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Hydrogen–fluorine exchange in NaBH₄–NaBF₄

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Hydrogen–fluorine exchange in the NaBH₄–NaBF₄ system is investigated using a range of experimental methods combined with DFT calculations and a possible mechanism for the reactions is proposed. Fluorine substitution is observed using in situ synchrotron radiation powder X-ray diffraction (SR-PXD) as a new Rock salt type compound with idealized composition NaBF₂H₂ in the temperature range T = 200 to 215 °C. Combined use of solid-state ¹⁹F MAS NMR, FT-IR and DFT calculations supports the formation of a BF₂H₂ complex ion, reproducing the observation of a ¹⁹F chemical shift at 144.2 ppm, which is different from that of NaBF₄ at 159.2 ppm, along with the new absorption bands observed in the IR spectra. After further heating, the fluorine substituted compound becomes X-ray amorphous and decomposes to NaF at 310 °C. This work shows that fluorine-substituted borohydrides tend to decompose to more stable compounds, e.g. NaF and BF₃ or amorphous products such as closo-boranes, e.g. Na₂B₁₂H₁₂. The NaBH₄–NaBF₄ composite decomposes at lower temperatures (300 °C) compared to NaBH₄ (476 °C), as observed by thermogravimetric analysis. NaBH₄–NaBF₄ (1 : 0.5) preserves 30% of the hydrogen storage capacity after three hydrogen release and uptake cycles compared to 8% for NaBH₄ as measured using Sievert’s method under identical conditions, but more than 50% using prolonged hydrogen absorption time. The reversible hydrogen storage capacity tends to decrease possibly due to the formation of NaF and Na₂B₁₂H₁₂. On the other hand, the additive sodium fluoride appears to facilitate hydrogen uptake, prevent foaming, phase segregation and loss of material from the sample container for samples of NaBH₄–NaF.

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† Electronic supplementary information (ESI) available: DFT results for the isolated ions BF_4^- and H_x^+ and calculated IR spectra, in situ SR-PXD measurements of NaBH_4 and $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2). ^{19}F MAS NMR spectra of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2-300). The X-ray diffractogram of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2-300) after NMR measurement. IR measurement of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.1, S1), IR spectra of the solid as a function of temperature, TPD-IR spectra as a function of temperature of the released gas, and Sieverts measurements of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2), $\text{NaBH}_4\text{-NaF}$ (1 : 0.25, S6) and NaBH_4 . Tables with thermal analysis data and Sieverts measurements data. See DOI: 10.1039/c3cp52815d

1 Introduction

Hydrogen has the highest gravimetric energy density but is difficult to store in a compact form, which may be achieved in the solid state.¹⁻⁷ Currently, metal borohydride materials are considered promising for hydrogen storage, however, the kinetics and thermodynamics of the hydrogen uptake and release need to be further improved.⁸⁻¹⁰ Anion substitution has recently been suggested as a new method to improve the hydrogen storage properties due to possible changes in the lattice energy, chemical pressure and metal-hydrogen bond strength.^{8,11} Fluorine substitution was reported for sodium hexahydroaluminum, Na_3AlH_6 ,¹² and ab initio calculations suggest a decreased enthalpy upon substitution, which is verified experimentally.^{13,14} Anion substitution in metal borohydride materials was reported for $\text{LiBH}_4\text{-LiX}$,

where $\text{X} = \text{Cl, Br, and I}$ in $\text{NaBH}_4\text{-NaCl}$, in $\text{Ca}(\text{BH}_4)_2\text{-CaX}_2$, $\text{X} = \text{Cl and I}$, and in $\text{Mg}(\text{BH}_4)_2\text{-MgX}_2$, $\text{X} = \text{Cl and Br}$.¹⁵⁻²⁴ The change in the hydrogen storage properties of anion-substituted metal borohydride using the heavier halides, Cl, Br or I, is small and may lead to a stabilization, which tends to facilitate hydrogen absorption.^{18,19,24} In contrast, calculations reveal that fluorine substitution in LiBH_4 is not thermodynamically favored but should indeed provide a destabilization of lithium borohydride.^{25,26} Furthermore, fluorine preferably exists on the same boron atom, i.e. formation of one BH_2F_2 is preferred compared to $2 \text{BH}_3\text{F}$.^{10,25,27,28} DFT also reveals that room temperature formation of solid solutions between LiBH_4 and LiBF_4 is not thermodynamically favoured.²⁵ Experimental reports indicate fluorine substitution in studies of $\text{MgB}_2\text{-LiF}$ and $\text{LiBH}_4\text{-TiF}_3$ and also for the $\text{KBH}_4\text{-KBF}_4$ system.²⁹⁻³¹

In this paper, the physical, structural and hydrogen storage properties of the $\text{NaBH}_4\text{-NaBF}_4$ composite are investigated using in situ synchrotron radiation powder X-ray diffraction (SR-PXD), solid-state magic-angle spinning (MAS) NMR spectroscopy, infrared spectroscopy (IR), simultaneous differential scanning calorimetry (DSC), thermogravimetric analysis (TGA), and Sieverts method. DFT calculations on isolated $\text{BF}_4\text{-xH}_x$ ions were also performed and spectral parameters were computed.

2 Experimental section

Sample preparation

Samples of $\text{NaBH}_4\text{-NaBF}_4$ in the molar ratio of 1 : 0.1 and 1 : 0.5, denoted S1 and S2, and reference samples of NaBH_4 and NaBF_4 , denoted R1 and R2, respectively, were ball milled (BM) using the same conditions comprising 15 times 2 min of milling each intervened by 2 min breaks to avoid heating of the samples.³² Ball milling was conducted under inert conditions in an argon atmosphere with a Fritsch Pulverisette P4 planetary mill using 80 mL tungsten carbide (WC) containers and a sample powder-to-ball mass ratio of approximately 1 : 30 (WC balls, o.d. 10 mm). Fractions, 0.5 g, of the sample $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) were transferred to corundum crucibles, placed in sealed argon-filled quartz tubes, and annealed in a furnace at a fixed temperature. The first sample was annealed at 200 °C for 72 hours and is denoted S2-200. The second and third samples were annealed at 275 and 300 °C, respectively, for 1 hour to analyze the decomposition reaction (S2-275 and S2-300). A hand mixed (HM, 10 min) sample of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5), denoted S3, was prepared using an agate mortar to examine the effect of ball milling. Samples S4 (1 : 1) and S5 (3 : 1) are hand mixed (HM, 10 min), containing physical mixtures of NaBH_4 and NaBF_4 .

Finally, a ball-milled sample of $\text{NaBH}_4\text{-NaF}$ (1 : 0.25) denoted S6 was prepared to investigate the properties of NaF used as an additive. For NMR measurements a sample of NaF was used as received, R3. All samples are listed in Table 1. The chemicals used were: NaBH_4 (Z99.99%, Aldrich), NaBF_4 (>98%, Aldrich) and NaF (>95%, Aldrich). The preparation and manipulation of all samples were performed in an argon-filled glovebox using a circulation purifier.

Theoretical calculations

Theoretical DFT calculations were performed on the isolated $\text{BH}_4\text{-xF}_x$ ions at B3-LYP/6-31G** level using the Gaussian program³³ with B3-LYP(6-31G**). Isotropic shielding tensors were computed with the Gauge-Independent Atomic Orbital (GIAO) method.³³

Table 1 List of investigated samples. The composition of the samples is given as relative molar ratios and molar fractions and the theoretical gravimetric hydrogen content is denoted $r_m(\text{H}_2)$. The sample preparation methods are either ball milling (BM) or hand-mixing in a mortar (HM) and in some cases combined with annealing (A) in an argon atmosphere

Notation	Materials	Molar ratio	$n(\text{NaBF}_4)/n(\text{total})$	Preparation	$r_m(\text{H}_2)$
S1	$\text{NaBH}_4\text{-NaBF}_4$	1 : 0.1	0.091	BM	8.4
S2	$\text{NaBH}_4\text{-NaBF}_4$	1 : 0.5	0.334	BM	4.3
S2-200	$\text{NaBH}_4\text{-NaBF}_4$	1 : 0.5	0.334	BM, A ^b	4.3
S2-275	$\text{NaBH}_4\text{-NaBF}_4$	1 : 0.5	0.334	BM, A ^c	—
S2-300	$\text{NaBH}_4\text{-NaBF}_4$	1 : 0.5	0.334	BM, A ^d	—
S3	$\text{NaBH}_4\text{-NaBF}_4$	1 : 0.5	0.334	HM	4.3

S4	NaBH ₄ -NaBF ₄	1 : 1	0.500	HM	2.7
S5	NaBH ₄ -NaBF ₄	1 : 0.33	0.250	HM	5.4
S6	NaBH ₄ -NaF	1 : 0.25	0.199 ^a	BM	6.3
R1	NaBH ₄	—	—	BM	10.7
R2	NaBF ₄	—	—	BM	—
R3	NaF	—	—	—	—

^a n(NaF)/n(total). ^b Annealed at 200 °C for 72 hours. ^c Annealed at 275 °C for 1 hour. ^d Annealed at 300 °C for 1 hour.

Synchrotron radiation powder X-ray diffraction

In situ synchrotron radiation powder X-ray diffraction (SR-PXD) data for sample S2 were measured at beamline BM01A at the Swiss-Norwegian Beam Lines (SNBL), European Synchrotron Radiation Facility (ESRF), Grenoble, France, using a MAR345 image plate detector. The samples were mounted in glass capillaries (0.5 mm o.d.) and sealed to prevent contact with air. The data were collected with a sample-to-detector distance of 250 mm, a 301 rotation of the capillaries during data collection and 30 s X-ray exposure time. The wavelength, $\lambda = 0.70082$ Å, was calibrated using an external standard, LaB₆. The sample was heated from room temperature (RT) to 450 °C at a heating rate of $DT/Dt = 5$ °C min⁻¹.

SR-PXD data for sample S2-200 were measured at the MAX-II synchrotron at beamline I711 in the research laboratory MAX-lab, Lund, Sweden using a MAR165 CCD detector system.³⁴ The sample was mounted in sapphire (Al₂O₃) single crystal tubes (0.79 mm i.d.) in an argon-filled glovebox.^{35,36} The experiment was conducted at $p(\text{Ar}) = 1$ bar, in the temperature range from RT to 385 °C ($DT/Dt = 5$ °C min⁻¹) and $\lambda = 0.94499$ Å. The data were collected with a sample-to-detector distance of 87 mm, an X-ray exposure time of 30 s per PXD pattern.

The data were integrated using the Fit2D program and analyzed using the Rietveld methods in the FullProf suite.^{37,38} The sequential refinement of the in situ SR-PXD data was performed to follow the change in composition and unit cell volumes. The intensity of selected Bragg reflections was integrated and normalized in order to illustrate changes in the sample composition as a function of temperature (the relative amount, $a_i(t) = I_i(t)/I_{i,\text{max}}$, of compound *i* at time *t*).

Solid-state MAS NMR spectroscopy

Solid-state ¹¹B, ¹⁹F and ²³Na magic-angle spinning (MAS) spectra were collected for samples S2, S2-275 and S2-300 on a Varian INOVA-400 (9.39 T) spectrometer using a home-built CP/MAS probe for 5 mm o.d. rotors. The ¹⁹F MAS NMR spectra were acquired on a Varian INOVA-300 (7.05 T) spectrometer employing the high-frequency ¹H/¹⁹F channel of a home-built CP/MAS NMR probe for 7 mm o.d. rotors. All spectra were obtained at ambient temperature using air-tight end-capped zirconia (PSZ) rotors packed in an argon-filled glovebox.

The ¹¹B, ¹⁹F, and ²³Na MAS NMR spectra and chemical shifts are referenced to neat F₃B O(CH₂CH₃)₂, neat CCl₃F, and a 1.0 M aqueous solution of NaCl, respectively. Simulations and least-squares fitting of the ²³Na MAS NMR spectra were performed using the STARS simulation software package.³⁹

Thermal analysis

Differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were performed simultaneously using a Netzsch STA449C Jupiter instrument at a heating rate of 5 °C min⁻¹ from RT to 450 °C (S2 and S3) or to 600 °C (S1, R1 and R2) in a flow of He (50 mL min⁻¹). The samples were placed in Al₂O₃ crucibles with a small hole in the lid to prevent the increase of pressure.

Mass spectroscopy

The gas release from the samples of NaBH₄-NaBF₄ (1 : 0.1, S1) and NaBH₄-NaBF₄ (1 : 0.5, S2) was investigated using a MKS Microvision-IP residual gas analyzer (RGA) by mass spectroscopy (MS) attached to an in-house-built temperature-programmed desorption (TPD) setup. The sample was contained in a stainless-steel autoclave and heated from RT to 600 °C ($DT/Dt = 2$ °C min⁻¹) under dynamic vacuum. The pressure in the autoclave was measured using an Alcatel ACC 1009 vacuum gauge. The ratios of selected gas components (H₂, B₂H₆, and BF₃) were roughly estimated from peak area of calibrated mass spectra. The calibration was performed using NaAlH₄ and NaBF₄ as sources of H₂ and BF₃ gases, respectively, to determine the linear relationship between the MS signal and pressure for each gas species. The coefficient for the B₂H₆ spectrum was determined by fitting the sum of these calibrated spectra with the total pressure. Due to fragmentation of the gas molecules during ionization, the most intense signals from B₂H₆ and BF₃ were mass 26 (B₂H₄⁺) and 49 (BF₂⁺) and these signals were used for the analysis.

Infrared spectroscopy

Gas-infrared (IR) spectroscopy measurements were performed using a Vertex 70 FT-IR spectrometer (Bruker Optics) in the range 4000 to 600 cm⁻¹ with 0.5 cm⁻¹ resolution. The sample holder was connected to the gas IR cell and the set-up was degassed to 10⁻⁵ mbar. IR spectra of the evolved gases were recorded while continuously heating the sample in a closed system from RT to 300 °C ($DT/Dt = 3$ °C min⁻¹) and then at a constant temperature of 300 °C for about 1 hour. The sample NaBH₄-NaBF₄ (1 : 0.1, S1, 0.083

g) was placed in a quartz tube under an argon atmosphere. After the experiment, the residual sample mass was 0.072 g corresponding to a mass loss of 0.011 g or ca. 13 wt%. Molecular H₂ is IR inactive and the measurement aimed to detect other gases such as boranes or BF₃. A negative signal is recorded in the 1800–1600 cm⁻¹ region corresponding to the water vapor of the background.

Temperature-dependent FTIR experiments on solid samples were performed using a BioRad Excalibur Instrument equipped with a Specac Golden Gate heatable ATR set-up. The spectral resolution was set to be 1 cm⁻¹.

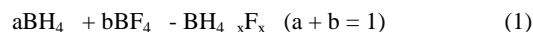
Sieverts measurements

Sieverts-type measurements were performed for samples of NaBH₄–NaBF₄ (1 : 0.5, S2) and NaBH₄ (R1) using a PCTpro 2000 instrument from Hy-Energy.⁴⁰ The samples were loaded in an autoclave and sealed in an argon atmosphere. The Sieverts-type desorption experiments were performed at p(H₂) = 1 bar from RT to 300 °C (DT/Dt = 4 °C min⁻¹), followed by constant temperature T = 300 °C for 2 h, heating from 300 to 550 °C (DT/Dt = 4 °C min⁻¹) and prolonged annealing at T = 550 °C. Hydrogen absorptions were conducted at a fixed temperature of 450 °C for 24 hours at p(H₂) = 130 bar.

3 Results and discussion

Theoretical calculations

DFT calculations on all 5 isolated BH_{4-x}F_x ions (x = 0 to x = 4) showed that these ions are stable, i.e. no imaginary vibrational frequency was found. The corresponding bond length and angles, the calculated IR spectra as well as the computed isotropic magnetic shielding tensor values are given in the ESI,† Tables S1–S3 and Fig. S1. The total energy (zero point corrected energy) is computed for the BH_{4-x}F_x ions (x = 0 to x = 4), which can be used to estimate the reaction energy (at 0 K) for reaction (1).



The calculated reaction energy for the formation of the ions BH₃F, BH₂F₂ and BHF₃ was 52, 54 and 28 kJ mol⁻¹, respectively. The results indicate that the formation of all mixed hydrogen–fluorine compounds is significantly endothermic (up to ca. 55 kJ mol⁻¹).

In situ SR-PXD

The samples of NaBH₄–NaBF₄ (1 : 0.5, S2 and 1 : 0.5, S2-200) were studied using in situ SR-PXD in the temperature range from RT to 385 °C. The first diffractogram in Fig. 1a measured at 23 °C for sample NaBH₄–NaBF₄ (1 : 0.5, S2-200) reveals Bragg diffraction peaks from NaBH₄ and o-NaBF₄. This suggests that no reaction occurred during ball milling and thermal activation of sample S2-200 (200 °C/72 h) prior to the SR-PXD analysis. During heating, the transformation from orthorhombic o-NaBF₄ to hexagonal h-NaBF₄ polymorphs is observed at 221 °C, in accordance with previous studies where this transition was observed at 227 °C.⁴¹ The Bragg reflections from h-NaBF₄ disappear at 273 °C, which is significantly lower than the reported melting point, T_{mp}(NaBF₄) = 357 °C.⁴¹ The diffracted intensity from NaBH₄ continuously decreases during heating from RT to 211 °C due to increasing thermal vibrations in the material. This is also observed for NaBH₄ (R1), see Fig. S2 in the ESI.† NaBH₄ in sample S2-200 decomposes between 211 and 320 °C, which is a significantly lower temperature than the range 450 to 500 °C observed for NaBH₄ (R1), see Fig. S2 (ESI†). Formation of NaF is observed in the temperature range 269 to 350 °C. Integrated, normalized diffracted intensities for selected well-resolved reflections from the observed compounds are visualized in Fig. 1b. The transformation from o- to h-NaBF₄ at 221 °C is fast and the decomposition of h-NaBF₄ is almost equally fast. Interestingly, the onset of sodium fluoride, NaF, formation occurs when almost all h-NaBF₄ is decomposed leaving a ‘gap’ with limited amounts of crystalline material in the sample. This suggests the presence of amorphous intermediates during decomposition of NaBH₄–NaBF₄.

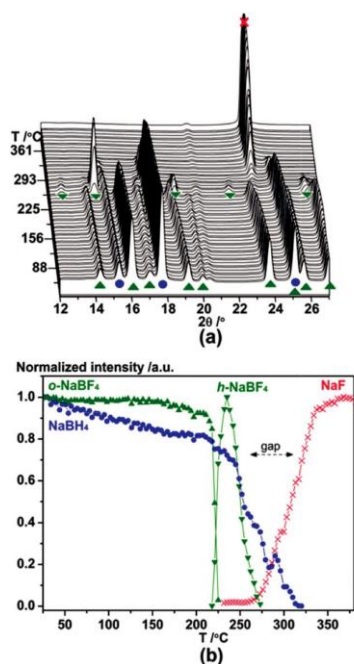


Fig. 1 In situ SR-PXD data (a) measured for $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2-200) in the temperature range of RT to 385 1C with $DT/Dt = 5 \text{ 1C min}^{-1}$, $\lambda = 0.94499 \text{ \AA}$, using beam line I711 at MAX-lab. (b) Normalized integrated diffracted intensities for the crystalline compounds in the sample. Symbols: \blacktriangle NaBH_4 ; \bullet $o\text{-NaBF}_4$; \square $h\text{-NaBF}_4$; \blacklozenge NaF .

In a similar in situ SR-PXD study of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) the same 'gap' was observed during decomposition, see Fig. S3 (ESI†). However, after disappearance of diffraction from $h\text{-NaBF}_4$ a few of the following diffractograms contain Bragg peaks from a new compound. Numerous diffraction experiments were conducted, also with other sample compositions not included in this publication, but only in one case was the new set of diffraction peaks is sufficiently intense to allow indexation (Fig. 2 and Fig. S3, ESI†), using a cubic unit cell, $a = 6.7616(6) \text{ \AA}$

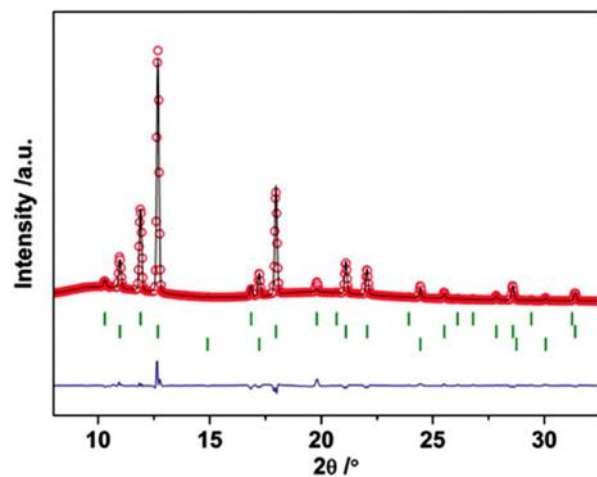


Fig. 2 Rietveld refinement of the in situ data of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) collected at $T = 208 \text{ 1C}$ with $\lambda = 0.70082 \text{ \AA}$. Symbols: observed data (red circles), calculated fit (black line) and the difference plot (blue line). Green tick marks indicate reflections from $\text{NaBH}_{2.1}\text{F}_{1.9}$ (top), NaBH_4 (mid) and NaF (bottom).

($V = 309.13(4) \text{ \AA}^3$, and possible space group $Fm\bar{3}m$). Thus, this compound may have a Rock salt type structure isomorphous to NaBH_4 but with a larger unit cell volume. A structural model for Rietveld refinement was constructed with fluorine and hydrogen statistically distributed on the same position as hydrogen in the NaBH_4 structure. The refined composition is $\text{NaBH}_{2.1}\text{F}_{1.9}$ (at $T = 208 \text{ 1C}$, see Fig. 2) in agreement with a unit cell volume increase of 21.0% ($V/Z = 77.3 \text{ \AA}^3$) compared to that for NaBH_4 ($V/Z = 63.9 \text{ \AA}^3$, $T = 208 \text{ 1C}$) and a decrease of 7.4% compared to NaBF_4 ($V/Z = 83.5 \text{ \AA}^3$, $T = 207 \text{ 1C}$).⁴¹ In fact, the unit cell volume for NaBH_4 in sample S2 (see Fig. 2) is slightly larger than the value for pristine NaBH_4 ($V/Z = 61.1 \text{ \AA}^3$ at $T = 210 \text{ 1C}$, see Fig. S2, ESI†). However, the fluorine substitution appears to be within the experimental uncertainty and cannot be estimated accurately.

NMR spectroscopy

The ^{11}B MAS NMR spectrum of the central and satellite transitions for the $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) sample before heating (Fig. 3a) contains two sets of resonances with centerbands at $d(^{11}\text{B}) = 1.7 \text{ ppm}$ and $d(^{11}\text{B}) = 41.9 \text{ ppm}$, corresponding to the isotropic chemical shifts of NaBF_4 and NaBH_4 , respectively.^{42,43} The centerband from NaBH_4 exhibits a linewidth of $\text{FWHM} = 0.6 \text{ ppm}$ in the ^1H decoupled ^{11}B MAS spectrum (Fig. 3a), whereas it is somewhat larger ($\text{FWHM} = 3.2 \text{ ppm}$) for the NaBF_4 centerband. Integration of all resonances from the central and satellite transitions for the two compounds gives a $\text{NaBH}_4\text{-NaBF}_4$ intensity ratio of 1.0 : 0.37 which is in fair agreement with the reactant ratio used in the preparation of the sample $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2). This result shows that no reaction occurs during ball milling of the $\text{NaBH}_4\text{-NaBF}_4$ mixture, in agreement with the X-ray diffraction results.

The ^{11}B MAS NMR spectrum of sample S2-300 after heat treatment (300 1C for 1 hour) is shown in Fig. 3b and exhibits resonances from NaBF_4 , NaBH_4 and a new compound with a centerband resonance at $d(^{11}\text{B}) = 15.5 \text{ ppm}$ which is assigned ($\text{FWHM} = 3.6 \text{ ppm}$) and NaF , $d(^{19}\text{F}) = 222.8 \text{ ppm}$ ($\text{FWHM} = 7.9 \text{ ppm}$). This is apparent from a comparison of the spectrum in Fig. S5a (ESI†) with a similar ^{19}F MAS NMR spectrum acquired for NaBF_4 (Fig. S5b, ESI†) and the chemical shift value, $d(^{19}\text{F}) = 221 \text{ ppm}$, reported for NaF .⁴⁶ An analysis of the intensities for the partly overlapping centerbands and spinning sidebands in the ^{19}F MAS NMR spectrum (Fig. S5a, ESI†) gives a ^{19}F intensity ratio of 1.0 : 0.49 for NaBF_4 and NaF , corresponding to a sample composition with a $\text{NaBF}_4 : \text{NaF}$ molar ratio of 1.0 : 1.95.

The ^{23}Na spectrum of the $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) sample (Fig. 4a) includes a narrow central-transition centerband from NaBH_4 at 8.4 ppm ($\text{FWHM} = 1.2 \text{ ppm}$) and a partly resolved second-order quadrupolar lineshape at about 20 ppm from NaBF_4 (Fig. 4c).^{41,47} ^{23}Na MAS NMR spectra of the central and satellite transitions for samples of NaBH_4 and NaBF_4 have been acquired (not shown), which allow determination of the ^{23}Na isotropic chemical shifts and quadrupole coupling parameters (Table 2) from simulations and least-squares fitting to the spinning sidebands from the satellite transitions.³⁹ The quadrupole coupling parameters for NaBF_4 (Table 2) are in good agreement with earlier reported parameters ($C_Q = 1008.4 \text{ kHz}$ and $Z_Q = 0.095$) determined from ^{23}Na single-crystal NMR at 23 1C.⁴⁸ Moreover, the ^{23}Na data determined for NaBH_4

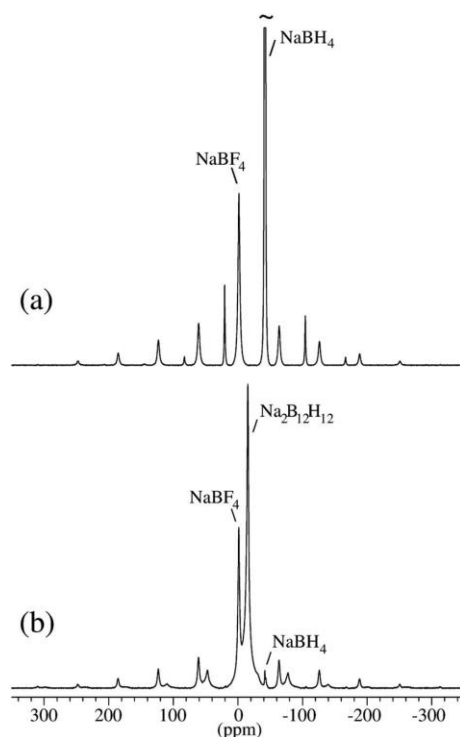


Fig. 3 ^{11}B MAS NMR spectra of the central and satellite transitions for (a) NaBH_4 - NaBF_4 (1 : 0.5, S2) and (b) NaBH_4 - NaBF_4 (1 : 0.5, S2-300) after heating to $T = 300$ IC for 1 h. The spinning sidebands from the satellite transitions associated with the centerband resonance at 15.5 ppm extend further than the selected spectral region shown in the figure. Both ^{11}B MAS NMR spectra have been acquired at 9.4 T with ^1H decoupling and a spinning speed of $n_R = 8.0$ kHz, using a short excitation pulse ($t_p = 0.5$ ms) and a relaxation delay of 30 s. The narrow resonance at 41.9 ppm from NaBH_4 is cut-off at 1/2 of its total height in (a) to $\text{Na}_2\text{B}_{12}\text{H}_{12}$ on the basis of the recently reported ^{11}B chemical shift ($d(^{11}\text{B}) = 15.4$ ppm, 9.4 T) for this compound.⁴⁴ The centerband resonance from $\text{Na}_2\text{B}_{12}\text{H}_{12}$ at $d(^{11}\text{B}) = 15.5$ ppm is slightly broader (FWHM = 3.4 ppm) than the centerband of NaBF_4 (FWHM = 3.1 ppm) and much broader than the center-band from NaBH_4 (FWHM = 0.7 ppm).

Examination of the intensities for the central-transition centerbands reveals relative ^{11}B intensities of 0.26 : 0.72 : 0.02 for NaBF_4 , $\text{Na}_2\text{B}_{12}\text{H}_{12}$, and NaBH_4 , corresponding to the molar ratios of 0.26 : 0.06 : 0.02, respectively, indicating that $\text{Na}_2\text{B}_{12}\text{H}_{12}$ is the principal decomposition product of the S2-300 sample. PXD data measured for sample S2-300 only reveal Bragg reflections from NaBF_4 and NaF (see Fig. S4, ESI[†]), which suggest that $\text{Na}_2\text{B}_{12}\text{H}_{12}$ and the small amount of NaBH_4 are X-ray amorphous, similar to amorphous LiBH_4 observed by ^{11}B MAS NMR in a study of $\text{Y}(\text{BH}_4)_3$.⁴⁵ The above-mentioned results are in accordance with the ^{19}F MAS NMR spectrum of the S2-300 sample (Fig. S5a, ESI[†]), which only includes resonances from NaBF_4 , $d(^{19}\text{F}) = 159.2$ ppm agree well with the quadrupole coupling parameters reported recently from static-powder ^{23}Na NMR experiments ($C_Q = 0.154$ 0.003 MHz, $Z_Q = 0.10$ 0.05).⁴⁹ The ^{23}Na MAS NMR spectrum of the sample S2-300 (Fig. 4b) shows clearly that all NaBH_4 has decomposed and that NaF (Fig. 4d) is the principal sodium-containing compound after the heat treatment. The absence of NaBH_4 is in accord with the corresponding ^{11}B MAS NMR spectrum (Fig. 3b) which only contains a very low-intensity peak from NaBH_4 (2% intensity). In addition, a centerband resonance at 17.4 ppm is observed, which partly overlaps with the central transition from NaBF_4 . This resonance is assigned to X-ray amorphous $\text{Na}_2\text{B}_{12}\text{H}_{12}$, following the observation of this phase in the ^{11}B NMR spectrum (Fig. 3b, $d(^{11}\text{B}) = 15.5$ ppm).

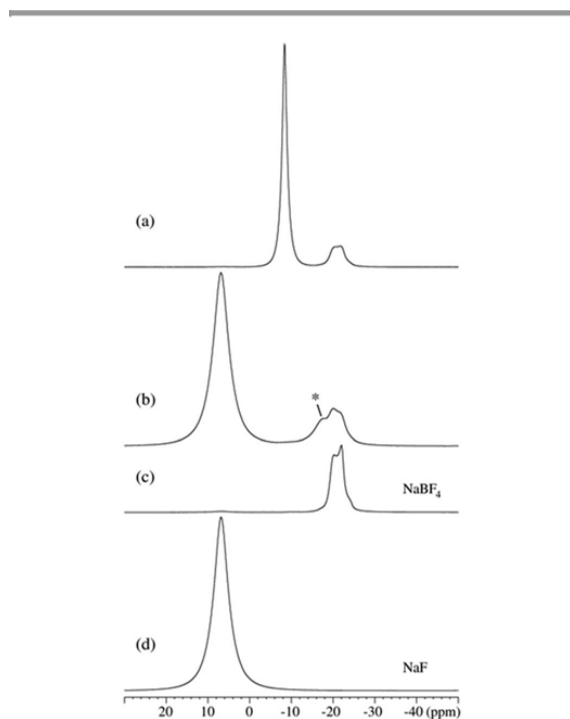


Fig. 4 ^{23}Na MAS NMR spectra (9.4 T, $n_R = 10.0$ kHz, $t_p = 0.5$ ms), illustrating the central-transition region for (a) $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2), (b) $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2-300) after heating to $T = 300$ 1C for 1 h and for samples of (c) NaBF_4 and (d) NaF . The spectra in (a) and (b) employed ^1H decoupling during acquisition. The asterisk in (b) indicates the centerband from the $\text{Na}_2\text{B}_{12}\text{H}_{12}$ decomposition product.

Table 2 ^{23}Na isotropic chemical shifts and quadrupole coupling parameters for NaBH_4 and NaBF_4 determined from ^{23}Na MAS NMR spectra of the central and satellite transitions

	$d_{\text{iso}}^{\text{a}}$ /ppm	C_Q^{b} /MHz	Z_Q^{b}
NaBH_4	8.40.2	0.147 0.002	0.08 0.01
NaBF_4	18.60.2	0.998 0.002	0.08 0.01

^a ^{23}Na isotropic chemical shift relative to a 1.0 M aqueous solution of NaCl . ^b The quadrupole coupling parameters are defined as $C_Q = (eQ/h)V_{zz}$ and $Z_Q = (V_{yy} V_{xx})/V_{zz}$, where V_{ii} are the principal elements of the electric field gradient tensor following the definition: $|V_{zz}| Z$, $|V_{xx}| Z |V_{yy}|$, Q is the nuclear electric quadrupole moment of ^{23}Na and e , the charge of the electron.

The sample S2 heat-treated at 275 1C (S2-275) has also been characterized by ^{11}B , ^{19}F , and ^{23}Na MAS NMR. The ^{23}Na MAS NMR spectrum (not shown) is dominated by the resonances from NaBH_4 and NaBF_4 in an approximate 2 : 1 ratio. Only a low-intensity resonance from NaF is observed, constituting 3.5% of the total central-transition intensities, thereby demonstrating that only a minor part of the sample has decomposed by heat-treatment at 275 1C. This is also apparent from the ^{11}B MAS NMR spectrum (Fig. 5a), which is dominated by the centerbands and spinning sidebands from NaBH_4 and NaBF_4 . However, a very low-intensity (0.004%) centerband at $d(^{11}\text{B}) = 15.5$ ppm from $\text{Na}_2\text{B}_{12}\text{H}_{12}$ can also be identified. More interestingly, the ^{19}F MAS NMR spectrum of the S2-275 sample (Fig. 5b) clearly reveals the presence of two new fluorine environments by the resonances at $d(^{19}\text{F}) = 144.2$ ppm and 150.6 ppm in addition to the dominating peak at $d(^{19}\text{F}) = 159.2$ ppm from NaBF_4 . The new resonances are ascribed to fluorine that substitutes for hydrogen in the BH_4 units of NaBH_4 . The SCF GIAO calculated isotropic ^{19}F magnetic shielding tensor yields a value of 360.5 ppm (absolute shielding) for fluorine in BF_4^- , and a value of 376.8 ppm for fluorine in BF_2H_2^- , corresponding to a positive shift of ca. 16 ppm (see Table S3, ESI†), similar to the one observed experimentally. In contrast, the calculated isotropic ^{11}B isotropic shifts for BF_4^- , BF_3H and BF_2H_2^- only exhibit a 3 ppm variation, which is within the experimental resolution, considering the line-widths of the centerband resonances. Thus, BF_4^- , BF_3H and BF_2H_2^- cannot be distinguished experimentally under the ^{11}B MAS NMR conditions used here.

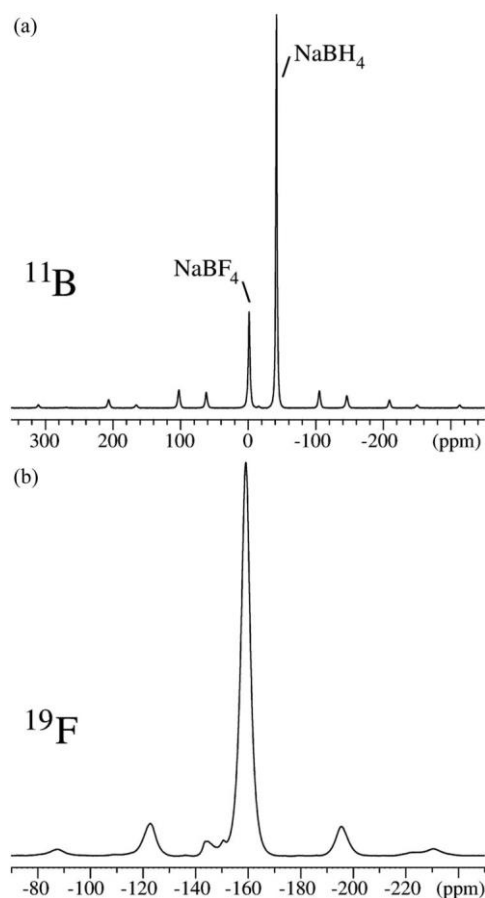


Fig. 5 ^{11}B and ^{19}F MAS NMR spectra (7.1 T, $n_R = 10.0$ kHz) of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5) after heating to $T = 275$ °C for 1 h (S2-275), obtained with relaxation delays of 10 s and 8 s, respectively.

Temperature-dependent infrared spectroscopy

The samples of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 1, S4) and $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.33, S5) were studied using FT-IR as a function of increasing temperature with steps of 10 °C from RT to 280 °C and then cooled to RT (see Fig. S6 and S7, ESI†). The initial spectra suggest the presence of a physical mixture, as no new bands besides those of NaBH_4 and NaBF_4 are observed (Fig. S8, ESI†). Upon heating, new bands at ca. 800 and 1200 cm^{-1} are observed at $T > 230$ °C. Fig. S9 (ESI†) compares the spectra of the sample $\text{NaBH}_4\text{-NaBF}_4$ (1 : 1, S4) measured at RT and after heating to 280 °C.

As a consequence, new bands are observed at 792, 900, 1198 and 1248 cm^{-1} . Besides the band at 792 cm^{-1} , all other new bands fall in the range of the frequencies calculated (for gaseous molecules) for intermediate $\text{BH}_4\text{-F}_x$ ions (see Fig. S9, ESI†), supporting the conclusions from the NMR experiments. It is interesting to note that the B-H stretching mode region (between 2000 and 2500 cm^{-1}) does not appear to be strongly changed by the heat treatment. Note that the B-H stretching modes are subject to strong Fermi resonances, making it difficult to analyze this spectral region.⁵⁰ The results for the 1 : 0.33 mixtures are similar to those of the 1 : 1 mixture (see Fig. S6 and S7, ESI†).

Residual gas analysis

The gas released from samples of $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.1, S1) and $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) was investigated by TPD-MS in the temperature range RT to 600 °C, see Fig. 6. NaBH_4 (R1) and NaBF_4 (R2) were also measured as references and a zoom (intensity 10) of Fig. 6a is provided in Fig. S12 (ESI†). The TPD-MS of NaBH_4 reveals hydrogen release in two steps, at $T = 476$ and 519 °C, respectively. The TPD-MS spectrum of NaBF_4 shows release of BF_3 at 398 °C. A large H_2 -signal with a peak temperature of 305 °C is observed for sample S2. Mass fragments of B_2H_6 and BF_3 were also detected in the same temperature range, see Fig. 6a. The integrals of the calibrated MS profiles can be used to estimate the relative amounts of the gases released. Sample $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) releases 89% H_2 together with minor fractions of B_2H_6 (3%) and BF_3 (5%).

For sample $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.1, S1) the relative amounts of H_2 , B_2H_6 , and BF_3 are 88, 4 and 8%, respectively. However, a major part of hydrogen is released at 483 1C while B_2H_6 and BF_3 are detected at 277 1C, see Fig. 6b. Interestingly, this hydrogen release is observed at reduced temperatures, 850 1C below pristine NaBH_4 . A MS signal corresponding to the mixed fluorine-hydrogen ion (BFH^+ , $m/z = 31$) is also detected in both samples, which may indicate decomposition of B-H-F containing compounds in the samples.

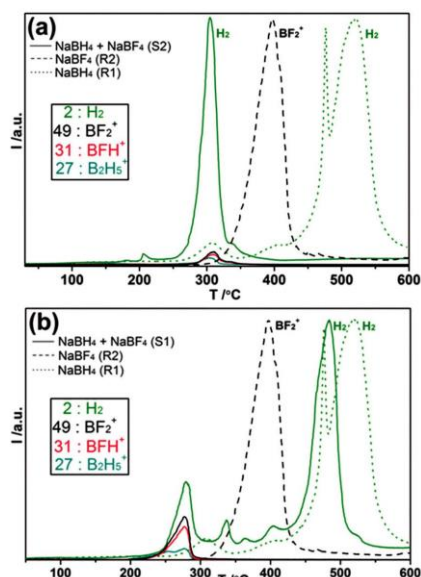


Fig. 6 TPD-MS measurements performed in the temperature range from RT to 600 1C ($\text{DT}/\text{Dt} = 2 \text{ 1C min}^{-1}$) for samples (a) $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) and (b) $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.1, S1). For comparison, both figures show data for the individual compounds NaBH_4 (R1) and NaBF_4 (R2). The mass fragments detected correspond to H_2 , B_2H_6 , and BF_3 .

Infrared spectra of the gases evolved during decomposition of the $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.1, S1) and $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.5, S2) samples were measured, see Fig. S10 and S11 (ESI[†]). The first IR signal appeared when the gas concentration in the cell was sufficient to reach the instrument sensitivity, which depends on the absorbance coefficient of each gas. The first signals for BF_3 and B_2H_6 were recorded at 90 1C, which means that desorption of these species started just below this temperature.

Thermal analysis

DSC and TGA measurements were conducted for $\text{NaBH}_4\text{-NaBF}_4$ (1 : 0.1, BM, S1), (1 : 0.5, BM, S2) and (1 : 0.5, HM, S3) and are compared with results for NaBH_4 (R1) and NaBF_4 (R2) (Fig. 7). The data were collected at temperatures from RT to above 450 1C (heating rate 5 1C min^{-1}) and the results are listed in Table S4 (ESI[†]).

The DSC profile of NaBH_4 (R1) shows endothermic signals at $T = 484$ and 540 1C assigned to melting and decomposition. The corresponding TGA mass loss (28 wt%, observed) between 477 and 600 1C is larger than the gravimetric hydrogen content of NaBH_4 , $r_m = 10.7 \text{ wt\% H}_2$, which may be due to melting and foaming of NaBH_4 during decomposition resulting in loss of

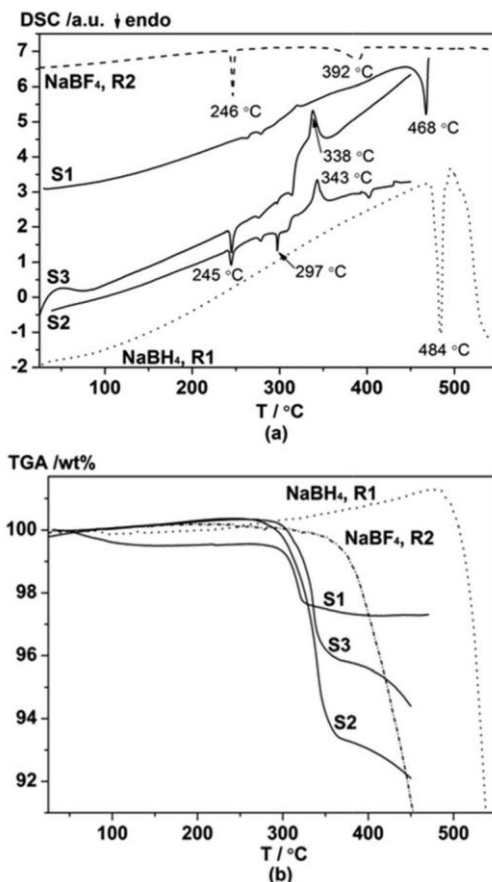
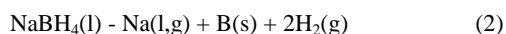
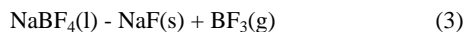


Fig. 7 (a) Differential scanning calorimetry (DSC) conducted from RT to >450 IC (DT/Dt = 5 IC min⁻¹) for NaBH₄-NaBF₄ (1 : 0.1, BM, S1), (1 : 0.5, BM, S2), (1 : 0.5, HM, S3), NaBH₄ (R1), and for NaBF₄ (R2). (b) Thermogravimetric analysis (TGA) conducted simultaneously with the DSC. The weight loss observed for samples S1–S3 at T o 380 IC appears to be related to the exothermic signal in the DSC.

material and possibly also decomposition of sodium hydride, NaH, and evaporation of sodium according to reaction scheme (1).^{51,52}



The DSC profile of NaBF₄ (R2) reveals an endothermic signal at T = 246 IC assigned to the o- to h-NaBF₄ polymorphic transformation. A broad endothermic signal with peak intensity at T = 392 IC is associated with an observed mass loss of 33 wt% observed from 392 to 600 IC. Full decomposition of NaBF₄ to NaF and BF₃ according to reaction scheme (3) corresponds to a calculated mass loss of $Dm/m(\text{BF}_3) = 61.8$ wt%, which occurs at temperatures above the melting point, $T_{\text{mp}}(\text{NaBF}_4) = 357$ IC.⁴¹



The DSC profile of NaBH₄-NaBF₄ (1 : 0.1, S1) shows weak endothermic signals at T = 263 and 278 IC, assigned to decomposition as observed by TPD-MS. A TGA mass loss of 2.3 wt% is recorded in the temperature range 300 to 320 IC. At 321 and 468 IC a weak exothermic and a stronger endothermic event is recorded and assigned to the formation of Na₂B₁₂H₁₂ and the melting of excess NaBH₄, respectively. For NaBH₄- NaBF₄ (1 : 0.5, BM, S2) and (1 : 0.5, HM, S3) endothermic signals are observed at T = 245, 278 and 297 IC for both samples and also at 314 IC for S3. The first endothermic event is assigned to the o- to h-NaBF₄ polymorphic transformation whereas the second event, at T = 278 IC, cannot directly be coupled with any reaction observed by in situ SR-PXD involving crystalline reactants. The endothermic events at 297 and 314 IC are correlated with the mass loss observed in the temperature range 300 to 350 IC of 7.0 and 4.5 wt% for S2 and S3, respectively, and also to the significant release of hydrogen detected by TPD-MS. A broad exothermic signal observed in the temperature range B315 to B350 IC with a peak value at T B 340 IC may be assigned to multiple reactions in the sample, e.g. formation of Na₂B₁₂H₁₂. The DSC and TGA profiles of the ball-milled and physically mixed samples of NaBH₄-NaBF₄ (1 : 0.5, BM, S2 and 1 : 0.5, HM, S3) are similar, but also reveal some differences, e.g. more solid-state chemical reactions in the HM sample in the temperature range B315 to 350 IC are stronger, which lead to a smaller mass loss.

Sieverts measurements

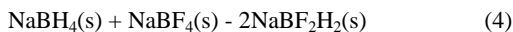
The reversible hydrogen storage properties of NaBH₄-NaBF₄ (1 : 0.5, S2) were investigated using the Sieverts approach, see Fig. S13 and Table S5 (ESI†). During the first desorption NaBH₄-NaBF₄ (1 : 0.5, S2) releases 9.1 wt% H₂-NaBH₄ and 3.6 and 3.2 wt% H₂-NaBH₄ during the second and third desorption, respectively. Thus, the reversible capacity of the system NaBH₄-NaBF₄ appears to be improved as compared to NaBH₄ (R1) used as a reference. NaBH₄ (R1) releases 6.0 wt% H₂ during 105 h (the first 12 h are shown in Fig. S13, ESI†) corresponding to 56% of the theoretical hydrogen capacity $r_m(\text{H}_2) = 10.7$ wt%, assuming formation of NaH. Complete dehydrogenation requires higher temperatures due to the back pressure of $p(\text{H}_2) = 1$ bar used during desorption. Rehydrogenation was performed at $T = 450$ °C, $p(\text{H}_2) = 130$ bar for 24 h, but the second and third dehydrogenation only release 0.69 and 0.65 wt% H₂, i.e. 6% of the theoretical capacity. NaBH₄ is expected to absorb hydrogen at higher temperatures, 550 to 700 °C.⁵¹ Recent research shows that addition of nano-porous carbon facilitates hydrogen uptake for bulk NaBH₄ significantly.⁵³

In order to address the possible effect of sodium fluoride, NaF, on the hydrogen storage properties a sample of NaBH₄-NaF (1 : 0.25, S6) was investigated. The first desorption of S6 resembles pure NaBH₄ with a total gas release of 4.9 wt% and 1.1 wt% in both second and third desorption, see Fig. S14 (ESI†). Thus, NaF appears to have a positive effect on hydrogen adsorption in NaBH₄ possibly by limiting the formation of foam and phase segregation and possibly also influenced by H-F exchange in NaBH₄.⁵²

The mechanism for hydrogen-fluorine exchange

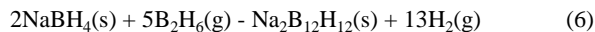
Hydrogen release from metal borohydrides is strongly dependent on the gas pressure.^{54,55} Decomposition of NaBH₄ at $p(\text{H}_2) = 0$ in the TGA experiment resulted in loss of the sample possibly by ‘foaming’, whereas a slow loss of 6 wt% H₂ over 105 h was observed at $p(\text{H}_2) = 1$ bar using the Sieverts method. Furthermore, the results presented here suggest that utilization of sodium fluoride as an additive may eliminate foaming of the sample.

A possible reaction mechanism for hydrogen-fluorine exchange in the NaBH₄-NaBF₄ system may be suggested based on the results presented in this paper. NaBH₄-NaBF₄ samples generally reveal decreasing amounts of crystalline material in the temperature range 250 to 310 °C, observed as a ‘gap’ in the diffraction data. In a few cases, weak diffraction from a new compound with the idealized composition, ‘NaBF₂H₂’, was observed, which may form according to reaction (4).

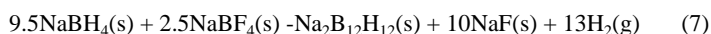


This new compound may account for the ¹⁹F NMR resonance observed at 144.2 ppm, shifted to higher frequency relative to NaBF₄ ($d(^{19}\text{F}) = 159.2$ ppm). This is further supported by the SCF GIAO calculations which predict a 16 ppm shift to a higher frequency for a BF₂H₂ unit relative to a BF₄ site.

Reaction (4) may occur in the phase boundary between individual NaBH₄ and NaBF₄ particles. This hydrogen-fluorine exchange reaction (4) may be the first of multiple reactions, which lead to amorphous products. The product from (4) may react with excess sodium borohydride and form diborane, B₂H₆, and the stable and inert salt sodium fluoride according to in situ SR-PXD data, see reaction (5).



The formed diborane may react with sodium borohydride and polymerize to the more stable closo-boranes, e.g. Na₂B₁₂H₁₂, see reaction (6). In fact, reactions (4)–(6) can be added to give the overall reaction (7).



Reaction (7) corresponds to a hydrogen mass loss of $r_m(\text{H}_2) = 4.31$ wt% H₂ and tends to suggest that >21 mol% NaBF₄ in

samples of NaBH₄-NaBF₄ corresponds to excess NaBF₄ and may lead to release of BF₃, as shown in eqn (3). The TGA results are in good agreement with reaction (7), i.e. sample NaBH₄-NaBF₄ (1 : 0.1, S1) releases half of this amount of gas, whereas S2 (0.666 : 0.334) releases slightly more. Interestingly, the major hydrogen release from NaBH₄-NaBF₄ (1 : 0.1, S1) is observed at significantly lower temperatures, B50 1C, as compared to NaBH₄. A drawback for the NaBH₄-NaBF₄ composite is the formation of stable closo-boranes, e.g. Na₂B₁₂H₁₂, which are generally considered difficult to rehydrogenate.^{56,57}

4 Conclusions

Direct observation of hydrogen-fluorine substitution in metal borohydrides was performed using in situ SR-PXD as a new Rock salt type compound with idealized composition NaBF₂H₂. Combined use of solid-state ¹⁹F MAS NMR and DFT calculations confirms the formation of a BF₂H₂ complex ion, which is also supported by combined use of FT-IR and DFT. This work shows that fluorine substituted borohydrides appear to be relatively unstable and tend to decompose to more stable compounds, e.g., the ionic compound NaF and the covalent, molecular BF₃ gas or amorphous products such as closo-boranes, e.g. Na₂B₁₂H₁₂. H-F exchange appears to be facilitated by less stable fluorine containing reactants (i.e. NaBF₄) as compared to the more stable reaction products formed during decomposition. The NaBH₄-NaBF₄ composite decomposes at lower temperatures (T B 300 1C) compared to NaBH₄ (T = 476 1C), preserves 30% of the hydrogen storage capacity after three hydrogen release and uptake cycles compared to 6% for NaBH₄ and more than 50% using prolonged absorption time. Thus, this work demonstrates that hydride-fluoride exchange in hydrogen storage materials may significantly change the physical properties. H-F exchange may facilitate hydrogen uptake, prevent foaming, phase segregation and loss of material during release of hydrogen by thermolysis. Furthermore, lightweight fluoride-containing materials are of increasing interest for other energy-related purposes, such as development of new types of batteries.

Acknowledgements

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