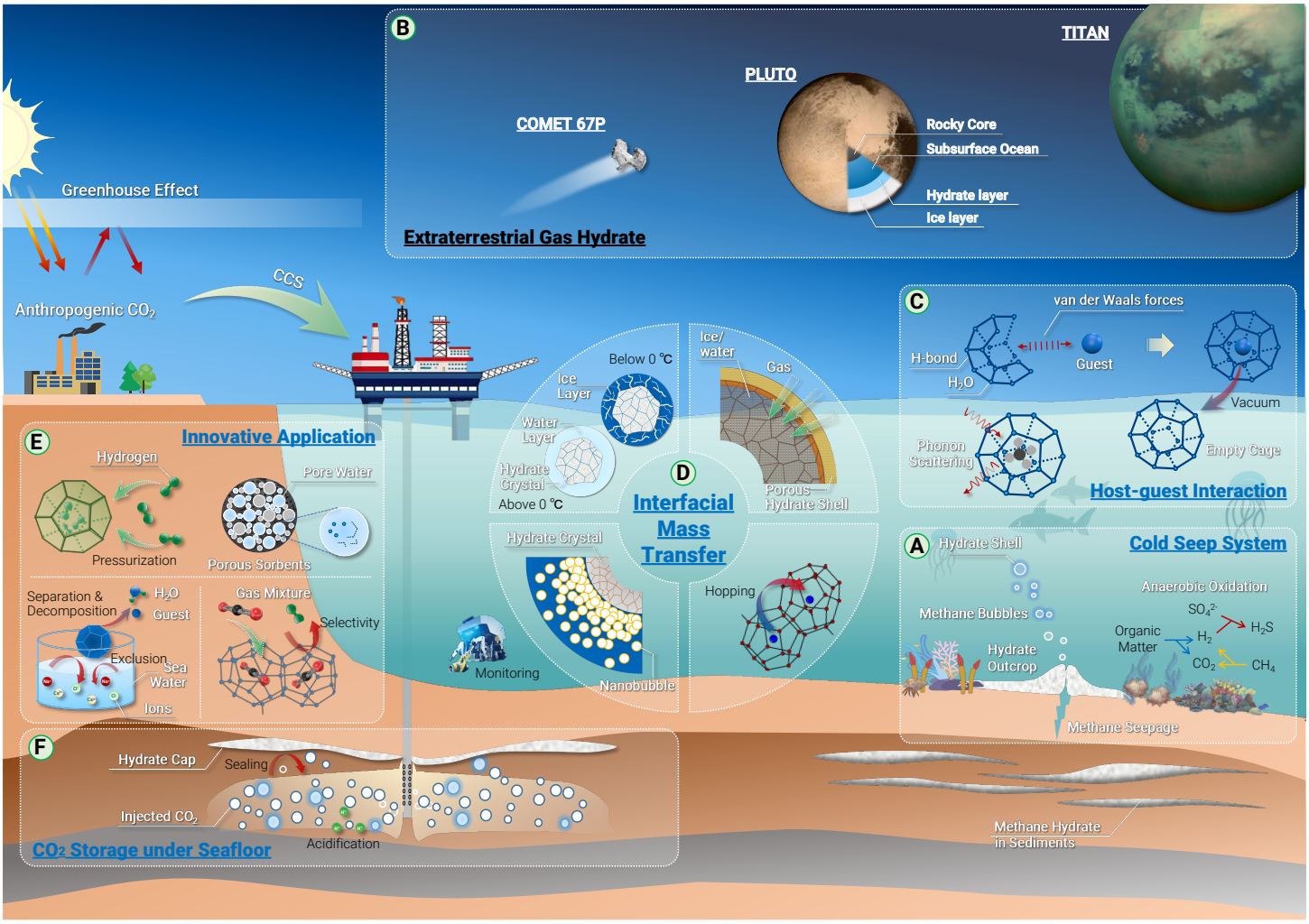

Figure 1. Physicochemical properties of gas hydrates and their role in nature and various industrial applications (A) Behavior of methane hydrate in the cold seep system. (B) Presence of methane hydrate in extraterrestrial bodies. (C) Effects of the host-guest interaction in the stability of the cage and physical properties of the hydrate. (D) Unique interfacial mass transfer behavior during phase transition. (E) Various hydrate-based applications. (F) "Self-sealing" effect of CO_2 hydrate during CO_2 storage in the marine sediments.

These together form a long-term stable and unique deep-sea cold seep ecosystem. The biogeochemical processes of the microorganisms enable more advanced consumers, such as bivalves, and polychaetes, to thrive on the seafloor, allowing life to evolve at the bottom of the dark, high-pressure oceans and providing researchers with an alternative perspective for exploring the origins of life. This vulnerable local methane carbon cycle is argued to

be able to regulate the Earth's climate from a long-term perspective and thus requires careful attention. There are evidences of massive gas release from hydrate dissociation into the seawater and atmosphere induced by ocean warming, challenging the previous sulfate filter assumption. Clearly, it is of crucial importance to improve our understanding on the dynamics of methane involved in the stability of gas hydrates as well as its interaction with the ocean. Specifically, attentions should be paid to the biological and geochemical effects of the multifarious microorganisms on the transformation of ascending gas bubbles into gas hydrates; this process is considered to contribute to filtering and blocking the escape of marine-derived methane into the atmosphere.

DOMINANT METHANE PHASE IN THE UNIVERSE

Besides on Earth, the existence of liquid water or ice has been widely confirmed or inferred in extraterrestrial environments. The structure of the H_2O ice in the comets carries significant information on the conditions of the solar nebula during planet formation. Being able to incorporate large quantities of volatile gases, clathrate hydrates have gained increasing interest in the solar system studies. There is evidence indicating the presence of clathrates in the coma of the Jupiter family comet 67P (see Figure 1B), providing important clues on the origin and evolution of the cometary nuclei. Methane hydrates are also believed as the dominant methane phase during the formation of the planets and satellites; specially, the methane in Titan is assumed to be mostly accreted as clathrate. Consequently, the physical properties of these methane hydrates, such as the thermal conductivity and the thermodynamic stability, are of particular significance in the models to predict and study a range of solid bodies in the solar system. Recent studies have identified the intrinsic ultralow thermal conductivity of the clathrate compared to ice due to the smaller density and higher complexity of the water network. This hydrate layer is thus considered to act as a thermal insulator to maintain a long-term subsurface ocean in Pluto. A potentially much increased pressure and declined temperature in the outer bodies will exert additional impact on the physical properties of the clathrates. As such, *in-situ* measurements and observations at extreme conditions are necessary to test these theories. The question of whether extraterrestrial life forms similar to cold seep ecosystems is also worthy of further discussion in astrobiology.

FASCINATING HOST-GUEST INTERACTIONS

Host-guest supramolecular materials exhibit intriguing physical properties, hence are of fundamental importance in various scenarios such as biomedicine, thermoelectrics, and photovoltaics. Two or more chemicals can be facially and reversibly integrated through the host-guest interactions, providing the probabilities to develop new materials with preferred performance. Specifically, methane hydrates are representative prototypes of hydrophobic hydration from a physical–chemical perspective, where water is orderly organized around hydrophobic solutes; a host-guest interaction *via* van der Waals forces and hydrogen bonds connecting host molecules coexist (see Figure 1C). Though weaker than the latter, the host-guest interaction could help stabilize the water networks, and thus is of crucial importance in the formation and decomposition of the cages. The interaction energy is calculated to be dependent on the guest size; consequently, one can experimentally produce empty clathrate (namely a new crystalline ice phase) by pumping a sufficiently small guest out of the cages.[2] Albeit with great challenges, a characterization and comparison of the properties of the water cages with/without guest fillers will shed light on the underlying nature of the host-guest interactions. It is also noteworthy that this interaction can be intensified by lattice compression. This has been found to trigger strong phonon scatterings and phonon localizations, resulting in significant suppression of thermal conductivity. It is also identified that the physical properties of the hydrates can be flexibly modulated by controlling the strength of the host-guest interaction. Therefore, a deeper comprehension of the host-guest interaction will offer an avenue to the design of materials with bespoke compositions, crystalline structures, and boosted performances. Further efforts are still necessary to experimentally quantify the interaction strength and integrate its effects in numerous models and programs for physical property predictions.

UNIQUE INTERFACIAL MASS TRANSFER BEHAVIOR

The hydrophobic nature of methane and its supersaturation in hydrate phase make the interfacial kinetic mass transfer during hydrate phase transition quite complicated. From a macroscopic view, thin gas hydrate shell will be formed at the gas-water interface upon hydrate formation; this shell will block the subsequent contact of gas and water hindering the reaction process (see Figure 1D). Yet microscopically, the initial hydrate shell is actually porous and cage less occupied, allowing gas and water to diffuse through ($\sim 10^{-12} m^2/s$ determined by *in-situ* CT). This process will densify the hydrate phase gradually, making the following hydrate formation a diffusion-limitation process. This might be similar to some surface coating reactions with solid phase generated. What should be different is that there exists a cage-to-cage hopping of methane molecules in the hydrate structure ($\sim 10^{-15}$ m^2/s). More interestingly, a much faster methane translational diffusion ($\sim 10^{-8}$ m^2/s) has been observed at the interface of sI-sII hydrate structures.[3] This could be a result of the enhanced diffusivity of methane inside the nanobubbles generated in the methane-water solution. To be specific, large quantities of methane will be released from the decomposing hydrate surface into the water, which is far beyond the dissolving capacity of the water. This will facilitate a metastable enrichment of gas molecules in the water as observed through the synchrotron X-ray technique; it explains the huge chemical activity gap of gas in hydrate phase and saturated water. Following this argumentation, the enriched gas molecules in water may well be in the form of nanobubbles as a consequence of the high entropic cost of the hydrophobic hydration. Due to their high surface area–to–volume ratio and most probably high pressure inside according to the Young-Laplace Law, nanobubbles are argued to play a role in the secondary hydrate formation (also known as the "memory effect"). Besides substantial gas release, the decomposition of hydrate will also produce water; an anomalous phenomenon concomitant when decomposition proceeds slightly below freezing point is that this water will transform into ice coating the hydrate crystals as a diffusion barrier, recognized as the "self-preservation". This would surprisingly help lock the gas inside the hydrate phase for even months at conditions far outside its thermodynamic stability. The abovementioned interfacial mass transfer mechanisms contribute to revealing the nature of hydrate formation and decomposition. Deeper understandings on further utilizing or breaking the mass transfer limitation are still required to better guide the application of gas hydrates in various energy-related scenarios (see below).

INNOVATIVE APPLICATIONS IN SUSTAINABLE CHEMISTRY

The molecular structure of methane hydrate enables a counterintuitive concentration of nonpolar hydrophobic methane gas in the hydrate lattice more than two orders of magnitude higher than its solubility in water.[4] This renders gas hydrates a potential candidate for energy gas storage and transportation at moderate conditions; of special interest is the capability to store hydrogen as clathrate under the pressure of only several megapascals and temperature above water freezing point aided by a second guest (see Figure1E). Yet there exists an energy density limit due to the well-organized gas molecules in water vacancies and thus the fixed mole and mass fraction. High pressure might contribute to improving the storage capacity by squeezing more than one guest in the individual cage, especially small molecules like hydrogen. Further pressurization (over 1 GPa) would enhance the dissolution of gas through reducing its molecular size to be integrated into a connected H-bound network. The storage performance can also be regulated by co-acting with porous solid sorbents, in which hydrates can form from the water imbibed within the pores enhancing gas uptake capacity. Notably, the solutes (like ions) in the water solution are basically excluded from the water cage structure during hydrate nucleation (some temporary cooperation may occur), thus the crystallization process can essentially be used for desalination and water treatment. By mechanically separating the solid hydrate crystals from the solution, one can decompose them into water and hydrate guests for recycling. Other energy-related applications may also involve gas capture or separation taking advantage of the different cage occupancies of various gas species, latent heat-based cold energy storage, etc. Despite pilot-scale tests of these hydrate-based techniques are launching, challenges remain towards an outstanding performance and economically viable application in industries.

UNDERESTIMATED ROLE IN MARINE CO_2 SEQUESTRATION

Geological storage of CO_2 is considered as an alternative method to mitigate greenhouse gas emission towards carbon neutrality in the context of high dependence on high-carbon energy currently. Oceans hold great potential for CO_2 sequestration in the form of dissolved CO_2 in the seawater, liquid CO_2 lake on the seafloor, as well as trapped CO_2 in the deep-sea sediments. Here one previously overlooked issue might be that CO_2 can widely form hydrate in deep sea conditions (e.g., over ~500 m water depth and at several degrees Celsius).[5] Consequently, the CO_2 lake would be a "hydrate lake" at deeper submarine basin, the solid phase of which could better avoid the CO_2 migration and leakage under geologic perturbation. This also applies in the sediment sequestration scenario where the formation of CO_2 hydrate will occupy the pore spaces and serve as a low permeable seal blocking the upward plume of CO_2 (see Figure 1F); its diffusion rate could be reduced by even 3 orders of magnitude. Besides, the formation of these hydrates will enhance the integrity and stability of the sediments as well. It should be noted that the availability of water and increased local salinity upon hydrate formation will hinder the sustained hydrate transformation. Acidification accompanying the CO_2 injection will also change the local seawater environment (like dissolving the organics) and significantly affect the hydrate formation behavior. Clearly, the abovementioned mass transfer issues are also present here; one open question is whether this hydrate-based storage is sufficiently stable at geological time scales. Further evaluation and monitoring of the entire CO_2 storage process are necessary for a safe and permanent CO_2 sequestration.

In summary, more than a form of unconventional natural gas, gas hydrates have become a multifaceted frontier encompassing physical chemistry, environmental science, and astrophysics. They evolve from a phenomenon initially observed in oil and gas pipelines to a rising star in the green and sustainable chemistry. Looking ahead, continued innovation and collaboration in hydrate-based technology could unlock its full potential as a cornerstone of a low-carbon energy system.

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DECLARATION OF INTERESTS

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