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A modeling study of the methane hydrate decomposition in contact with the external surface of zeolite

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Electronic Supplementary Information

SI Characteristics of methane adsorbed in silicalite-1

SI.a Potential and structural models.

The utilized potential models are described in the main article, see DOI:10.1039/b000000x. Zeolite structure was constructed from $1 \times 1 \times 2$ unit cells (u.c.) of the orthorhombic silicalite-1 framework.¹

SI.b Molecular dynamics simulations.

The velocity Verlet integrator with $\Delta t = 0.5$ fs, damped shifted-force Wolf method for electrostatic interactions,^{2,3} damping parameter 0.2 Å⁻¹, interaction cutoff distance of 10 Å, 3D periodic boundary conditions. Simulations at 298 K in an NVT statistical ensemble with the temperature controlled via a chain of Nosé-Hoover thermostats.⁴ Methane loading was varied from 2 to 12 mol./u.c. A typical MD run consisted of a 500 ps equilibration stage followed by an 1 ns production period with saving interval of 0.05 ps. The interaction of methane with the silicalite structure was characterized by the computation of methane adsorption energy and self-diffusion coefficient. The latter was obtained from the mean squared displacement *vs*. time dependence using the Einstein relationship and the coefficient was averaged over *N* runs, where *N* is given by N = 96/Mwith *M* being the methane loading.

SI.c Results.

Adsorption energy. The computed adsorption energy E_a is equal to -21.9 (2.6) kJ/mol and it is an excellent agreement with the value of -21.8 kJ/mol obtained by Nicholas and co-workers.⁵ Fritzsche *et al.*⁶ have reported E_a from -21.6 to -22.6 kJ/mol using the same potential model for the host-guest interactions. The adsorption energy is also in line with the experimental values equal to -18.4 kJ/mol⁷ and -20.9 kJ/mol,⁸ where the experimental energy was computed as $E_a = RT - \Delta H$ with ΔH being the measured isosteric heat of adsorption.

Self-diffusion coefficient. Table S1 reports self-diffusion coefficient D_s of methane in silicalite at different loadings. Computed values of D_s are in an excellent agreement with experimental results obtained by PFG NMR spectroscopy⁹ and with results of previous modeling studies.^{10,11}

	D_s , 10^{-9} m ² s ⁻¹		
Loading (mol./u.c.)	This work	Experiment ^a	Previous simulations
2	12.3 (1.5)	_	$11.1^b, 12.35^c$
4	10.6 (1.2)	13.0	8.5 ^b , 12.14 ^c
8	7.5 (1.0)	9.5	$5.1^b, 9.05^c$
12	5.4 (0.7)	6.0	$2.7^b, 5.25^c$

Table S1: Self-diffusion coefficient of methane in silicalite (values in parentheses are the RMS errors).

^a ref. 9, ^b ref. 10, ^c ref. 11.

SII Characteristics of bulk methane hydrate

SII.a Potential and structural models.

The utilized potential models are described in the main article, see DOI:10.1039/b000000x. Methane hydrate (MH) sI structure was built of $2 \times 2 \times 2$ unit cells with the initial atomic coordinates and lattice parameter taken from ref.12.

SII.b Molecular dynamics simulations.

Simulations in NVT and NPT statistical ensembles using Berendsen barostat¹³ and a chain of Nosé-Hoover thermostats⁴ for the pressure and temperature control, respectively. A typical NPT run lasted 1.2 ns from which the first 200 ps were conducted in the NVT ensemble to equilibrate the system at the desired value of temperature. Then, the simulation continued for 1 ns in the NPT ensemble at the nominal pressure P = 1 bar; characteristics were computed by averaging their instantaneous values over the last 500 ps. If not explicitly stated otherwise, all results were obtained for the temperature of 150 K. See section SI.b for other details.

SII.c Results.

Temperature dependence of lattice parameter. The temperature dependence of the MH lattice parameter a_0 at P = 1 bar is shown in Fig. S1, where it is compared with experimental results^{14,15} and data of previous simulations.^{16,17} It is worthy of note that the difference between the experimental and simulated a_0 values is less than 1.5 % for the system where the lattice constant is determined by non-bonded interactions.



Figure S1: Temperature dependence of the lattice parameter a_0 at P = 1 bar.

Energetic characteristics. The interaction energy of methane with the clathrate water structure is equal to -20.8 (0.2) kJ/mol and -19.5 (0.5) kJ/mol for the molecule in the $5^{12}6^2$ and 5^{12} cages, respectively. A homogeneous melting temperature was obtained to be equal to 370 K. Two phase (hydrate + water) coexistence MD simulations in the NPT ensemble[†] have shown that the exchange of water molecules between the two phases begins at *ca*. 250 K, whereas the methane molecules start to diffuse into the liquid phase at 265 K; the increase in the methane mobility is accompanied by a sharp increase of the system volume. Both the melting temperature estimates are in the range of literature values.^{18–21}

Radial distribution functions. Figure S2 shows pair radial distribution functions for the oxygen-oxygen and carbon-oxygen atom pairs. The number of oxygen atoms around the carbon atom obtained from the running coordination number is equal to 20 and 24 for methane in the small and large clathrate cages, respectively.

Vibrational spectra. Figure S3 displays the power spectrum of the hydrogen atoms of CH_4 molecules. The vibrational spectrum of H atoms in a "free" methane molecule[‡] is characterized by peaks at 1364 (v_4), 1535 (v_2), 2925 (v_1), and 3093 (v_3) cm⁻¹. A blue frequency shift of the v_1 mode of the CH_4 molecules in the small clathrate cages as compared to the frequency of those in the large cages agrees with the experimental

[†]The simulations were performed for a system of 18 sI MH u.c. and 948 water molecules.

[‡]Computed for a system of one methane molecule in 255 argon atoms at 110 K.

findings²² and results of previous MD simulations.²³ On the other hand, the present model overestimates the absolute value of the frequency shift that may suggest too repulsive interactions between the methane and water molecules in the 5^{12} cages.



Figure S2: Oxygen-oxygen and carbon-oxygen pair radial distribution functions g(r) in MH at 150 K.



Figure S3: Power spectrum of hydrogen atoms of methane molecules in the low- (a), mid- (b), and high-frequency (c) regions at 150 K. Black solid line and red dashed line correspond to the spectra for molecules in the large and small clathrate cages, respectively.

20 0.054 0.048 10 0.042 y-coordinate (A) 0.036 0.030 0 0.024 0.018 -100.012 0.006 -20 0.000 500 1000 1500 2000 2500 3000 3500 4000 Time (ps)

SIII Water density evolution in the methane hydrate-silicalite system at 150 K

Figure S4: Time-dependence of water number density profile (in $Å^{-3}$) between the silicalite surfaces at 150 K. The upper and lower limits of the *y*-axis correspond to mean positions of the upper and lower silicalite surfaces, respectively. Horizontal dashed lines delimit layers used in the structure analysis (see Fig. 1 in the main article).

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