Supporting Information

Atomic Hydrogen Production from Semi-Clathrate Hydrates

Dong-Yeun Koh, Hyery Kang, Juwoon Park, Woongchul Shin and Huen Lee*

Department of Chemical and Biomolecular Engineering (BK21 program) and graduated school of EEWS, KAIST, 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Republic of Korea .

Fax: +82-42-350-3910; Tel: +82-42-350-3917;

E-mail: hlee@kaist.ac.kr

Table of Contents

Reference in Fig. S5

Hashimoto, S.; Murayama, S.; Sugahara, T.; Sato, H.; Ohgaki K.; *Chem. Eng. Sci.* **2006**, 61, 7884-7888

Experimental Section

Deionized water with ultrahigh purity was supplied from Merck (Germany) and the TBABh, TBAB, TBAF, TBAOH, THF, Me_4NOH and D_2O were supplied by SIGMA-ALDRIGH Inc. H_2 and N_2 gas with a purity of 99.995mol% was supplied by Special Gas (Korea). Solutions of proper mole-composition of TBABh, TBAB, TBAF, TBAOH, THF, Me_4NOH were frozen at 210K for at least 24 hour and were then ground to a fine power (~200μm) in liquid nitrogen. For TBABh solution, NaOH (molar ratio of OH^-/BH_4^- = 0.05) was added to prevent premature hydrolysis reaction. The grounded powders were pressurized by H_2 or N_2 at 210K for at least 1 week. The formed hydrate samples were stored in liquid nitrogen and gamma-ray irradiated as 30 kGy (15 kGy per 1hr) by a ^{60}Co γ-ray source at KAERI in Jeongup, Korea.

The polycrystalline samples were measured at 77K by an X-band ESR spectrometer (JEOL FA200) at a modulation of 100 kHz using a modulation width of 0.5 mT, a microwave power of 1 mW and a sweep time of 4 minutes. 5 grams of each sample was carefully transferred to a quartz tube placed in a liquid nitrogen environment. This low-temperature condition was maintained during ESR experiments. The XRD patterns were obtained using Rigaku D/max-IIIC diffractometer with CuKα as a light source (λ=1.5406) at a generator voltage of 40 kV and a generator current of 300 mA. Low temperature stage attached to XRD kept the working temperature to 93K and step scan mode of 0.01^o/3s was applied.

The equilibrium pressure and temperature were determined by checking the routine PT trajectory, which consisted of hydrate formation and dissociation stages. The cooling rate was 0.5 K/h and the heating rate was 0.2 K/h. A 4-wire type PT-100Ω (±0.05% full-scale accuracy) and a PMP4070 device from Druck Inc. were used as temperature and pressure sensing device. The direct-release experiments were conducted at 293K and were repeated three times for reliability.

Fig. S1

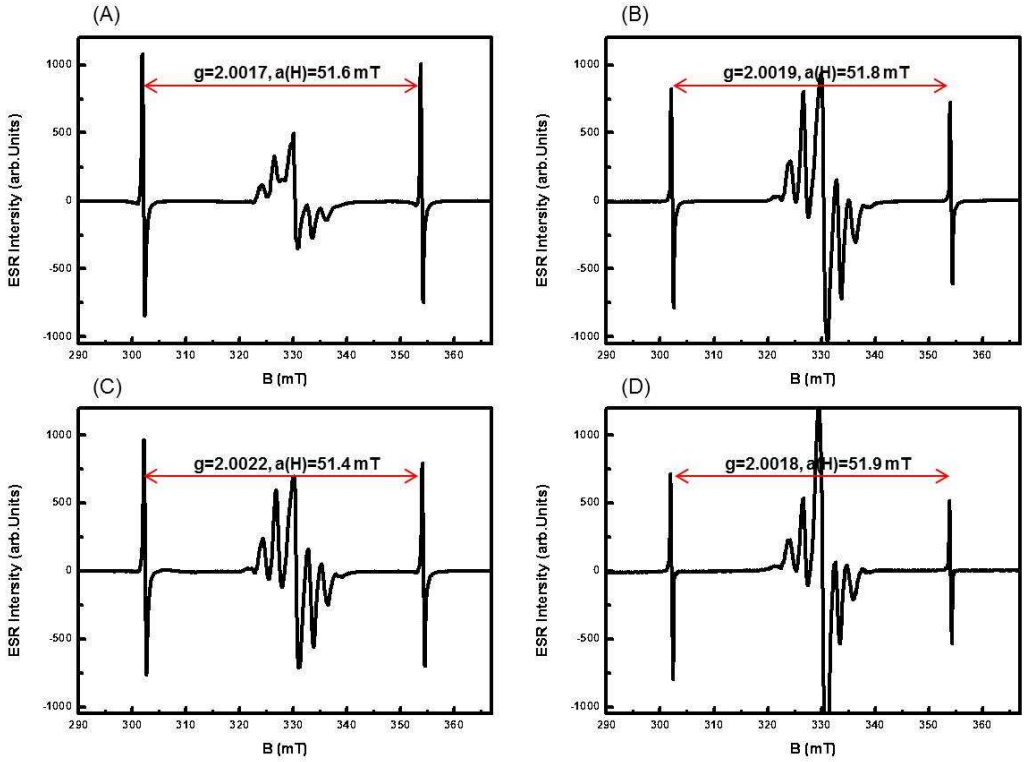
(A)
g=2.0017, a(H)=51.6 mT
(B)
g=2.0019, a(H)=51.8 mT
(C)
g=2.0022, a(H)=51.4 mT
(D)
g=2.0018, a(H)=51.9 mT
ESR Intensity (arb.Units)
B (mT)

Fig. S2

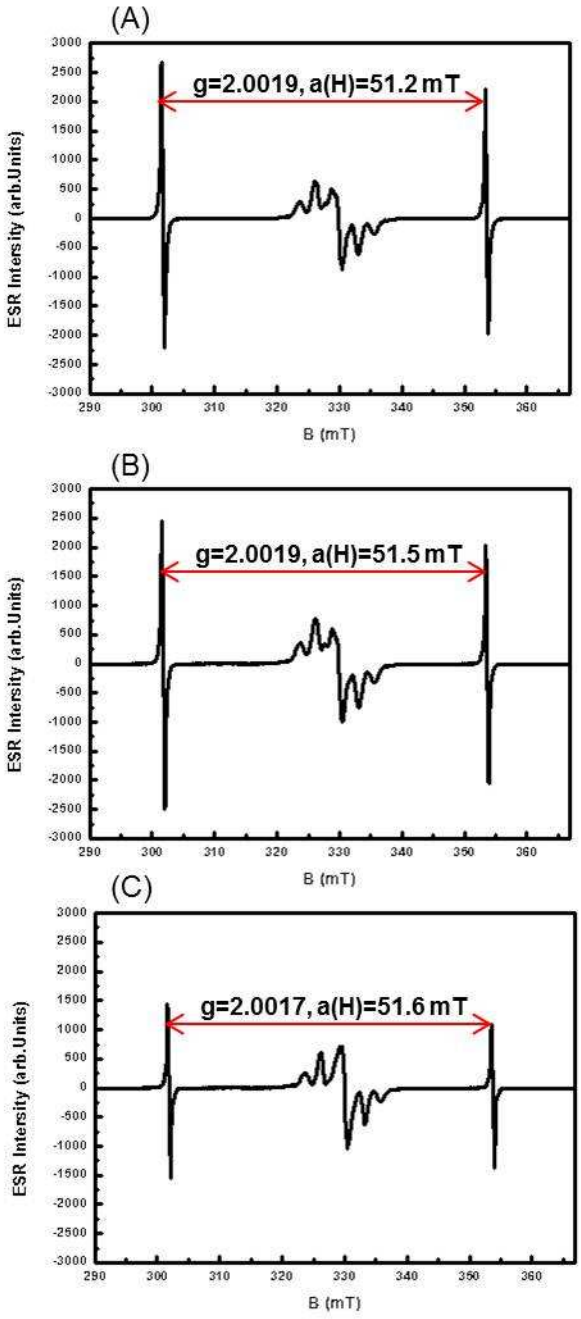
(A)
g=2.0019, a(H)=51.2 mT
ESR Intersity (arb.Units)
B (mT)
(B)
g=2.0019, a(H)=51.5 mT
ESR Intersity (arb.Units)
B (mT)
(C)
g=2.0017, a(H)=51.6 mT
ESR Intersity (arb.Units)
B (mT)

Fig. S3

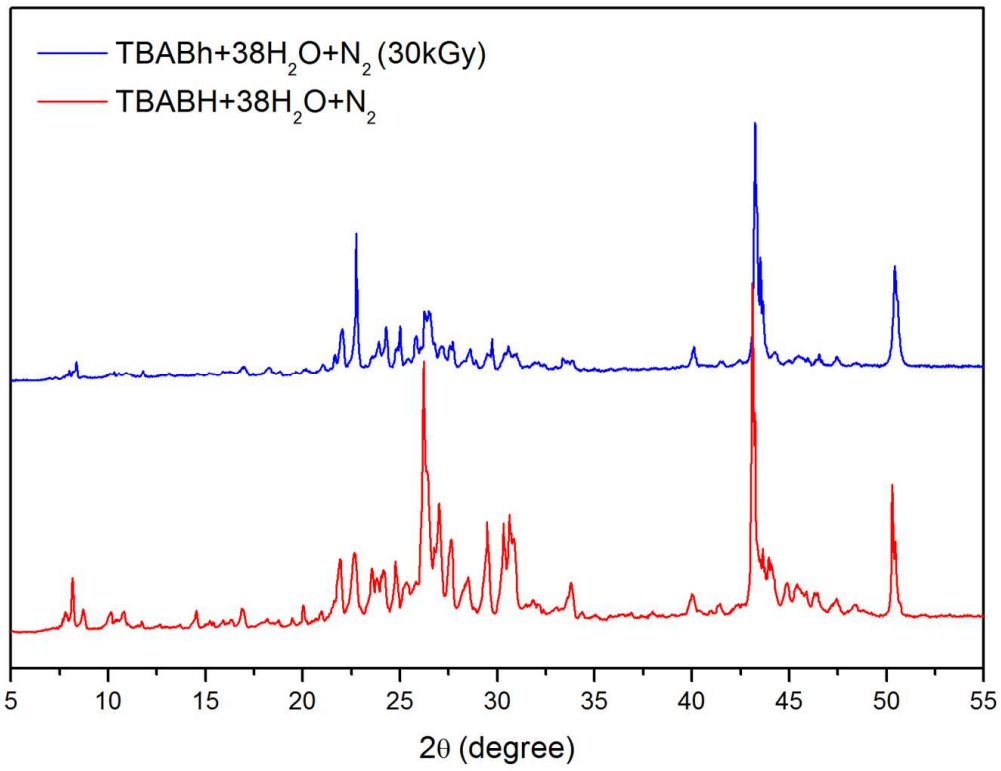
TBABh+38H2O+N2 (30kGy)
TBABH+38H2O+N2
5
10
15
20
25
30
35
40
45
50
55
2θ (degree)

Fig. S4

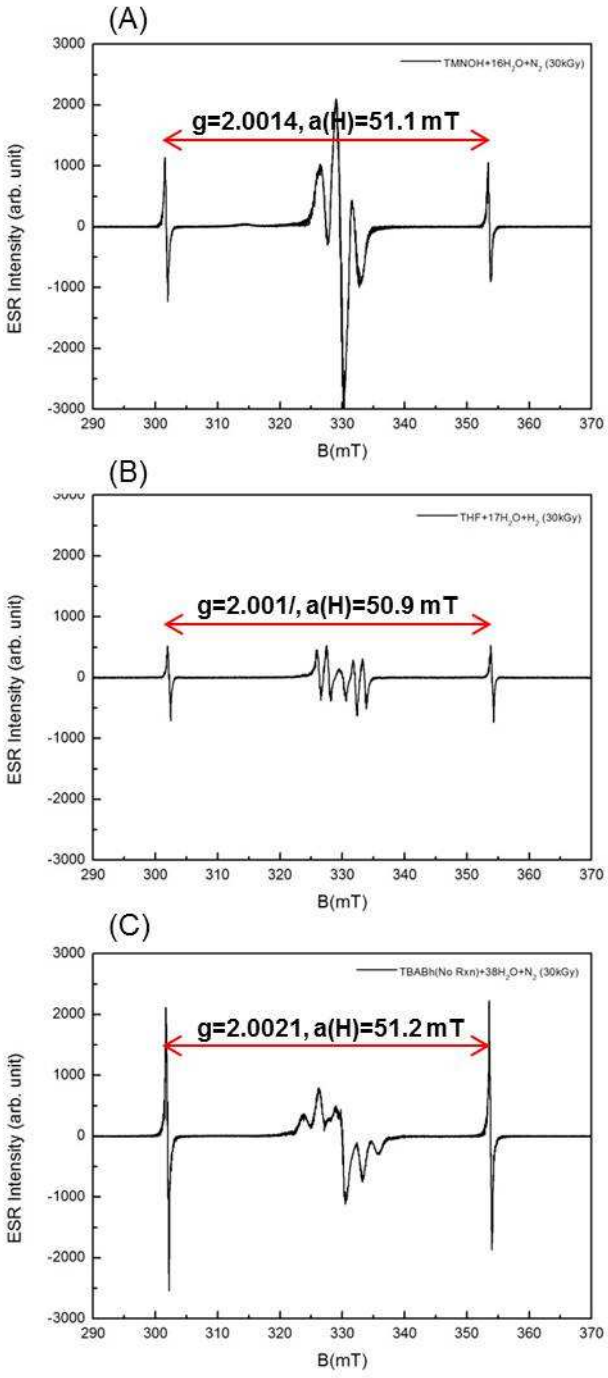
(A)
TMNOH+16H2O+N2 (30kGy)
g=2.0014, a(H)=51.1 mT
ESR Intensity (arb. unit)
B(mT)
(B)
THF+17H2O+N2 (30kGy)
g=2.001/, a(H)=50.9 mT
ESR Intensity (arb. unit)
B(mT)
(C)
TBABh(No Rxn)+38H2O+N2 (30kGy)
g=2.0021, a(H)=51.2 mT
ESR Intensity (arb. unit)
B(mT)

Fig. S5 (This figure is newly inserted in the revision. Here, we don't provide the full range data set, but this can show the general PT equilibrium trend.)

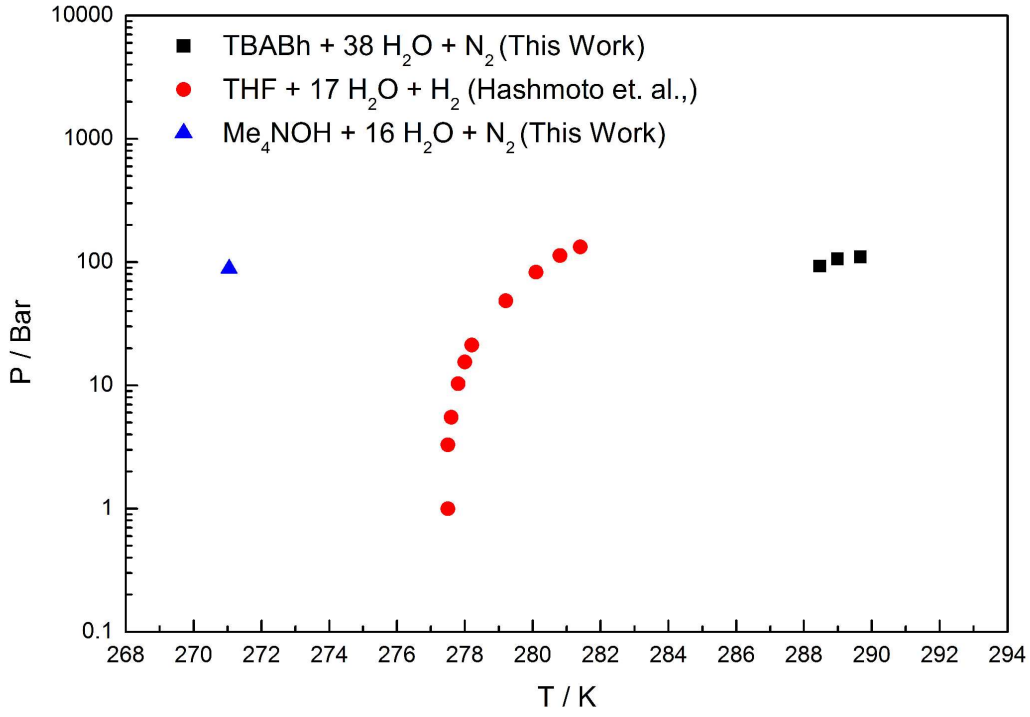

Table S1.

NIGM type	Dose of □-ray (kGy)	Released amount (ml/g)
N_2	0 (before the irrdiation)	24.52 ± 0.24
	30	24.86 ± 0.81
H_2	0 (before the irrdiation)	19.47 ± 0.21
	30	19.27 ± 0.24