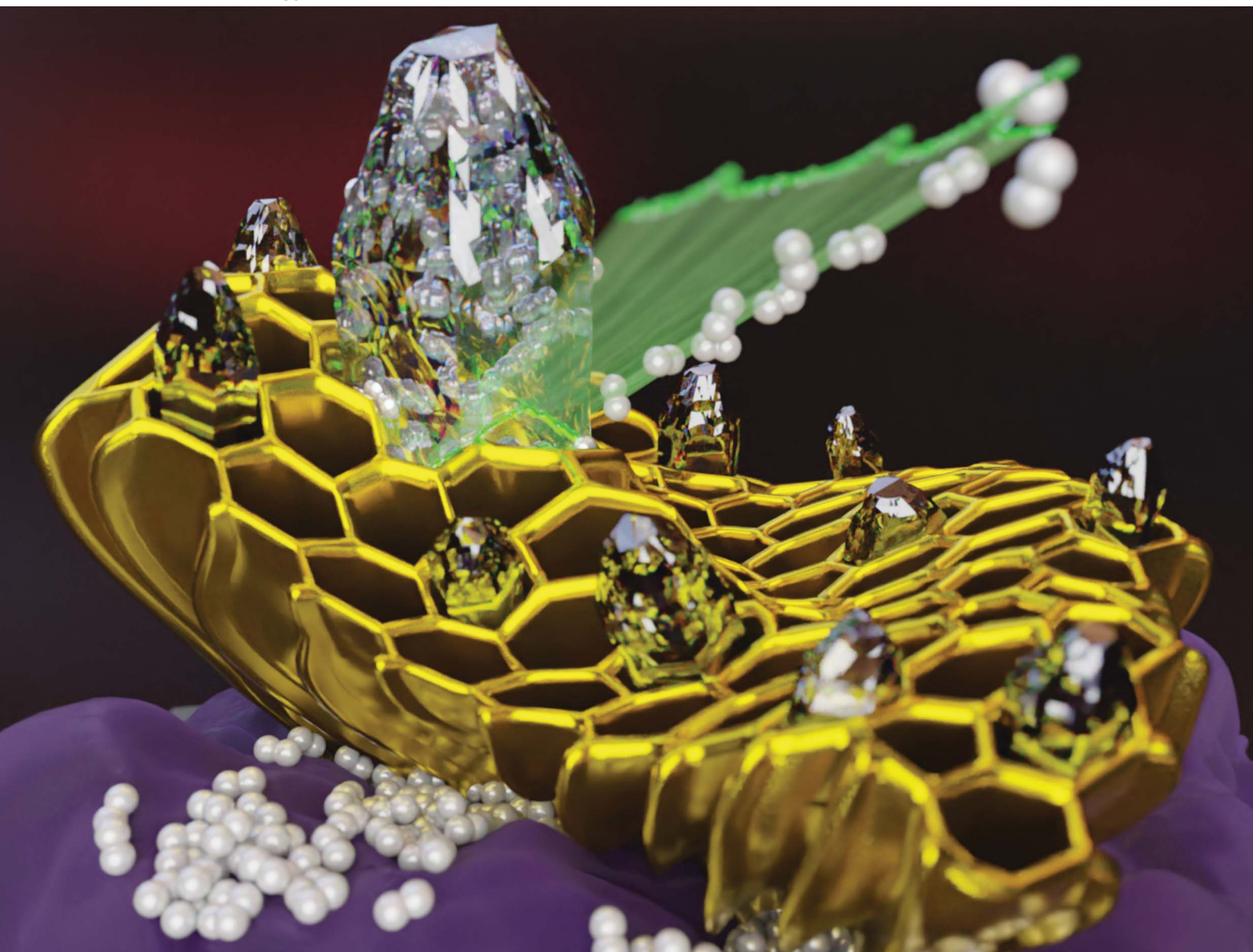


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**PAPER**

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# Surface modification of mesostructured cellular foam to enhance hydrogen storage in binary THF/H<sub>2</sub> clathrate hydrate†

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This study introduces solid-state tuning of a mesostructured cellular foam (MCF) to enhance hydrogen (H<sub>2</sub>) storage in clathrate hydrates. Grafting of promoter-like molecules (e.g., tetrahydrofuran) at the internal surface of the MCF resulted in a substantial improvement in the kinetics of formation of binary H<sub>2</sub>-THF clathrate hydrate. Identification of the confined hydrate as sII clathrate hydrate and enclathration of H<sub>2</sub> in its small cages was performed using XRD and high-pressure <sup>1</sup>H NMR spectroscopy respectively. Experimental findings show that modified MCF materials exhibit a ~1.3 times higher H<sub>2</sub> storage capacity as compared to non-modified MCF under the same conditions (7 MPa, 265 K, 100% pore volume saturation with a 5.56 mol% THF solution). The enhancement in H<sub>2</sub> storage is attributed to the hydrophobicity originating from grafting organic molecules onto pristine MCF, thereby influencing water interactions and fostering an environment conducive to H<sub>2</sub> enclathration. Gas uptake curves indicate an optimal tuning point for higher H<sub>2</sub> storage, favoring a lower density of carbon per nm<sup>2</sup>. Furthermore, a direct correlation emerges between higher driving forces and increased H<sub>2</sub> storage capacity, culminating at 0.52 wt% (46.77 mmol of H<sub>2</sub> per mole of H<sub>2</sub>O and 39.78% water-to-hydrate conversions) at 262 K for the modified MCF material with fewer carbons per nm<sup>2</sup>. Notably, the substantial H<sub>2</sub> storage capacity achieved without energy-intensive processes underscores solid-state tuning's potential for H<sub>2</sub> storage in the synthesized hydrates. This study evaluated two distinct kinetic models to describe hydrate growth in MCF. The multistage kinetic model showed better predictive capabilities for experimental data and maintained a low average absolute deviation. This research provides valuable insights into augmenting H<sub>2</sub> storage capabilities and holds promising implications for future advancements.

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## 1. Introduction

2022 was a critical year for the European Union, both in terms of changing the traditional energy import routes and hastening its

energy transition towards low-emission alternative fuels. This complements the recommendation of the 27th United Nations Climate Change Conference to prioritize decarbonization.<sup>1</sup> Hydrogen (H<sub>2</sub>) is a clean energy carrier with a >200% higher energy density than methane (CH<sub>4</sub>) (H<sub>2</sub> ~120 MJ Kg<sup>-1</sup>; CH<sub>4</sub>: ~50 MJ Kg<sup>-1</sup>). With a predicted global H<sub>2</sub> demand of 95 million tonnes by 2030, H<sub>2</sub> is considered to be a crucial pillar of the future energy system, especially for industrial sectors.<sup>2,3</sup> Despite H<sub>2</sub>'s potential, its safety and processability (*i.e.* storage and transportation) remain major challenges limiting the development of novel H<sub>2</sub> technologies and delaying the deployment of an H<sub>2</sub> economy.<sup>4</sup> Chemi- and physi-sorption based H<sub>2</sub> storage has often been touted as an alternative to conventional storage of molecular H<sub>2</sub> in high-pressure tanks or *via* liquefaction, which comes with a variety of drawbacks.<sup>5,6</sup> While sorption based storage can exhibit superior gravimetric and/or volumetric H<sub>2</sub> storage densities, many materials potentially exceed the DOE target of 5.6 wt% H<sub>2</sub> for mobile applications.<sup>7-9</sup> H<sub>2</sub> release is often energy intensive and not fully reversible. To confront slow kinetics, poor reversibility, cycling instability, and

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thermal management issues, substantial R&D resources are committed to the field of materials science.<sup>6,10</sup>

Gas hydrates or clathrate hydrates are crystalline materials formed under favorable thermodynamic conditions when suitable guest ( $H_2$  in this work) molecules are incorporated in the cages of 3-dimensional hydrogen bonded solid water ( $H_2O$ ) structures.<sup>11</sup> Because of its renewable and environmentally friendly nature as the principal storage medium is  $H_2O$ , clathrate based  $H_2$  storage technology has regained significant momentum.<sup>12,13</sup> Minimal temperature or pressure swings outside the hydrate stability zone enable swift recovery of the stored molecular  $H_2$  without losing  $H_2O$  or promoter molecules.<sup>14–16</sup> Recently, gas recovery from clathrate hydrate was even demonstrated without melting the solid water phase, further improving the energy balance of the process.<sup>17</sup> Pure  $H_2$  clathrates entered the focus of attention when Mao *et al.*<sup>15</sup> reported that classical sII hydrate structures allow to encapsulate respectively two and four hydrogen molecules in each of its sixteen dodecahedra (small) and eight hexakaidecahedron (large) cages. In this scheme, complete occupancy would deliver a total  $H_2$  storage capacity of 5 wt%. Neutron diffraction analysis by Lokshin *et al.*,<sup>18</sup> however, refuted the claims of double occupancy of  $H_2$  in small cages. Regardless of this occupancy debate, the exceedingly high pressures (between 0.75 and 3.1 GPa) required to stabilize pure  $H_2$  clathrate hydrate in the bulk remain a major factor limiting deployment of bulk  $H_2$  clathrate hydrate in  $H_2$  storage and transportation applications. To resolve this aspect and make  $H_2$  clathrates industrially viable, binary clathrate hydrates incorporating both  $H_2$  and promoter molecules have been put forward.<sup>13</sup>

Stoichiometric concentrations of thermodynamic promoters (e.g. tetrahydrofuran (THF); 5.56 mol%) can stabilize binary promoter-gas sII clathrate hydrate structures at pressures as low as 5 MPa and 279.6 K, albeit at the expense of storage capacity for the gas.<sup>12,13,16,19,20</sup> Promoter molecules typically occupy a significant fraction of larger clathrate cages, indeed leaving mostly only small cages open for gas enclathration. In an attempt to enable a higher  $H_2$  storage density, various studies have proposed strategies for reducing the concentrations of these thermodynamic promoters below the stoichiometric concentration.<sup>21–24</sup> These strategies were, however, contested by claims that the  $H_2$  storage capacity at reduced pressure and elevated temperature is dependent on the promoter concentration. Optimization of the promoter concentration would therefore not allow the storage capacity to be enhanced.<sup>25–28</sup>

While much attention has been focused on cage occupancies and determining overall  $H_2$  storage capacities with different thermodynamic promoters (THF being cited as the best promoter thus far),<sup>13,19,29</sup> the constraints on enclathration kinetics and the mass transfer rate have largely been overlooked, causing further impediments to foster this technology. While mechanical mixing can potentially assist in enhancing its kinetics, gas enclathration is typically a slow process due to insufficient contact between gas and liquid phases<sup>27,30,31</sup> (in this case between  $H_2$  and  $H_2O$  + promoter molecules). Mixing on top is an energy-intensive operation as the viscosity of the system increases with increasing conversion.<sup>32–34</sup> As an alternative to

mechanical mixing of the bulk gas–liquid system, pre-synthesized pure promoter molecules, including THF, have been made to come into contact with  $H_2$  gas at high-pressure to convert the pure promoter-molecule clathrate hydrate into binary clathrate hydrate. Melting of the binary clathrate hydrate to a liquid phase upon gas release however renders this strategy unsuitable for continuous cycles.<sup>27,35–38</sup> Enhancing the kinetics of synthesizing a binary  $H_2$  hydrate from a bulk aqueous phase under mild thermodynamic conditions in a process incorporating recycling of the  $H_2O$  and promoter molecules therefore remains a major challenge.

A limited number of publications report the option to accelerate the kinetics of binary clathrate hydrate formation by incorporating porous materials in an unstirred reactor.<sup>25,35,39–45</sup> This paves the way for further research on quiescent and porous systems that could propel clathrate-based  $H_2$  technology to new frontiers. While the literature clearly demonstrates enhanced growth of clathrate hydrate with increasing the surface-to-volume ratio, the process is affected by multiple factors including surface chemistry, pore morphology, and wettability.<sup>27,30</sup> Pore size and network morphology not only affect the gas–liquid contact, but together with the surface chemistry of the pores, they also profoundly impact the local organization of  $H_2O$ ,<sup>46</sup> thereby directly affecting clathrate hydrate nucleation. Molecular simulations by Bai *et al.*<sup>47</sup> also show that gas hydrate nucleation occurs more easily on less hydrophilic surfaces. This is supported experimentally by J. Wang *et al.*<sup>48</sup> who reported the induction time of gas clathrate hydrate formation to be more than 8 times shorter in hydrophobic materials than in hydrophilic materials. Hydrophobic nano-confinement indeed induces a reorganization of the hydrogen bonding structure of  $H_2O$ , towards a more ice-like tetrahedrally bonded organization which appears to promote clathrate hydrate nucleation.<sup>39,42,46,49–60</sup>

Given the advantages of hydrophobic surfaces in gas hydrate nucleation, the present work attempts to design and synthesize porous materials enabling the enclathration kinetics of binary  $H_2$  clathrate hydrates to be boosted. Consequently, this study focuses on silica-based mesoporous materials that have been comprehensively designed in terms of pore networks and with pore diameters exceeding 17.3 Å.<sup>11</sup> Such pore size should allow the accommodation of an sII clathrate hydrate unit cell, while functionalization with a promoter molecule (THF) could assist in stabilizing  $H_2$  clathrate hydrate and potentially allow its concentration in the aqueous phase to be reduced. The chosen silica material, specifically mesostructured cellular foam (MCF), offers several advantages due to its relatively large pores in the mesoporous region, which, in turn, facilitate network accessibility. As THF today still is the best promoter molecule for binary  $H_2$  clathrate hydrate formation, the MCF pore surface was functionalized with tetrahydro furfuryloxypropyl triethoxysilane, a THF-like molecule that can be grafted on silica surfaces while retaining high mobility due to its long ether chain. To evaluate if the grafted THF-like molecules assist in perturbing the  $H_2O$  structure and lowering the nucleation barrier, binary  $H_2$ -THF clathrate hydrate formation was studied as a function of temperature (268 K, 265 K, and 262 K; 7 MPa





initial pressure) in grafted and pristine MCF foams, evaluating kinetics as well as H<sub>2</sub> storage capacity.

## 2. Experimental methods

### 2.1. Materials

Table 1 lists all the chemicals used in this work and all of them were used without any purification. H<sub>2</sub> (99.99% purity) was supplied by Air Liquide Benelux Industries and for the liquid phase deionized H<sub>2</sub>O was used.

### 2.2. Synthesis and characterization methods

The MCF silica material was synthesized *via* a previously reported template approach.<sup>61</sup> In a typical experimental procedure, the triblock copolymer P123 (EO<sub>20</sub>PO<sub>70</sub>EO<sub>20</sub>) surfactant was dissolved in a solution of HCl acidified H<sub>2</sub>O and stirred overnight. Next, appropriate amounts of etching agent ammonium fluoride (NH<sub>4</sub>F) and swelling agent 1, 3, 5-trimethylbenzene (mesitylene) were added and the mixture was equilibrated at 308–313 K for 1 h while stirring. Next, tetraethylorthosilicate (TEOS) was added dropwise to the stirred solution over a timeframe of 30 minutes (approximately 1 mL min<sup>-1</sup>). Subsequently, the newly formed white precipitate was aged at 313 K for 20 h while stirring. The synthesis was finalized by transferring the white precipitate to an autoclave and subjecting it to hydrothermal treatment for 24 h at 373 K. Afterwards, the solid was recovered by filtering, subsequently rinsed with distilled H<sub>2</sub>O, and then dried. The molar ratio of the precursors used in the synthesis was as follows: 1 TEOS: 5.87 HCl: 194 H<sub>2</sub>O: 0.017 P123: 0.031 NH<sub>4</sub>F: 0.815 1, 3, 5-trimethylbenzene. Before using it in the subsequent experiments, the dry material was calcined at 550 °C for 6 hours, raising the temperature from 295 to 823 K at 1 K per minute. The resulting product was denoted as MCF (n-f) and will be referred to as such throughout this manuscript.

After the synthesis, the MCF silica material underwent surface modification using tetrahydro furfuryloxypropyl triethoxysilane, drawing inspiration from a previously documented approach.<sup>62</sup> Prior to the procedure, each batch of 1.2 g of the MCF material was subjected to overnight drying at 473 K under atmospheric pressure. Subsequently the dried batches were introduced in a glovebox under an argon atmosphere and each batch was suspended in 30 ml toluene. Subsequently a mixture of toluene and tetrahydro furfuryloxypropyl triethoxysilane (0.002 moles for f-1 and 0.006 moles for f-2) was added to the stirred suspension. The resulting mixture was sealed and

continuously stirred for 72 h at 353 K. The resulting solid phase was isolated by filtration and thoroughly rinsed with toluene to eliminate any remaining unreacted triethoxysilane. Finally, the material was dried overnight at 373 K. The resulting products were denoted as MCF (f-1) and MCF (f-2) and will be referred to as such throughout this manuscript.

The material's porosity was evaluated using N<sub>2</sub>-sorption, conducted on an automated Quantachrome Quadrasorb system at 77 K. Before analysis, the samples underwent degassing at 393 K for 16 h. *In situ* diffuse reflectance infrared FT (DRIFT) measurements were performed using a Nicolet 6700 Fourier transform IR (FT-IR) spectrometer. To prepare the samples for analysis, they were diluted in KBr (2 wt%) and heated under vacuum to 393 K. Following a 30-min equilibration time and keeping the temperature constant, 100 scans were performed in the region of 4000–500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>. Thermogravimetric analyses (TGA) were conducted using a Mettler Toledo TGA/DSC 3+ star system, in cups of 150 μL and 80 mL min<sup>-1</sup> flow of pure O<sub>2</sub>. The TGA results were cross-referenced with the N<sub>2</sub>-sorption analysis (BET surface area) to estimate the surface functional group density of the modifier molecule. This methodology was previously validated and documented in the existing literature.<sup>63,64</sup> The analysis of the TGA-profile considered the mass loss between 423 K and 1073 K, assuming that toluene, used as a solvent and rinsing agent in the post-synthesis modification protocol, had evaporated below this temperature.

### 2.3. Experimental setup and procedure

The schematic layout of the experimental setup employed in this work is presented in Fig. 1. The binary H<sub>2</sub>-THF hydrate formation tests were performed in a Swagelok stainless steel cylindrical reactor (316L-50DF4-150; designed pressure: 34.4 MPa) with an effective inner volume of 150 cm<sup>3</sup>. The temperature within the reactor was kept cold and stable (measured using a K-type thermocouple, ± 0.1 K; Testo SE & Co. KGaA) by immersing it in a circulating water–ethylene glycol bath (CORIO CP-1000F, JULABO GmbH, stability: ± 0.03 K). The pressure in the reactor was monitored every second using a pressure transmitter acquired from KELLER AG für Druckmesstechnik (PAA3X-30 MPa; range of 0–30 MPa absolute, with ± 0.01% FS accuracy).

All experiments were performed in accordance with the previously reported standard procedure.<sup>45,64,65</sup> In summary, the reactor was thoroughly cleaned with H<sub>2</sub>O and dried to remove contaminants/impurities before commencing any experiment.

Table 1 Description of chemicals

| Chemical name  | Purity           | Source        |
|--|------------------|---------------|
| P123 (EO <sub>20</sub> PO <sub>70</sub> EO <sub>20</sub> ) | Average Mn ~5800 | Sigma-Aldrich |
| Ammonium fluoride (NH <sub>4</sub> F)                      | 95%              |               |
| 1, 3, 5-trimethylbenzene (mesitylene)                      | 99%              |               |
| Tetraethylorthosilicate (TEOS)                             | 99%              |               |
| Toluene  | 99%              |               |
| Tetrahydro furfuryloxypropyl triethoxysilane               | 97%              |               |



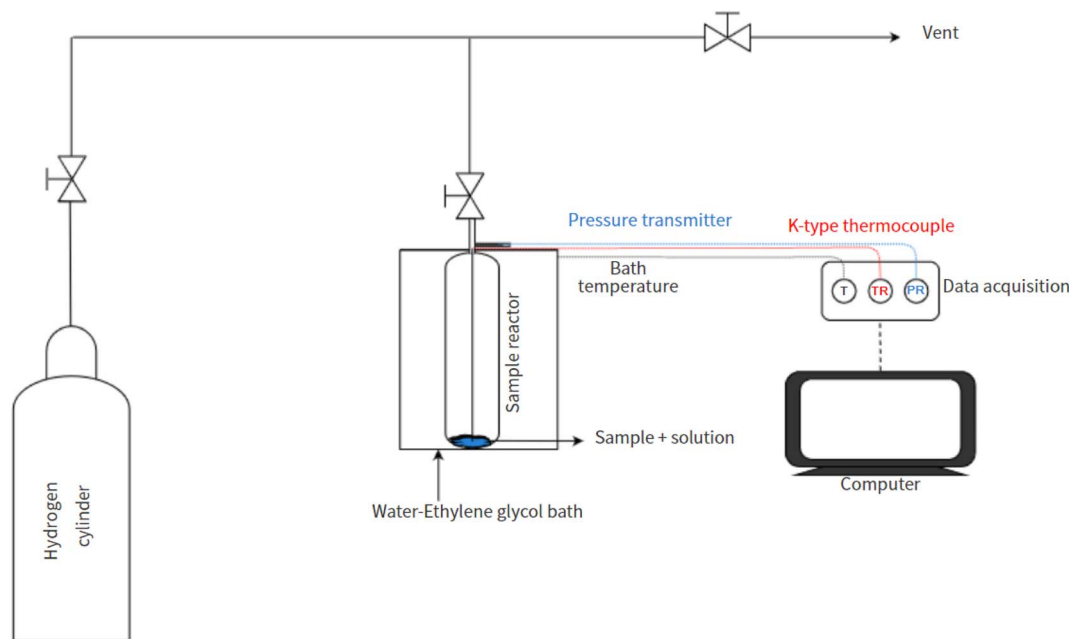


Fig. 1 The schematic of the experimental setup.

To carry out the  $H_2$  uptake experiments, 5.56 mol% THF solution was added to 0.5 g of the synthesized material (dried overnight at 343 K) based on 100% pore volume saturation. To remove any atmospheric gases the reactor was subsequently subjected to at least 10 rapid pressurization (0.2 MPa) and depressurization (0.12 MPa) cycles with  $H_2$  gas. The reactor was then immersed in a water–ethylene glycol bath at 298 K before gradual pressurization with  $H_2$  gas to 7 MPa. Sufficient time was allowed for the system to stabilize under these thermodynamic conditions before cooling the reactor to the experimental temperature. The maximal  $H_2$  storage capacity of the binary  $H_2$ -THF clathrate hydrate was considered to have been attained when no considerable pressure reduction ( $0.02 \pm 1 \times 10^{-4}$  MPa in 30 min) was observed. Each experiment in this study was performed in triplicate.

The amount of  $H_2$  gas consumed during hydrate formation at any given real-time was quantified using the compressibility factor equation of state as shown in eqn (1):

$$\Delta n_{H_2,t} = \frac{V_r}{RT} \left[ \left( \frac{P}{z} \right)_{t=0} - \left( \frac{P}{z} \right)_{t,t} \right] \quad (1)$$

with  $\Delta n_{H_2,t}$  being the moles of  $H_2$  gas consumed at time  $t$ ;  $V_r$  is the gas-phase volume in the reactor measured using the helium expansion method;<sup>65</sup>  $R$  is the ideal gas constant;  $T$  and  $P$  respectively are the temperature and pressure within the reactor and  $z$  is the compressibility of  $H_2$  gas calculated using the Lemmon–Huber–Leachman correlation.<sup>66</sup>

The normalized  $H_2$  gas uptake ( $NG_t$ ) and the percentage of  $H_2O$  to hydrate conversion were quantified using eqn (2) and eqn (3) and 4, respectively.

$$NG_t = \frac{\Delta n_{H_2,t}}{n_{H_2O}} \text{ (moles of } H_2 \text{ / moles of } H_2O \text{)} \quad (2)$$

$$WtH(\%) = \frac{(\Delta n_{H_2,t} + \Delta n_{THF}) \times H_n}{n_{H_2O}} \times 100 \quad (3)$$

$$\Delta n_{THF} = \Delta n_{H_2,t} \times \frac{\text{number of large cages}}{\text{number of small cages}} \quad (4)$$

with  $n_{H_2O}$  representing the moles of  $H_2O$  introduced into the reactor;  $\Delta n_{THF}$  is the moles of THF consumed for hydrate formation, assuming that THF solely occupies the hexakaidecahedron cages of the expected sII clathrate hydrate, and  $H_n$  is the hydration number, which is considered to be 5.67 in order to comply with previously reported binary  $H_2$ -THF sII clathrate hydrate studies.<sup>45,67</sup>

The volumetric gas storage capacity was determined using eqn (5),<sup>19</sup>

$$\text{Volumetric } H_2 \text{ storage capacity} \left( \frac{\text{volume of gas at STP}}{\text{volume of hydrate}} \right) = K \times NG_t \quad (5)$$

$$K = \frac{v}{(\rho_{\text{hyd}} \times n_{\text{wh}})} \quad (6)$$

$$M_{w,\text{hyd}} = (136 \times 18.01) + (8 \times 72.11) + (16 \times 2.016) \quad (7)$$

$$\rho_{\text{hyd}} = \frac{M_{w,\text{hyd}}}{(A \times \lambda^3)} \quad (8)$$

where the proportionality coefficient  $K$  is defined as shown in eqn (6),  $v$  is the gas volume under STP conditions ( $22.4 \text{ cm}^3 \text{ mmol}^{-1}$  of gas),  $M_{w,\text{hyd}}$  is the molecular weight ( $\text{g mol}^{-1}$ ) of sII clathrate hydrate considering the thermodynamic promoter used in this study (THF) and is calculated as shown in eqn (7),



$n_{\text{wh}}$  is the mole of H<sub>2</sub>O per mole of sII clathrate hydrate (*i.e.* 136), and  $\rho_{\text{hyd}}$  (g cm<sup>-3</sup>) is the hydrate density, calculated using eqn (8), with  $A$  the Avogadro constant ( $6.023 \times 10^{23}$  mol<sup>-1</sup>)<sup>68</sup> and  $\lambda$  the sII hydrate lattice parameter which is 17.145 Å when THF is used as a promoter and pressurized with H<sub>2</sub> gas in the bulk.<sup>69</sup>

The rate of H<sub>2</sub> hydrate formation was determined by applying a discrete first-order forward difference approach, as shown in eqn (9), where  $\Delta t$  (1 min) is the time difference between two observations.

$$\frac{dN_t}{dt} = \left( \frac{d\Delta n_{\text{H}_2}}{dt} \right) \approx \frac{\Delta n_{\text{H}_2,t+\Delta t} - \Delta n_{\text{H}_2,t}}{\Delta t} \quad (9)$$

#### 2.4. Characterization of the confined clathrate hydrate phase

The crystal structure of the clathrate hydrate phase formed in an MCF (f-1) host material mixed with an amount of 5.56 mol% THF solution corresponding to 100% of its pore volume, and subsequently pressurized to 7 MPa with H<sub>2</sub> gas and cooled to 265 K, was established by transmission X-ray diffraction using a B STOE STADI P combi diffractometer with a focusing Ge(111) monochromator (CuK $\alpha_1$  radiation,  $\lambda = 0.154$  nm) in a high throughput set-up in transmission geometry. Samples were collected from the reactor, ground in a mortar filled with liquid nitrogen (LN<sub>2</sub>) and finally transferred to a sample holder which had been submerged in LN<sub>2</sub> up until the transfer. The metal sample holder was retrofitted with a Kapton® bottom film to withstand the low LN<sub>2</sub> temperature (77 K) required for the stability of the clathrate hydrate phase at atmospheric pressure. PXRD data were recorded using a 140° curved image plate position sensitive detector (IP PSD) from  $-17.5$  to  $62.5^\circ 2\theta$ . To account for reflections originating from the MCF host material, a diffraction pattern of the dry MCF (f-1) material was recorded as a reference. X-ray diffraction experiments at liquid nitrogen (LN<sub>2</sub>) temperature (77 K) and atmospheric pressure were performed in a metal sample holder with a Kapton® bottom film. The low temperature ensured the stability of the clathrate hydrate phase under these conditions. Before XRD analysis, the H<sub>2</sub>-THF clathrate hydrate samples were first ground in a mortar filled with LN<sub>2</sub> and then transferred to the metal sample holder which had been submerged in LN<sub>2</sub> up until the transfer.

Incorporation of H<sub>2</sub> in 5<sup>12</sup> cages of the sII clathrate hydrate lattice was observed using *in situ* high-pressure <sup>1</sup>H nuclear magnetic resonance (NMR) spectroscopy at 800 MHz. <sup>1</sup>H NMR spectra were acquired using a static 5 mm BBO probe head operating at a Larmor frequency of 801.25 MHz and a Bruker Avance Neo console. The temperature was regulated using a BCU II unit. In order to minimize the <sup>1</sup>H background signal of the host material and facilitate identification of all components in spectra, the MCF (f-1) material was rinsed 3 times with D<sub>2</sub>O and subsequently dried at 363 K under vacuum. Approximately 30 mg of dried D-exchanged MCF (f-1) sample was packed in a 5 mm high-pressure NMR cell built according to the design by Houllberghs *et al.*<sup>70</sup> before adding 60  $\mu\text{L}$  of a 5.56 mol% THF-D<sub>2</sub>O mixture to the system. The tube was pressurized to 7 MPa

with H<sub>2</sub> gas before transferring to a pre-cooled (265 K) NMR probe head and allowing the system to equilibrate for 10 h. Following shimming, 48 transients were recorded for each <sup>1</sup>H NMR spectrum using a 30° pulse with 18 kHz RF strength and a repetition delay of 10 s. Chemical shift referencing was carried out with respect to TMS, using ethylbenzene (10% in chloroform-d) as a secondary reference with  $\delta$  (<sup>1</sup>H) = 1.22 ppm. Spectral decomposition was performed using dmFit software using Gaussian lineshapes.<sup>71</sup>

### 3. H<sub>2</sub>-THF binary hydrate kinetics

The kinetic regime of post-induction time H<sub>2</sub> gas uptake was analyzed using the widely adopted Johnson-Mehl-Avrami-Kolmogorow (JMAK) model,<sup>72-80</sup> as shown in eqn (10). This model was established to describe the kinetics of phase change under isothermal/isotropic conditions with a linear growth rate and random nucleation.

$$\alpha_{\text{wH}} = 1 - \exp(-k(t)^n) \quad (10)$$

where  $\alpha_{\text{wH}}$  is water-to-hydrate conversion at time  $t$ ,  $k$  is the crystallization rate constant and  $n$  is the Avrami exponent.

However, in a later phase of hydrate growth, the kinetics of hydrate crystallization is often impeded due to the poor diffusion of guest gas (H<sub>2</sub>) or H<sub>2</sub>O through the hydrate layer.<sup>81,82</sup> Considering this, the kinetics of the experimental data were also analyzed by adopting Hay's two-stage crystallization kinetic model,<sup>83</sup> as given in eqn (11), which can represent both the initial hydrate growth based on the JMAK model (first term in eqn (11)) and the hydrate growth owing to diffusion (second term in eqn (11)),

$$\alpha_{\text{wH}} = \alpha_{\text{P}}(1 - \exp(-k_{\text{P}}t^n))(1 + (k_{\text{S}}t^{0.5})) \quad (11)$$

where  $\alpha_{\text{wH}}$  is the water-to-hydrate conversion at time  $t$  and  $\alpha_{\text{P}}$  is the water-to-hydrate conversion at the end of the reaction-controlled primary crystallization process.  $k_{\text{P}}$  and  $k_{\text{S}}$  are the rate constants for reaction-controlled primary and diffusion-controlled secondary crystallization growth, respectively.  $n$  is the Avrami exponent. Additional details about the analysis are provided in the Results and discussion section.

The efficacy of the kinetic models in predicting water-to-hydrate conversion is evaluated using average absolute deviation (AAD) as shown in eqn (12),

$$\text{AAD} = \frac{1}{N} \sum_{i=1}^N |E_i^\alpha - P_i^\alpha| \quad (12)$$

$N$  is the number of datasets and  $E_i^\alpha$  and  $P_i^\alpha$  are experimental and predicted water-to-hydrate conversion respectively.

## 4. Results and discussion

#### 4.1. Host material characterization

N<sub>2</sub>-sorption (Fig. 2a) proved the successful formation of the MCF (n-f) material. The presence of the swelling agent pushed for the formation of considerably larger pores as compared to



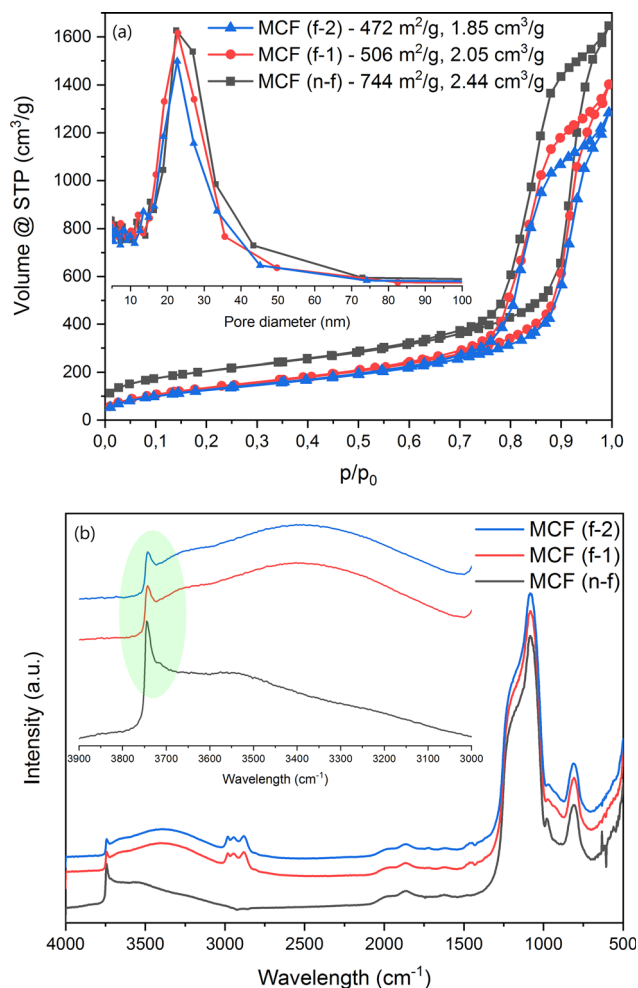


Fig. 2 (a: top)  $N_2$  sorption and (b: bottom) *in situ* DRIFT analyses of the materials.

a standard SBA-15 material.<sup>84</sup> The maximum size of the ultra-big mesopores determined by the BJH method is approx. 22 nm, while the BET surface area and total pore volume reach  $744 \text{ m}^2 \text{ g}^{-1}$  and  $2.44 \text{ cm}^3 \text{ g}^{-1}$ , respectively. Following the procedure of post-synthesis modification, a decrease in both surface area and total pore volume is observed (Fig. 2a), serving as an initial confirmation of the successful grafting process. The most important band observed during the *in situ* DRIFT spectral analysis refers to the presence of silanol groups on the surface, localized at around  $3745 \text{ cm}^{-1}$  (Fig. 2b). The decreased intensity of this band after the grafting procedure suggests the chemical attachment of the modifier molecule. In other words, fewer Si-OH groups are present on the surface of the material after the modification procedure takes place, which directly implies that these groups are involved in the surface reactions. Next, the features belonging to the silica material are present in all the samples, while the bands at around 2981, 2944, 2881 and  $1456 \text{ cm}^{-1}$  are related to the  $\text{CH}_x$  groups of the modifier.<sup>62,85</sup>

Thermogravimetric analysis (Fig. S1†) showed a consistent mass loss above 423 K for the modified MCF materials (12–13%). It is clear that increasing the amount of the modifier did not achieve a considerably higher modification degree. This

might be connected to the surface becoming saturated with the modifier molecule, leading to steric interactions that restrict the chemical grafting process. The carbon content exhibits variation between the two modified samples, resulting in an approximately 7% increase in the density of the groups on the surface of MCF (f-2), totaling  $0.75 \text{ g nm}^{-2}$  compared to MCF (f-1). To conclude here, all the results presented above suggest a successful modification of the MCF material with the THF-ending molecule.

#### 4.2. Characterization of the clathrate hydrate phase

The identity of clathrate hydrate was confirmed to be sII clathrate hydrate using XRD analysis of the product obtained with MCF (f-1) as a porous host. Next to the sII clathrate hydrate also hexagonal ice was found (Fig. S2†). At present it cannot be distinguished if the impurity was formed in the reactor or by condensation and subsequent freezing of moisture from the air during the XRD analysis.

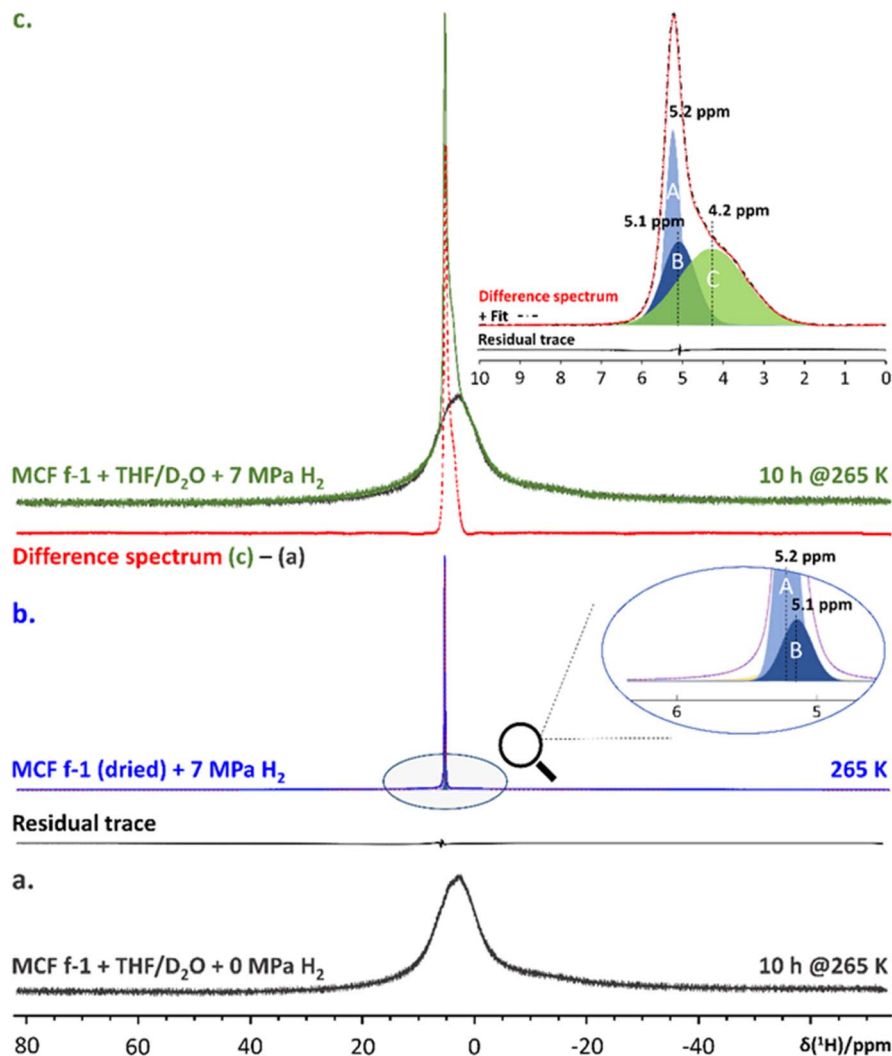
Enclathration of  $\text{H}_2$  in  $5^{12}$  cages of the sII hydrate structure was demonstrated using *in situ* high-pressure  $^1\text{H}$  NMR spectroscopy (Fig. 3). Subtracting the  $^1\text{H}$  NMR spectrum of pure THF sII clathrate hydrate confined in MCF (f-1) (Fig. 3a) from the spectrum of the binary  $\text{H}_2$ -THF clathrate hydrate formed at the same temperature in the presence of 7 MPa of  $\text{H}_2$  pressure (Fig. 3c) yielded a difference spectrum containing the resonance of gaseous  $\text{H}_2$  and  $\text{H}_2$  occupying the small cage of the clathrate hydrate (Fig. 3c, inset). To identify the signature of gaseous  $\text{H}_2$  and enable assignment, the  $^1\text{H}$  NMR spectrum of a dry MCF (f-1) material pressurized with 7 MPa  $\text{H}_2$  gas was measured (Fig. 3b). Decomposition of this spectrum revealed two resonances at 5.1 and 5.2 ppm respectively, which are associated with gaseous  $\text{H}_2$  in the presence of the host material. Decomposition of the difference spectrum between confined binary  $\text{H}_2$ -THF clathrate hydrate and confined pure sII THF clathrate hydrate revealed the presence of 3 spectral components (Fig. 3c, inset), two of which (A and B) were also present in the spectrum of the dry host material pressurized with  $\text{H}_2$  gas. The third resonance (C) at 4.2 ppm can therefore unequivocally be assigned to  $\text{H}_2$  molecules residing in the  $5^{12}$  cages of the sII hydrate structure. A similar resonance was reported by Lee *et al.*<sup>21</sup> in their pioneering work on binary sII  $\text{H}_2$ -THF clathrate hydrate.

#### 4.3. Effect of functionalized porous materials on $\text{H}_2$ storage

The storage capacities of  $\text{H}_2$  in the binary  $\text{H}_2$ -THF clathrate hydrate were investigated using an unstirred reactor filled with  $\approx 0.5 \text{ g}$  of porous material and 5.56 mole% of aqueous THF solution. All the experiments were conducted at 265 K with an initial  $\text{H}_2$  gas pressure of 7 MPa and all systems were saturated with a stoichiometric solution (5.56 mol%), corresponding to 100% of pore volume saturation of each material. The host material consisting of hydrophilic silica-based materials (MCF) and the same material grafted with THF-like functional groups (hydrophobic) were used in the experiments to evaluate the impact of the grafting on hydrate formation rates and  $\text{H}_2$  storage capacities. The primary distinctions between materials







**Fig. 3** (a).  $^1\text{H}$  NMR spectrum of MCF (f-1) + 5.56 mole% THF/ $\text{D}_2\text{O}$  + 0 MPa  $\text{H}_2$  measured after equilibration for 10 hours at 265 K (black trace). (b).  $^1\text{H}$  NMR spectrum of  $\text{D}_2\text{O}$ -exchanged and subsequently dried MCF (f-1) pressurized with 7 MPa  $\text{H}_2$  recorded at 265 K (blue trace). (Inset): zoom-in highlighting the most relevant spectral components, *i.e.*, 'A' and 'B', and their corresponding chemical shifts. The added residual trace reflects the accuracy of the modelled fit (dotted red trace). (c).  $^1\text{H}$  NMR spectrum of MCF (f-1) + 5.56 mole% THF/ $\text{D}_2\text{O}$  + 7 MPa  $\text{H}_2$  after 10 hours at 265 K (green trace). The red trace below shows the  $^1\text{H}$  NMR spectrum obtained from computing the difference between spectra (c) and (a). (Inset): spectral decomposition of the resulting difference spectrum. The different components, *i.e.*, A, B and C, are color coded in accordance with previous decompositions. The residual trace reflects the accuracy of the modelled fit (dashed/dotted black trace).

are their pore volumes and the number of carbons per  $\text{nm}^2$  as a result of functionalization. Table 2 summarizes the list of experimental conditions,  $\text{H}_2$  storage capacities and other analyzed outcomes from this work. Note that porous media can influence the phase equilibrium of hydrate formation and thus can serve as thermodynamic inhibitors, shifting the phase boundaries to significantly higher pressures and lower temperatures compared to bulk systems. Such effects are expected to become increasingly important as the pore size decreases and the hydrophilicity increases.<sup>49,86,87</sup> To assess the occurrence of such effects in our study, a comparative phase equilibrium analysis of binary  $\text{H}_2$ -THF clathrate hydrates in the MCF (f-1) material and in the bulk system was performed. As can be seen from Fig. S3,<sup>†</sup> the presence of a porous host indeed induces a small shift in the phase diagram (up to 4 K at the

lowest experimental temperature), but overall its effect is limited given the large mesopore size of 25 nm and the more hydrophobic nature of the grafted tetrahydrofurfuryloxypropyl triethoxysilane functional groups. This small thermodynamic penalty does however not outweigh the observed kinetic promotion, where dispersion of the aqueous phase throughout the modified porous matrix coupled with favourable pore wall-water interactions enables larger amounts of clathrate hydrate to be formed under non-stirred conditions in hours rather than days as compared to non-confined, bulk systems under similar experimental conditions.

Fig. 4 shows the amount of  $\text{H}_2$  enclathrated during binary  $\text{H}_2$ -THF hydrate formation in MCF (f-1 and f-2) hydrophobic and MCF (n-f) hydrophilic silica based porous materials. Time zero in this figure corresponds to the commencement of

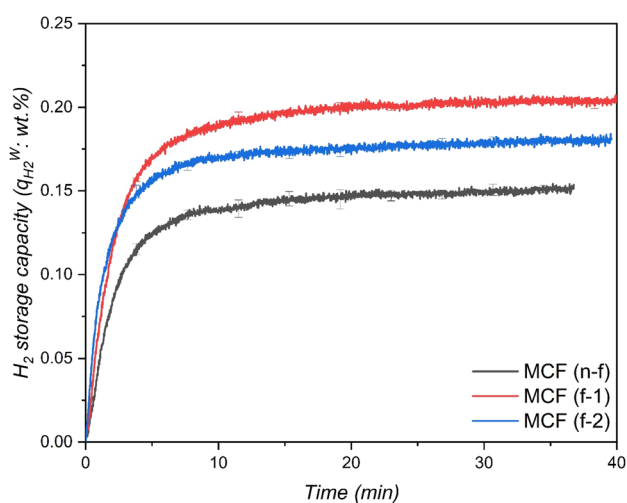




**Table 2** Summary of experimental observation for H<sub>2</sub>/THF(5.56 mol%)/H<sub>2</sub>O hydrate in THF-like functionalized and non-functionalized silica based porous materials under different thermodynamic conditions<sup>a</sup>

| Porous system | <i>P</i> (MPa) | <i>T</i> (K) | NG <sub>r</sub> (mmoles of H <sub>2</sub> per mole of H <sub>2</sub> O) | WtH (%) | <i>q</i> <sub>H<sub>2</sub></sub> <sup>W</sup> (wt%) | <i>q</i> <sub>H<sub>2</sub></sub> <sup>A</sup> (wt%) | <i>q</i> <sub>H<sub>2</sub></sub> <sup>T</sup> (wt%) | Volumetric H <sub>2</sub> storage (v/v) |
|---------------|----------------|--------------|---|---------|--|--|--|---|
| MCF(n-f)      | 7              | 265          | 13.53   | 11.50   | 0.15   | 0.30   | 0.10   | 13.58                                   |
| MCF(f-2)      | 7              | 265          | 16.15   | 13.73   | 0.18   | 0.27   | 0.11   | 16.21                                   |
| MCF(f-1)      | 7              | 265          | 18  | 15.31   | 0.21   | 0.34   | 0.13   | 18.06                                   |
| MCF(f-1)      | 7              | 268          | 14.06   | 11.96   | 0.16   | 0.27   | 0.1  | 14.12                                   |
| MCF(f-1)      | 7              | 262          | 46.77   | 39.78   | 0.52   | 0.88   | 0.33   | 46.95                                   |

<sup>a</sup>  $q_{H_2}^W$  (wt%) =  $\frac{m_{H_2}}{(m_{H_2O} + m_{H_2})} \times 100$ ,  $q_{H_2}^A$  (wt%) =  $\frac{m_{H_2}}{(m_{solid} + m_{H_2})} \times 100$ ,  $q_{H_2}^T$  (wt%) =  $\frac{m_{H_2}}{m_{tot}} \times 100$ ,  $m_{H_2}$  = mass of H<sub>2</sub>,  $m_{H_2O}$  = mass of H<sub>2</sub>O,  $m_{solid}$  = mass of solid, and  $m_{total}$  = mass of H<sub>2</sub>O + mass of solid + mass of H<sub>2</sub>.



**Fig. 4** H<sub>2</sub> storage capacity in THF-like functionalized MCF (f-1 and f-2) hydrophobic and non-functionalized MCF (n-f) hydrophilic porous materials at 265 K with an initial pressure of 7 MPa.

hydrate formation observed from the first temperature spike due to the exothermic nature of the process and all three gas uptake curves also demonstrate the consistency of hydrate formation with a minor standard deviation. As shown in Fig. 4, all three materials exhibit rapid hydrate formation before tapering off to a steady state, and the characteristic time  $t_{90}$ , defined as the time required for the system to reach 90% of the maximum obtained gas uptake, was less than 7.5 min for all the systems, implying that this parameter could be a critical criterion in evaluating the kinetic performance of gas uptake as well as hydrate formation. It can also be seen from the figure that the THF-like functionalized materials MCF (f-1 and f-2) showed an excellent promoting effect on H<sub>2</sub> storage compared to non-functionalized material MCF (n-f) despite having a pore volume  $\sim$ 16% and 24% lower than MCF (n-f), respectively. For instance, MCF (f-1), at 265 K, attained a maximum H<sub>2</sub> storage capacity ( $q_{H_2}^W$ ) of 0.21 wt%, which corresponds to  $\sim$ 15.31% of water-to-hydrate conversion and 18 mmol H<sub>2</sub> per mol H<sub>2</sub>O, while MCF (n-f) attained only 0.15 wt% and  $\sim$ 11.50% of water-to-hydrate conversion which is 28.6% and 24.8% less than MCF (f-1), respectively. It is also evident from the gas uptake curves that there also exists an optimal amount of tuning THF-like

moieties for enhancing the H<sub>2</sub> storage, where lowering the number of carbons per nm<sup>2</sup> showed a better gas uptake compared to MCF (f-2) having  $\sim$ 7% higher carbons per nm<sup>2</sup> (which is relatively more hydrophobic than MCF (f-1)) and MCF (n-f) which is a completely hydrophilic material. It is also important to mention that in order to corroborate the suggestions from Lee *et al.*,<sup>21</sup> THF-like functionalized and non-functionalized materials were also tested with 0.1 and 0.3 mol% THF solution; however, no clathrate formation was observed at 265 K for a period of 6 h. The induced hydrophobicity generated by the organic molecules grafted on the surface of the MCF directly affects the interaction of the material with water. In this regard, as already proved before, the organic groups are not allowing the water to interact very strongly with the surface of the SiO<sub>2</sub> material and provide a favorable environment for stabilizing clathrate cages and promoting the encapsulation of hydrogen molecules within those cages.<sup>54,57</sup> On top of this, one can assume that the enhanced mobility induced by the ether (containing 5 atoms) linker may allow the THF-ending group to have an influence on the water structure disruption, lowering nucleation barrier.<sup>88</sup>

#### 4.4. Effect of temperature on H<sub>2</sub> storage

The material that demonstrated higher H<sub>2</sub> uptake at 265 K was further investigated at two different temperatures to determine its H<sub>2</sub> storage capacities. Typically, lower temperatures for hydrate formation demonstrate higher driving force at constant pressure indicating improved gas enclathration. However, few studies<sup>89,90</sup> reported that the gas storage capacities increased with an increase in temperature, implying that lowering the driving force enhances gas storage capacity. In this perspective, two different temperatures, one lower than 265 K and one higher than 265 K were chosen to investigate the effect of the hydrate formation rate and H<sub>2</sub> enclathration. The corresponding experiments were performed at 262 K and 268 K with an initial H<sub>2</sub> gas pressure of 7 MPa and both the systems were saturated with 5.56 mol% of THF solution, which corresponded to 100% of pore-volume saturation. Fig. 5 exhibits H<sub>2</sub> storage capacity of the systems at 268 K, 265 K and 262 K. As can be seen, the temperature has a significant impact on the hydrate formation rate and H<sub>2</sub> storage capacities, where a decrease in temperature from 268 K to 262 K resulted in a substantial



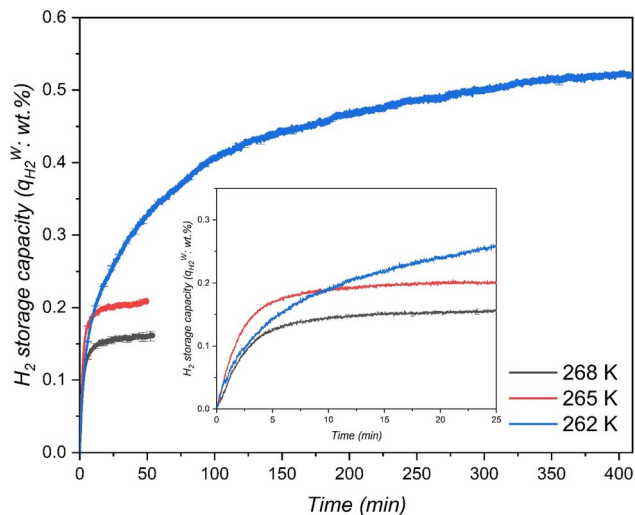


Fig. 5 H<sub>2</sub> storage capacity in the THF-like functionalized MCF (f-1) porous material at three different temperatures with an initial pressure of 7 MPa.

increase in H<sub>2</sub> enclathration, attaining a maximum storage capacity of ~0.52 wt% at the lowest temperature. These findings are consistent with Tian and Zhang simulation work,<sup>91</sup> which

indicated that the maximal H<sub>2</sub> storage capacity in a binary H<sub>2</sub>-THF hydrate can be obtained at 260 K at constant pressure. Similarly, results from Liu *et al.*<sup>92</sup> also support our findings by demonstrating that THF hydrate formation diminishes with increasing temperature, which consequently affects H<sub>2</sub> enclathration in the small cages (5<sup>12</sup>).

Meanwhile, the material MCF (f-1) also showed higher H<sub>2</sub> storage capacity than H<sub>2</sub>/THF hydrate systems and relatively similar storage capacities compared to H<sub>2</sub>/1,3-dioxolane systems using stirring reactors (Table 3). Nevertheless, it is worth mentioning that the pressures used in these stirring systems are at least 75% higher than the pressures used in this work. This indicates that the surface grafted THF-like functionalized porous materials show better mass transfer performance for a static/unstirred H<sub>2</sub> storage system compared to stirring systems (which are energy intensive). Nevertheless, at the end of hydrate growth reaching a steady state the total H<sub>2</sub> storage capacity at 262 K was 2.47 and 3.25 times higher than that in the case of 265 K and 268 K respectively, which corresponds to 39.78% water-to-hydrate conversion and 46.77 mmol H<sub>2</sub> per mol H<sub>2</sub>O. Fig. 6 also displays rapid hydrate growth in the first 2 min at all the temperatures, where the initial rate of hydrate formation increased with decreasing temperature from

Table 3 H<sub>2</sub> storage capacity in all hydrates below 15 MPa using promoters (stoichiometric conc.)

| System                      | P (MPa) | T (K)  | H <sub>2</sub> storage capacity (wt%) | Occupancy of 5 <sup>12</sup> cages <sup>a</sup> (%) | Ref. |
|-----------------------------|---------|--------|---------------------------------------|---|------|
| This work                   | 7       | 268    | 0.16                                  | 6.08  | —    |
|                             | 7       | 265    | 0.21                                  | 7.97  |      |
|                             | 7       | 262    | 0.52                                  | 19.84   |      |
| Powdered THF hydrate        | 6.7     | 270    | 0.36                                  | 13.63   | 27   |
|                             | 12.2    |        | 0.46                                  | 17.70   |      |
|                             | 6.2     |        | 0.38                                  | 14.56   |      |
|                             | 12.1    |        | 0.55                                  | 21.13   |      |
|                             | 12.4    |        | 0.32                                  | 12.28   |      |
| Powdered THF hydrates       | 10.7    | 277.15 | 0.19                                  | 7.23  | 38   |
|                             | 11.4    |        | 0.26                                  | 9.90  |      |
| Powdered THF hydrates       | 6.5     | 269.5  | 0.23                                  | 8.75  | 99   |
|                             | 6.5     | 269.5  | 0.23                                  | 8.75  |      |
|                             | 6.5     | 269.5  | 0.20                                  | 7.61  |      |
|                             | 8.4     | 269.5  | 0.25                                  | 9.52  |      |
|                             | 6.5     | 269.5  | 0.23                                  | 8.75  |      |
|                             | 3.6     | 269.5  | 0.19                                  | 7.23  |      |
|                             | 6.5     | 266.7  | 0.26                                  | 9.90  |      |
|                             | 6.5     | 269.5  | 0.23                                  | 8.75  |      |
|                             | 6.5     | 275.1  | 0.21                                  | 7.99  |      |
|                             | 6.5     | 278.2  | 0.14                                  | 5.25  |      |
| THF-bulk solution/stirring  | 7.0     | 278.2  | 0.14                                  | 5.25  | 67   |
|                             | 5.0     | 278.2  | 0.12                                  | 4.40  |      |
|                             | 5.0     | 278.2  | 0.13                                  | 4.76  |      |
|                             | 5.0     | 278.2  | 0.10                                  | 3.92  |      |
| Powdered THF hydrate        | 5.0     | 265.1  | 0.18                                  | 6.85  | 100  |
|                             | 5.0     | 269    | 0.16                                  | 6.10  |      |
|                             | 5.0     | 273.2  | 0.15                                  | 5.71  |      |
| Powdered DXN hydrate        | 12.0    | 233    | 0.4                                   | 15.25   | 101  |
| THF-bulk solution/stirring  | 13      | 279.2  | 0.183                                 | 6.96  | 102  |
| DIOX-bulk solution/stirring | 12.3    | 271.15 | 0.216                                 | 8.22  | 20   |
| THF in porous media         | 11.6    | 270    | 0.4                                   | 15.25   | 41   |
| ECP-bulk solution           | 12.2    | 273.25 | 0.310                                 | 11.81   | 37   |

<sup>a</sup> Estimated based on two H<sub>2</sub> molecules in a single small cage.



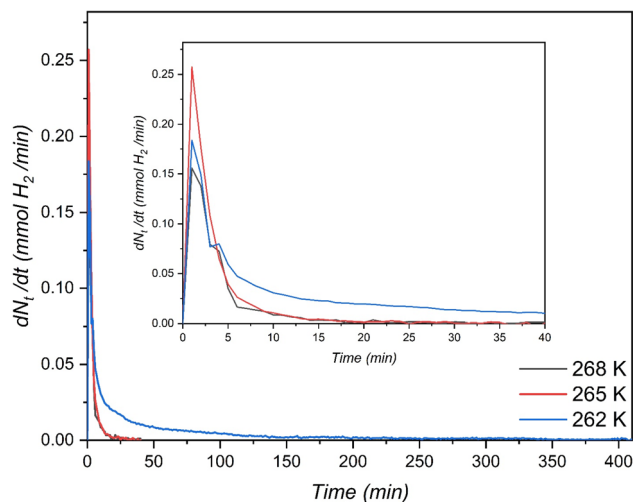


Fig. 6 Rate of H<sub>2</sub>-THF binary hydrate formation in the THF-like functionalized (f-1) porous material at three different temperatures with an initial pressure of 7 MPa.

268 K to 265 K and then dropped down quickly to near-zero after 30 min. However, lowering the temperature to 262 K showed a slight decrease in the initial rate of hydrate formation (which is evident from Fig. 5 (inset)) compared to 265 K, followed by a very gradual reduction, and reaching near-zero at about 350 min, indicating diffusion-controlled hydrate growth. Further explanation of hydrate growth kinetics is presented in the next section.

It could be intriguing to compare the findings of various research groups endeavoring to enhance H<sub>2</sub> storage in clathrate hydrates. Nevertheless, a direct comparison of the absolute values pertaining to the hydrate growth rate, maximum gas stored capacity, and other parameters obtained from different research laboratories might not be a reliable way to ascertain which one leapfrogged the other as the experimental procedures, reactor setups, and methodologies employed by different groups could significantly influence the results, which could also be a major contributing factor to the observed differences in kinetics of hydrate formation, possibly involving mass transfer limitations. However, it is exemplary to make a comparison between the studies focusing on H<sub>2</sub> storage capacity in the binary H<sub>2</sub>-THF clathrate hydrate, which is presented in Table 3.

Scientifically, it is well-established that under extremely high pressures, H<sub>2</sub> can form sII hydrate, reaching 5.6 wt%, with both small (5<sup>12</sup>) and large cages (5<sup>12</sup>6<sup>4</sup>) accommodating two and five H<sub>2</sub> molecules, respectively.<sup>15,93</sup> However, when THF (a thermodynamic promoter) is introduced in stoichiometric concentrations, the H<sub>2</sub> molecules can only occupy small cages, while large cages are left for THF. Consequently, the overall storage capacity decreases to 1.3 wt% and 2.5 wt% when one and two H<sub>2</sub> molecules occupy a small cage, respectively. From the data presented in Table 3, it is evident that in a H<sub>2</sub>-promoter (stoichiometric conc.) H<sub>2</sub>O system under various thermodynamic conditions, the maximum H<sub>2</sub> storage capacity falls below 1.3 wt%. This indicates that either the fractional H<sub>2</sub> occupancy

in the small cages is less than 1 or not all small (5<sup>12</sup>) cages are filled under those specific conditions. However, this limitation can be overcome by increasing the pressure of the system, which leads to an enhancement in H<sub>2</sub> storage capacity. Furthermore, Table 3 demonstrates that by employing solid-state tuning of the material, it is possible to improve the H<sub>2</sub> storage capacity significantly even at relatively low pressures when compared to values reported in the literature. While powder-THF hydrate exhibits better H<sub>2</sub> enclathration, it is essential to note that the fine THF hydrate particles revert to a liquid phase upon melting. This characteristic makes them unsuitable for continuous cycles of H<sub>2</sub> storage and release, thereby limiting their practical applicability in certain situations.

#### 4.5. Kinetic analysis

In this study, the formation kinetics of hydrates at different temperatures were investigated using two distinct kinetic models, as mentioned earlier. The predicted kinetic curves of hydrate formation from the JMAK model<sup>73</sup> (eqn (10)) are depicted in Fig. S4,† and the corresponding values of the rate constant (*k*) and the Avrami kinetic exponent (*n*) were determined and are presented in Table S1.† The Avrami kinetic exponent (*n*) is commonly used to interpret the growth geometry and the degree of crystallization during hydrate formation in a porous medium.<sup>94</sup> The value of the Avrami exponent (*n*) can provide insights into the growth dimension of hydrate crystals. A value of *n* = 3 indicates instantaneous three-dimensional growth from a spherical nucleus, *n* = 2 suggests instantaneous two-dimensional growth, and *n* = 1 signifies one-dimensional growth. However, interestingly, the regressed exponent values (*n*) obtained for the entire growth period, as shown in Table S1,† are consistently less than 1 for all conditions. This indicates that the hydrate crystals experienced instantaneous one-dimensional growth, followed by a decrease in hydrate nucleation and growth rates. This decrease in growth rates could be attributed to the presence of mass transfer resistance in the system. Similar low Avrami exponent values for hydrate growth were also reported by other researchers.<sup>77,95,96</sup> Conclusively, the predictive power of the JMAK model revealed limitations in evaluating the hydrate growth at both the beginning or later stages of the growth kinetics.

The limitations of single-step kinetic models have led to a preference for using an integrated multistep model, which offers a more accurate representation of hydrate kinetics. To achieve this, the model proposed by Hay<sup>83</sup> has been adopted and adapted for evaluating the hydrate growth kinetics at both the reaction-controlled stage (primary growth) and the diffusion-controlled stage (secondary growth). Hay's model, in a more detailed version, was previously described in their earlier work on crystallization kinetics.<sup>97,98</sup> This integrated approach allows for a more comprehensive understanding of the hydrate formation process by considering the distinct contributions of both primary and secondary growth stages. By incorporating these stages into the model, a more accurate depiction of the overall hydrate kinetics can be obtained,



improving our insights into the complex nature of hydrate formation. As indicated in eqn (11), the total water-to-hydrate conversion ( $\alpha_{\text{WH}}$ ) can be categorized into two components: the water-to-hydrate conversion in the primary growth stage and the secondary growth stage, as shown in eqn (13).

$$\alpha_{\text{WH}} = \alpha_{\text{WH,P}} + \alpha_{\text{WH,S}} \quad (13)$$

Here,  $\alpha_{\text{WH,P}}$ , the primary crystal growth stage, attributed to the rapid nucleation and hydrate growth was analyzed using the JMAK model (eqn (14)), assuming that the primary growth stage ends before the onset of the diffusion-controlled regime *i.e.*, the secondary growth stage ( $\alpha_{\text{P}}$ ).

$$\alpha_{\text{WH}} = \alpha_{\text{P}}(1 - \exp(-k_{\text{p}}t^n)) \quad (14)$$

where  $k_{\text{p}}$  is rate constant for primary crystallization growth and  $n$  is the Avrami exponent. Eqn (14) can also be rewritten by applying a double logarithm as shown in eqn (15).

$$\ln(-\ln(1 - \alpha_{\text{WH,P}}/\alpha_{\text{P}})) = n \ln(t) + \ln(k_{\text{p}}) \quad (15)$$

In this analysis, exponent  $n$  was set to 1 assuming one-dimensional growth and the value of the adjustable parameter,  $\alpha_{\text{P}}$ , was chosen from the best linear fit to eqn (15) based on the coefficient of determination ( $R^2$ ) (for MCF (f-1) at 265 K: Fig. S5†). Finally, the corresponding value of  $\ln(k_{\text{p}})$  was obtained from the intercept. The water-to-hydrate conversion in the secondary hydrate growth stage is defined as shown in eqn (16).

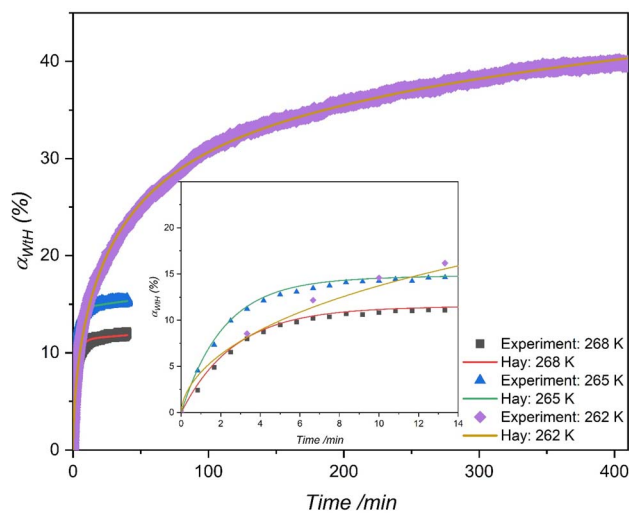
$$\alpha_{\text{WH,S}} = \alpha_{\text{WH,P}}(k_{\text{s}}t^{0.5}) \quad (16)$$

By substituting eqn (16) and eqn (14) into (eqn (13)), the complete kinetic model for the process is derived, as described in (eqn (11)). The kinetic rate constant governing the secondary growth or crystallization stage was determined by plotting  $\left[\left(\frac{\alpha_{\text{WH}} - \alpha_{\text{P}}}{\alpha_{\text{P}}}\right)\right]$  against  $t^{0.5}$  and calculating the slope of the resulting linear fit. These rate constants and  $\alpha_{\text{P}}$ , obtained from this study, are summarized in Table 4 and the predicted kinetic curves of hydrate formation from the Hay model are depicted in Fig. 7.

Table 4 reveals that the secondary kinetic rate constant ( $k_{\text{s}}$ ) decreases to a lower value after the initial growth stage, regardless of the driving force applied. This reduction can be attributed to slower conversion rates due to mass transfer resistance within these porous media, particularly upon reaching a certain water-to-hydrate conversion level.

**Table 4** Regressed values of rate constants ( $k_{\text{p}}$  and  $k_{\text{s}}$ ), from the Hay<sup>83</sup> model

| System    | $T$ (K) | Multistep kinetic model              |                                      | AAD  |
|-----------|---------|--------------------------------------|--------------------------------------|------|
|           |         | $k_{\text{p}}$ ( $\text{min}^{-1}$ ) | $k_{\text{s}}$ ( $\text{min}^{-1}$ ) |      |
| MCF (f-1) | 268     | 0.38                                 | 0.012                                | 0.16 |
|           | 265     | 0.48                                 | 0.015                                | 0.18 |
|           | 262     | 0.17                                 | 0.022                                | 0.23 |



**Fig. 7** Comparing the multistep kinetic model (Hay)<sup>83</sup> to experimental data for water-to-hydrate conversion (%) in the THF-like functionalized (f-1) porous material at three different temperatures with an initial pressure of 7 MPa.

Furthermore, the multistage kinetic model consistently demonstrated superior predictive capabilities for hydrate kinetics compared to the JMAK model, as evident from the AAD values. Moreover, the multistage model allows for an insightful examination of the contributions of primary and secondary-stage hydrate growth to the overall water-to-hydrate conversion. For instance, at 262 K, as shown in Fig. S6(c)†, the secondary stage contributes to around 30% of the overall water-to-hydrate conversion. This suggests that the growth of hydrates, equally driven by primary and diffusion-controlled stages, significantly influenced the slow rate of hydrate formation from inception, leading to relatively low-rate constants at very low temperatures. These findings highlight the significance of the multistage kinetic model in understanding hydrate formation dynamics.

#### 4.6. Clathrate hydrate formation pathway

The kinetic model conclusively indicates that the formation pathway for  $\text{H}_2$ -THF hydrate in porous media involves the concurrent occurrence of primary hydrate growth and diffusion-controlled secondary growth. Unlike sequential pathways where a separate THF hydrate forms first followed by  $\text{H}_2$  enclathration, primary growth here involves the direct formation of  $\text{H}_2$ -THF hydrate (as can be seen from Fig. 8, where a single sharp exothermic peak representing hydrate nucleation coincides with a significant pressure drop, signifying simultaneous hydrate formation and  $\text{H}_2$  enclathration occurring at the same time). This initial stage is characterized by rapid hydrate growth within the pore space, where the growing hydrate crystal makes it progressively more challenging for  $\text{H}_2$  molecules to reach the growing crystal front creating a diffusion limitation. Despite the diffusion limitations, the inherent high diffusivity of  $\text{H}_2$  within clathrate hydrates allows for continued crystal growth until steric hindrance (impingement) occurs. This initial burst of





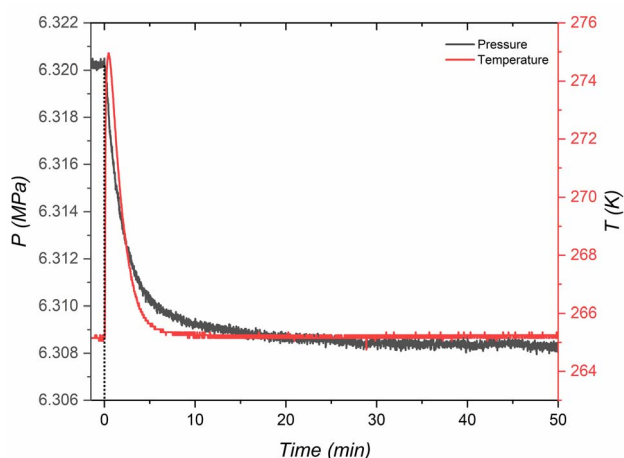


Fig. 8 A single sharp exothermic peak representing hydrate nucleation coinciding with a significant pressure drop inferring simultaneous THF hydrate formation and H<sub>2</sub> enclathration for MCF (f-1) at 265 K.

growth (as observed from relatively high  $k_p$ ) corresponds to primary crystallization, while the interplay between continued growth and the increasing influence of diffusion limitations ( $k_s < k_p$ ) reflects the concept of secondary growth.

## 5. Conclusion

This study introduces a new strategy to expedite H<sub>2</sub> storage *via* clathrate hydrates by solid-state tuning of silica-based porous materials (MCF) by grafting promoter-like molecules (THF), leading to a notable enhancement in H<sub>2</sub> enclathration kinetics and storage capacities within a binary H<sub>2</sub>-THF hydrate, as compared to conventional bulk stirring systems. The performance of the materials was evaluated under the conditions of 100% pore volume saturation with a stoichiometric concentration of THF solution (5.56 mol%), at 7 MPa in a range of different temperatures (262 K, 265 K, and 268 K) using a volumetric approach. The findings revealed that the modified MFC materials (MCF (f-1) and (f-2)) can enhance the overall H<sub>2</sub> storage capacity compared to the non-modified material (MCF (n-f)). This enhancement could potentially be attributed to the induced hydrophobicity achieved by grafting organic molecules onto the surface of MCF (n-f), which directly influenced the interaction of the material with H<sub>2</sub>O, creating a conducive milieu for stabilizing clathrate cages and promoting the encapsulation of H<sub>2</sub> within these cages. Additionally, the mobility engendered by the ether linker is hypothesized to enable the THF-ending group to function as a promoter, perturbing the water structure and lowering the nucleation barrier. MCF (f-1) and MCF (f-2) achieved a maximum H<sub>2</sub> gas uptake of 0.21 wt% and 0.18 wt%, respectively, as opposed to MCF (n-f) which reached 0.15 wt% at 265 K. It is also evident from the gas uptake curves that there also exists an optimal amount of tuning the material that enhances the H<sub>2</sub> storage, where a lower number of carbons per nm<sup>2</sup> showed a better gas uptake. Furthermore, the results also show that the H<sub>2</sub> storage capacity

increases with an increase in driving force (*i.e.*, a decrease in temperature), where a maximum storage capacity of 0.52 wt% corresponding to 46.77 mmols of H<sub>2</sub> per mole of H<sub>2</sub>O and 39.78 water-to-hydrate conversions was achieved at 262 K in MCF (f-1). An intriguing aspect of these results is the substantial H<sub>2</sub> storage capacity observed without necessitating supplementary energy-intensive procedures such as agitation or crystal grinding. This underscores the potential of solid-state tuning of porous materials as promoters for H<sub>2</sub> storage within artificially synthesized hydrates. Additionally, this work also employed two distinct models for kinetic analysis of hydrate formation and growth in MCF (f-1) at all driving forces. Notably, the multistage kinetic model exhibited better predictive capabilities for the experimental data (water-to-hydrate conversion), with a commendably low average absolute deviation (AAD). Conclusively, it is also recommended to conduct a comprehensive molecular-level investigation to glean a more profound comprehension of the solid-state tuning effects on the supporting materials in enhancing H<sub>2</sub> storage capacities. Additionally, these insights can contribute to the refinement and upscaling of clathrate-based H<sub>2</sub> storage processes, thereby paving the way for further technological advancements.

## Conflicts of interest

The authors declare no competing financial interest.

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