Mechanochemical reactions and hydrogen storage capacities in MBH₄-SiS₂ systems (M=Li or Na).

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Table S1. TPD results of ball milled NaBH₄-SiS₂ mixtures at different molar ratios. Numbers in parentheses represent data from the second desorption cycle after hydrogen absorption.

<table>
<thead>
<tr>
<th>Ratio  NaBH₄:SiS₂</th>
<th>wt. % H₂ (after absorption)</th>
<th>Tₒms (after absorption)</th>
<th>wt. % of total H₂ (after absorption)</th>
</tr>
</thead>
<tbody>
<tr>
<td>2:1</td>
<td>3.3 (1.0)</td>
<td>124 (270)</td>
<td>69 (30.3)</td>
</tr>
<tr>
<td>5:1</td>
<td>2.1</td>
<td>134</td>
<td>29.6</td>
</tr>
<tr>
<td>6:1</td>
<td>2.4</td>
<td>159</td>
<td>32</td>
</tr>
</tbody>
</table>

Fig. S1. TPD of the ball milled (a) 2NaBH₄-SiS₂ mixture (1st decomposition), (b) 2NaBH₄-SiS₂ mixture after rehydrogenation. (Red lines represent temperature profile; black lines, the amounts of released hydrogen).
Characterization of the as-milled products by FT-IR Analysis

The FT-IR spectra were measured for the ball milled 2:1 and 6:1 mixtures. (Fig. S3). The 2:1 mixture showed a broad signal in the frequency range between 2000 cm\(^{-1}\) and 2500 cm\(^{-1}\), which does not agree well with the characteristic modes of the pristine LiBH\(_4\). The appearance of broad signals corresponding to B-H stretches (2200-2500 cm\(^{-1}\) and 1000-1400 cm\(^{-1}\)) and a notable decrease in the signal intensities suggested that the [BH\(_4\)] groups were significantly distorted. Such distortions can be explained by the presence of an S\(^{2-}\) anion in a close proximity to [BH\(_4\)] groups in the newly formed product. The FT-IR spectrum of the 6:1 sample featured B-H stretches similar to LiBH\(_4\), suggesting that structurally symmetrical BH\(_4^-\) anions are statistically dominant in the material. Most likely, asymmetrical motifs in the 6:1 sample, which are similar to those in the 2:1 material, overlap with an overwhelming number of symmetrical [BH\(_4\)] moieties and thus are not visible in the FT-IR spectra.
**Fig. S3.** FT-IR spectra of the ball-milled LiBH₄-SiS₂ mixtures. The spectra of the starting materials are presented for comparison.

**Fig. S4.** The TPD of the 6:1 LiBH₄-SiS₂ mixture ball-milled for 18 hours in a Si₃N₄ vial upon heating to different temperatures.
**Fig. S5.** The XRD patterns from the 6:1 LiBH$_4$-SiS$_2$ mixture ball-milled for 18 hours in a Si$_3$N$_4$ vial at room temperature (RT) and after heating to the different temperatures.

**Fig. S6.** The XRD patterns from the ball-milled, decomposed and rehydrogenated NaBH$_4$-SiS$_2$ mixtures of different molar ratios.
Fig. S7. $^{11}$B$^1$H CPMAS NMR spectra of LiBH$_4$-SiS$_2$ mixtures (2:1 and 6:1) after dehydrogenation and subsequent rehydrogenation (black lines). The $^{11}$B NMR spectra were acquired using $v_R = 12.5$ kHz, $v_{RF}$(H) = 100 kHz for a hard $\pi/2$ pulse and 50 kHz for cross polarization and for H decoupling during acquisition, effective $v_{RF}$(11B) = 37 kHz for cross polarization, $\tau_{CP} = 1$ ms, $\tau_{RD} = 1$ s, and NS = 640. The corresponding $^{11}$B DPMAS spectra are superimposed for comparison (grey lines). The short $\tau_{CP}$ resulted in the disappearance of relatively sharp peaks around -17 ppm and -42 ppm, because of the slow $^1$H→$^{11}$B polarization transfer in mobile components such as closo-borane (-17 ppm) and BH$_4^-$ anion (-42 ppm).

Fig. S8. $^{11}$B DPMAS NMR spectra of the ball-milled 6:1 LiBH$_4$-SiS$_2$ mixture after heating to different temperatures and after rehydrogenation.