## Supporting Information

# Facile preparation and dehydrogenation of unsolvated KB<sub>3</sub>H<sub>8</sub>

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#### **General procedures**

All manipulations were carried out using standard Schlenk line or in a glove box filled with high purity nitrogen. Due to the activity of the reagents, all compounds were stored and handled under an inert atmosphere except during measurements.

Reagents

Sodium borohydride (NaBH<sub>4</sub>) ( $\geq$ 97%), acetonitrile ( $\geq$ 99.5%), diethyl ether ((C<sub>2</sub>H<sub>5</sub>)<sub>2</sub>O) ( $\geq$ 99.5%), and tetrahydrofuran (C<sub>4</sub>H<sub>8</sub>O) ( $\geq$ 99.5%) were purchased from SCRC. Sodium ( $\geq$ 99.7%), potassium ( $\geq$ 99.7%), and cuprous chloride (CuCl) ( $\geq$ 97%) were purchased from Aladdin and used as received. THF and Et<sub>2</sub>O were dried by refluxing over sodium wire, distilled and stored over potassium mirror.

### Na/K alloy preparation

To prepare the Na/K alloy, 8.4g bulky potassium and 0.9g sodium was loaded into a 500ml reaction flask in glove box. A silvery white liquid NaK alloy will form after slow agitation by magnetic bar.

### Unsolvated KB<sub>3</sub>H<sub>8</sub> preparation

500ml 1 M BH<sub>3</sub>·THF solution was prepared by the reaction of excess CuCl with NaBH<sub>4</sub> in THF at 40 °C. <sup>s1</sup> The solution was immediately transferred to the Na/K alloy prepared above under N<sub>2</sub> atmosphere and stirred overnight at room temperature. After the solid residue was filtered off, the solvent was distilled off under reduced pressure. Then, the resulting solid product was washed by  $15ml\times3$  Et<sub>2</sub>O and dried under vacuum to get 4.16g unsolvated KB<sub>3</sub>H<sub>8</sub>. The yield is 67% based on NaBH<sub>4</sub>. Pyrolysis of KB<sub>3</sub>H<sub>8</sub>

0.5g KB<sub>3</sub>H<sub>8</sub> was loaded into a glass tube with one end connected to a N<sub>2</sub> stream line and another end connected to a 50 ml cold trap filled with 10 ml anhydrous tetrahydrofuran (THF). The THF cold trap was cooled to -78 °C by dry ice, and the system was flushed by N<sub>2</sub> flow before pyrolysis. Then, the glass tube was slowly heated to 250 °C and kept for 2h. During the pyrolysis, the gaseous products carried out by the N<sub>2</sub> flow was collected by the THF cold trapped. After the pyrolysis, the glass tube was brought into glove box to collect the solid residue.

#### Instruments and characterization

Simultaneous thermo-gravimetric analysis and mass spectrometry (TGA-MS) was conducted under 1 atm argon in the temperature range of room temperature to 400 °C at a heating rate of 5 °C min<sup>-1</sup> using a netzsch STA 409 C analyzer equipped with a quadrupole mass spectrometer for the analysis of the evolved gas. The targeted gaseous products monitored by MS were H<sub>2</sub> (2) and B<sub>5</sub>H<sub>9</sub> (60). Meanwhile, desorption properties for the sample were also evaluated using Sievert's volumetric methods with heating rate of 5 °C min<sup>-1</sup> under 1 atm argon. Differential scanning calorimetry (DSC) was performed simultaneously on a Netzsch STA 409 PC with pure argon as the purge gas. Powder X-ray diffraction (XRD) patterns were obtained with a Bruke X'PERT diffractometer (Cu Ka radiation, 16Kw). During the XRD measurement, samples were mounted in a glove box, and an amorphous polymer tape was used to cover the surface of the powder to avoid oxidation. FT-IR (Magna-IR 550 II, Nicolet) analyses were conducted to determine the chemical bond. The solid residue after thermal decomposition was characterized using solid state magic angle spinning (MAS) NMR. This was performed in a field of 6.9 T using 5 mm rotors spinning at 5 kHz. <sup>11</sup>B was examined, at 94.6 MHz and room temperature. The free induction decays (FIDs) following 3  $\mu$ s  $\pi/2$  RF pulses were signal averaged over about 30 min (4000 scans), with high-power hydrogen decoupling. The shift reference was liquid BF<sub>3</sub>·Et<sub>2</sub>O at 0 ppm. Liquid NMR samples were prepared under argon in 5 mm Wilmad 507-PP tubes fitted with J. Young Teflon valves. <sup>11</sup>B spectra were measured on Bruker AVII-400 spectrometers. Chemical shifts are reported in ppm units, referenced to BF<sub>3</sub>·Et<sub>2</sub>O for <sup>11</sup>B chemical shift.



Fig. S1. <sup>11</sup>B NMR spectrum of the as-prepared BH<sub>3</sub>·THF (δ 0 ppm).



Fig. S2. TG/DSC results of KB<sub>3</sub>H<sub>8</sub> with a heating rate of 5 °C min<sup>-1</sup> in argon.



Fig. S3. TPD results of  $KB_3H_8$  and  $KB_3H_8$  ball-milled with AlCl<sub>3</sub>, FeCl<sub>3</sub> and ZrCl<sub>4</sub>, with a heating rate of 5 °C min<sup>-1</sup> in argon.



Fig. S4. TG (solid lines), and MS (symbols) results of KB<sub>3</sub>H<sub>8</sub> (a), AlCl<sub>3</sub>/ 3KB<sub>3</sub>H<sub>8</sub> (b), FeCl<sub>3</sub>/ 3KB<sub>3</sub>H<sub>8</sub> (c) and ZrCl<sub>4</sub>/ 4KB<sub>3</sub>H<sub>8</sub> (d) composites, with a heating rate of 5 °C min<sup>-1</sup> in argon.  $\bullet$  H<sub>2</sub>, m/e=2,  $\bigcirc$  B<sub>2</sub>H<sub>6</sub>, m/e=26,  $\diamondsuit$  B<sub>5</sub>H<sub>9</sub>, m/e=60,  $\precsim$  B<sub>6</sub>H<sub>10</sub>, m/e=71.



Fig. S5. <sup>11</sup>B NMR spectrum of gaseous products of KB<sub>3</sub>H<sub>8</sub> after heated at 250 °C in THF. B<sub>2</sub>H<sub>6</sub> ( $\delta$  0ppm, quart), B<sub>5</sub>H<sub>9</sub> ( $\delta$  -13.9ppm, -53.8ppm) B<sub>6</sub>H<sub>10</sub> ( $\delta$  14.2 ppm) and unknown phase ( $\delta$  -7.7 ppm) were detected according to this results.



Fig. S6. <sup>11</sup>B solid NMR spectrum of the solid residue of KB<sub>3</sub>H<sub>8</sub> after heated at 250 °C. The main peaks are identified as BH<sub>4</sub><sup>-</sup> ( $\delta$  -38.5 ppm), B<sub>12</sub>H<sub>12</sub><sup>2-</sup> ( $\delta$  -15.6 ppm), B<sub>10</sub>H<sub>10</sub><sup>2-</sup>( $\delta$  -30.1, -1.67 ppm). The most distant little peaks ( $\delta$  55.2 ppm, -131.7 ppm) are spinning sidebands.



Fig. S7. Solution <sup>11</sup>B NMR spectrum of the thermal decomposition products of KB<sub>3</sub>H<sub>8</sub> at 250 °C dissolved in CH<sub>3</sub>CN. The main peaks are ascribed to  $B_{10}H_{10}^{2-}$  ( $\delta$  -0.13 ppm, -28.2 ppm) and  $B_{12}H_{12}^{2-}$  ( $\delta$  -14.7 ppm).



Fig. S8. XRD pattern of the pyrolysis products of  $KB_3H_8$  after heated at 250 °C.



Fig. S9. DSC results of the  $KB_3H_8$  composites ball-milled with  $AlCl_3$ ,  $FeCl_3$  and  $ZrCl_4$  with a heating rate of 5 °C min<sup>-1</sup> in argon.



Fig S10. XRD results of the mixtures of  $KB_3H_8$  ball-milled with AlCl<sub>3</sub> (a), FeCl<sub>3</sub> (b) and ZrCl<sub>4</sub>(c) and their decomposition products. (d). FTIR spectrum of the mixtures of  $KB_3H_8$  ball-milled with AlCl<sub>3</sub>, FeCl<sub>3</sub> and ZrCl<sub>4</sub>.

References:

s1. W. D. Chen, G. T. Wu, T. He, Z. Li, Z. P. Guo, H. K. Liu, Z. G. Huang and P. Chen, *International Journal of Hydrogen Energy*, 2016, **41**, 15471-15476.