

Supplementary Information

Significantly Enhanced Dehydrogenation Properties of Calcium Borohydride Combined with Urea

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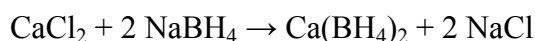
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Experimental details:

Materials

Ca(BH₄)₂ was synthesized by means of the metathesis of CaCl₂ and NaBH₄ in tetrahydrofuran (THF) solution according to our previous report [S1]:



CO(NH₂)₂ (99%) (Kermel chemicals of Tianjin, China) was used without further purification. Ca(BH₄)₂·4CO(NH₂)₂ was synthesized by balling milling Ca(BH₄)₂ and CO(NH₂)₂ in the molar ratio of 1:4 on a Retsch PM400 under argon atmosphere for 2 hours. To reduce heat effect in ball milling, the mill was set to revolve for 60 s in one direction and pause for 15 s, and then revolve in reversed direction. To avoid oxygen and moisture contaminations, all the manipulations are conducted inside a glove box filled with purified argon (O₂ < 1.0 ppm; H₂O < 1.0 ppm).

Characterization

Structural identifications were carried on a PANalytical X'pert diffractometer (Cu radiation, 40 kV, 40 mA). FT-IR measurements were conducted on a Varian 3100 unit in DRIFT mode. Temperature-programmed desorption (TPD) using purified Argon as carrier gas was conducted on a home-made system [S2] combined with a micro-reactor and an on-line mass spectrometer (HPR20, from Hiden). *Ca.* 50 mg sample was loaded and temperature was raised from room temperature to 500 °C at a ramping rate of 2 °C min⁻¹. Differential Scanning Calorimetry (DSC) measurements were done on a Netzsch STA449C thermal analysis system. Dynamic flow mode and a heating rate of 2 °C/min were applied to 5 mg sample. Volumetric release for quantitative measurements of hydrogen desorption were carried out on a HyEnergy PCT apparatus (PCTPro 2000). ¹¹B solid-state MAS NMR experiments were conducted at room temperature on a Bruker Advance III 500 NMR spectrometer at a frequency of 128.28 MHz, using a 4 mm MAS NMR probe and the ¹¹B NMR signals were referenced to BF₃·Et₂O at 0 ppm.

Figures and Tables

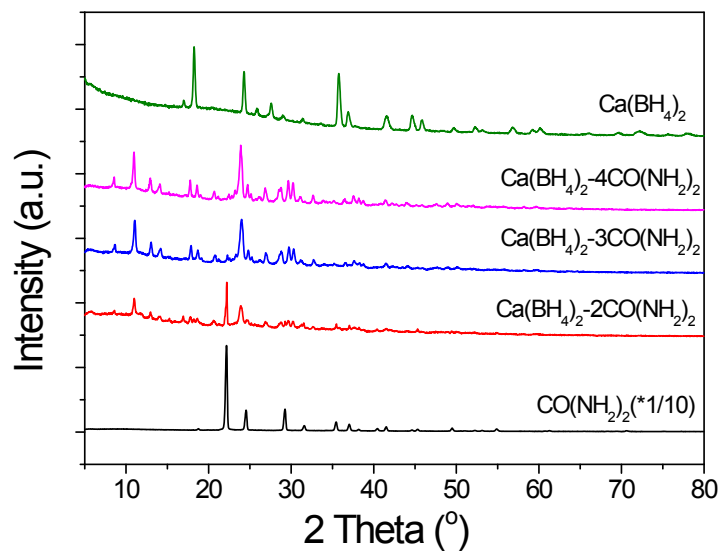


Fig. S1 XRD patterns of $\text{Ca}(\text{BH}_4)_2$, $\text{CO}(\text{NH}_2)_2$, and $\text{Ca}(\text{BH}_4)_2\text{-CO}(\text{NH}_2)_2$ in different molar ratios.

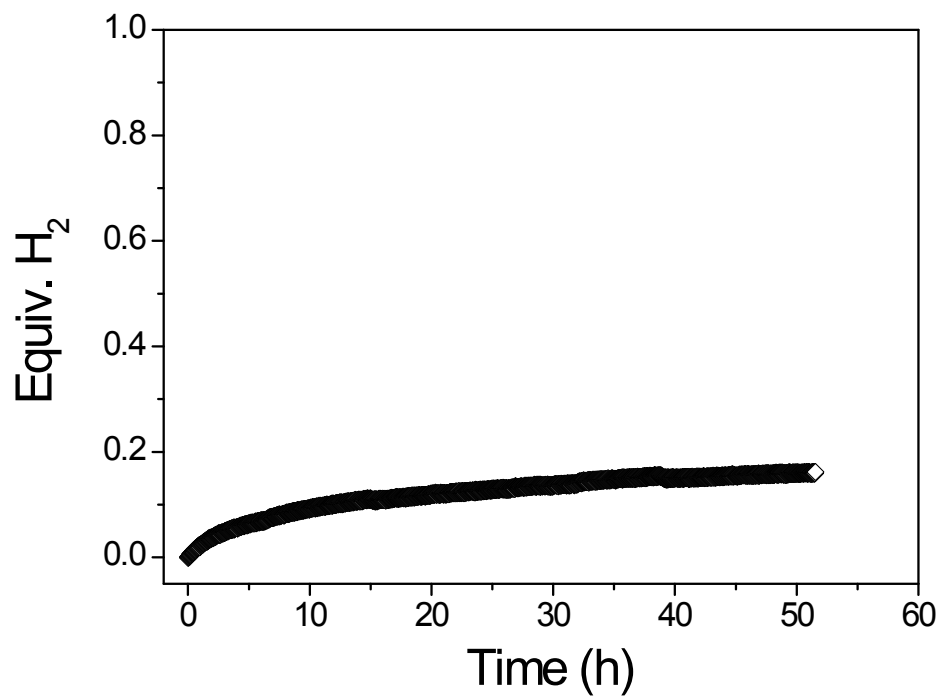


Fig. S2 Time dependence of hydrogen desorption from pristine Ca(BH₄)₂ at 250 °C.

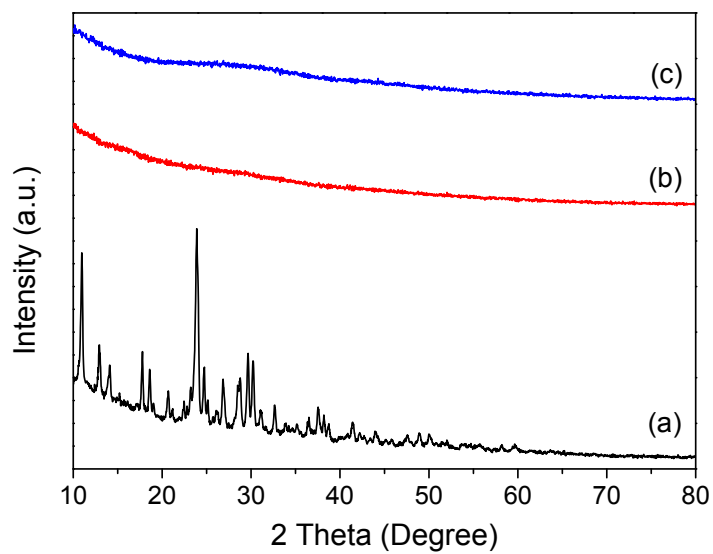


Fig. S3 XRD patterns of (a) $\text{Ca}(\text{BH}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ and its dehydrogenated products collected at different temperatures (b) at 150 °C and (c) 250 °C.

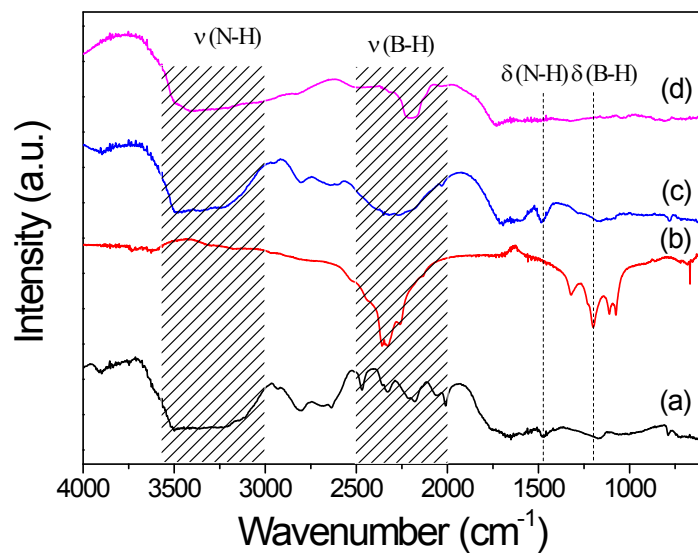


Fig. S4 FT-IR spectra of (a) $\text{CO}(\text{NH}_2)_2$, (b) $\text{Ca}(\text{BH}_4)_2$, (c) $\text{Ca}(\text{BH}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$, and (d) post-dehydrogenated $\text{Ca}(\text{BH}_4)_2 \cdot 4\text{CO}(\text{NH}_2)_2$ samples collected at 250 °C.

Reference:

[S1] H. L. Chu, S. J. Qiu, L. X. Sun and G. T. Wu, *J. Renewable Sustainable Energy*, 2014, **6**, 013105.

[S2] H. L. Chu, Z. T. Xiong, G. T. Wu, J. P. Guo, T. He and P. Chen, *Dalton Trans.*, 2010, **39**, 10585-10587.