Electronic Supplementary Material (ESI) for Sustainable Energy & Fuels. This journal is © The Royal Society of Chemistry 2020

# Supplementary Information

## Boric acid: the first effective inorganic promoter for methane hydrate

## formation under static conditions

Yanxian Zeng,<sup>a</sup> Xiaochun Niu,<sup>a</sup> Dongjun Lei,<sup>a</sup> Zhengwen Liu,<sup>a</sup> Zhengmei Zhu,<sup>a</sup> and Weixing Wang\*<sup>a</sup>

<sup>a</sup>Key Laboratory of Enhanced Heat Transfer and Energy Conservation of the Ministry of Education, School of Chemistry and Chemical Engineering, South China University of Technology, Guangzhou, Guangdong 510640, China.

\*Correspondence to: <a href="mailto:cewxwang@scut.edu.cn">cewxwang@scut.edu.cn</a>

### Materials

Boric acid (99.99%), sodium iodide (NaI, 99.5%), and sodium dodecyl sulfate (SDS, 97%) were purchased from *Aladdin* Co. Ltd., China. L-leucine (98%) was purchased from Shanghai Bio Science & Technology Co. Ltd., China. Sodium disilicate (Na<sub>2</sub>Si<sub>2</sub>O<sub>5</sub>, 99%) was purchased from Shandong Yousuo Chemical Technology Co., Ltd., China. Methane (99.9%) was purchased from Shengying Gas Co. Ltd., China.

#### Methane hydrates formation in a static reactor

To perform the methane uptake kinetic experiments, sample solution (20.0 g for the sample with an initial pressure of 9.5 MPa, 10.0 g for the sample with an initial pressure of 5.5 MPa) was loaded into a high-pressure stainless-steel vessel with a volume of 82 cm<sup>3</sup> (Kerui Instruments Co., Gongyi, Henan, China). The temperature of the coolant was controlled by using a programmable thermal circulator (DWHW-10, Kerui Instruments Co., Gongyi, Henan, China). The sample temperature in the high-pressure cell was measured using a type K thermocouple (-250 to 400 °C, Tianyi Cekong Co., Henan, China). The methane gas pressure was monitored using a high-accuracy gauge pressure transmitter (0–20 MPa, Tianyi Cekong Co., Henan, China). Both the thermocouple and the transmitter were connected to a digital universal input panel meter (ZNHW, Kerui Instruments Co., Gongyi, Henan, China), to communicate with the computer. Prior to each experiment, the cell was purged with methane three times to remove the air, and then pressurized to the desired pressure (starting pressure was 9.5 MPa unless otherwise specified) at the designated temperature. The temperature (T), pressure (P), and time (t) were automatically interval-logged using SuperCx 3.0 software (Kerui Instruments Co., Gongyi, Henan, China). The apparatus is shown schematically in Fig. S1.

### Calculation of methane uptake kinetics<sup>1, 2</sup>

The methane storage capacity was defined gravimetrically in terms of the mass of absorbed of methane per unit mass of the aqueous solution at 273 K. Capacities were calculated using the pressure change that occurs in the reaction vessel. The free space volume of the vessel was obtained by subtracting the sum volume of methane clathrate hydrate, unreacted water, and the additive. Taking into account non-ideality factors, GASPAK v3.41 software (Horizon Technologies, USA) was employed to calculate the gas enclathration capacity. We assume that the liquid and gas phases inside the vessel were exclusively formed from the solution and the guest gas, respectively, neglecting any dissolution of the guest gas into the liquid phase and any mixing of the water vapor in the gas phase.

#### Raman spectroscopic analysis

Methane hydrate (0.5 wt% boric acid) was stabilized below 180 K using liquid nitrogen prior to venting the excess methane. The recovered methane hydrate sample was kept in liquid nitrogen for subsequent analysis. Raman spectroscopic characterization was carried out on a Horiba Jobin Yvon LabRAM Aramis confocal Raman microscope (Nd-YAG laser with a wavelength of 532 nm). The methane hydrate sample was measured at the atmospheric pressure and the temperature of around 180 K to prevent dissociation.



Fig. S1 Schematic diagram of the experimental apparatus.



**Fig. S2** Methane uptake kinetics for bulk water and boric acid aqueous solutions at 273 K (initial pressure, 9.5 MPa, local enlargement of Fig. 1a).



**Fig. S3** Recyclability of 0.5 wt% boric acid aqueous solution during cooling and heating under methane pressure (temperature ramp:  $4.0 \text{ K h}^{-1}$ ).



**Fig. S4** Methane hydrate (0.5 wt% boric acid) dissociated without foaming upon degassing (left), and methane hydrate (0.2 wt% SDS) was subject to copious and persistent foaming upon degassing (right).



**Fig. S5** Raman spectrum of methane hydrate (0.5 wt% boric acid). Inset: local enlargement of Raman spectrum (2880 to 2950 cm<sup>-1</sup>), Black line: experimental data; Blue lines: Gaussian-fit peaks of 2905 cm<sup>-1</sup> for methane in M-cage (5<sup>12</sup>6<sup>2</sup>), and 2916 cm<sup>-1</sup> for methane in S-cage (5<sup>12</sup>); Red line: cumulative fit peak.



**Fig. S6** Methane uptake kinetics for 0.5 wt% boric acid aqueous solution at 273 K (initial pressure, 5.5 MPa).



Fig. S7 Methane uptake kinetics for 0.5 wt% SDS aqueous solution at 273 K (initial pressure, 5.5 MPa).



Fig. S8 Methane hydrate grew upward on the vessel wall (left: 0.5 wt% boric acid; right: 0.2 wt% SDS).



**Fig. S9** Methane uptake kinetics for the aqueous solutions of boric acid and SDS at 273 K (initial pressure, 9.5 MPa).

- 1 W. Wang, C. L. Bray, D. J. Adams and A. I. Cooper, *J. Am. Chem. Soc.*, 2008, **130**, 11608-11609.
- 2 Y. Liu, B. Chen, Y. Chen, S. Zhang, W. Guo, Y. Cai, B. Tan and W. Wang, *Energy Technol.*, 2015, **3**, 815-819.