Thermal decomposition of sodium borohydride covered with polyethyleneimine

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Abstract

In order to use hydrogen as an energy carrier in the future as part of real-life technologies, efficient storage media, e.g. for mobile applications, are necessary. Here, borohydrides are attractive hydrogen storage materials because of their low mass and high hydrogen density. One of the promising candidates is sodium borohydride ($NaBH_4$) if its degradation at atmosphere can be hindered and its hydrogen release temperature can be lowered. To achieve this goal, $NaBH_4$ can be covered with a polyethyleneimine (PEI) layer [1]. We characterized changes the hydrogen desorption path of $NaBD_4$ induced by PEI coverage using quadrupole mass spectrometry and differential scanning calorimetry. In order to compare both hydrogen release paths we performed in situ X-ray diffraction (XRD) measurements at beamline BL9 of DELTA synchrotron radiation source using native and PEI-coated $NaBH_4$ while heating the samples up to 700°C with focus on phase transition, oxidation, and the initial stage of PEI-promoted hydrogen release.

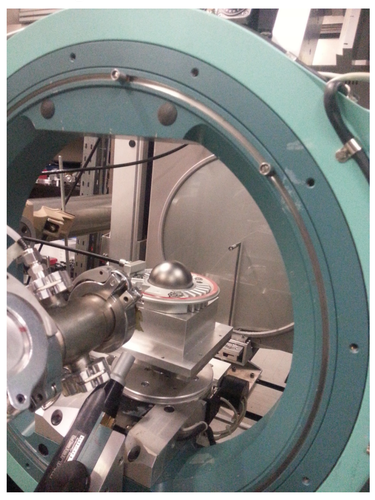
X-Ray diffraction and experimental setup

XRD measurements were performed at beamline BL9 at DELTA, Dortmund, using a MAR345 image plate scanner [2].
The photon energy was 27 keV with a beamsize of 0.8 x 1 mm^2.

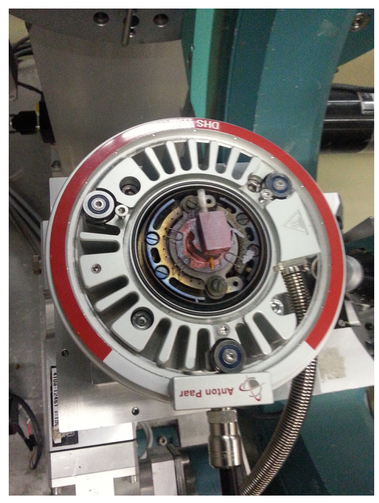
Samples (PEI/$NaBH_4$, $NaBH_4$, PEI) were filled in quartz glass capillaries and heated under vacuum and in air with an Anton Paar DHS 1100 domed hot stage.

In situ measurements were performed in the temperature range from 30°C – 700°C

Diffraction patterns were analyzed using FIT2D []



Diffractometer at beamline BL9 of DELTA synchrotron



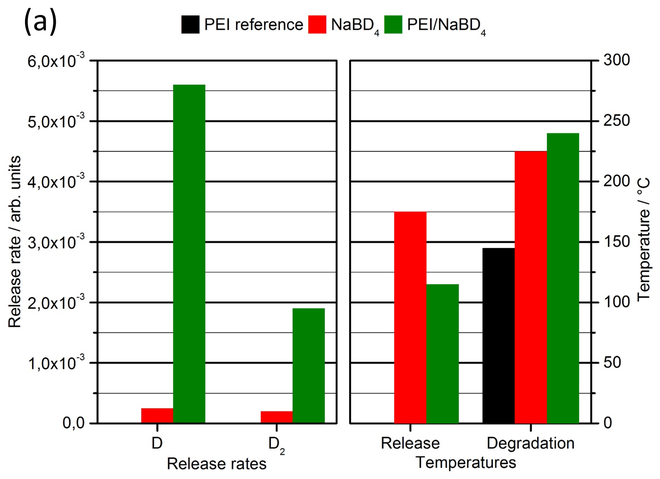
Anton Paar DHS 1100 domed hot stage with copper sample holder

Quadrupole mass spectrometry (QMS) and differential scanning calorimetry (DSC)

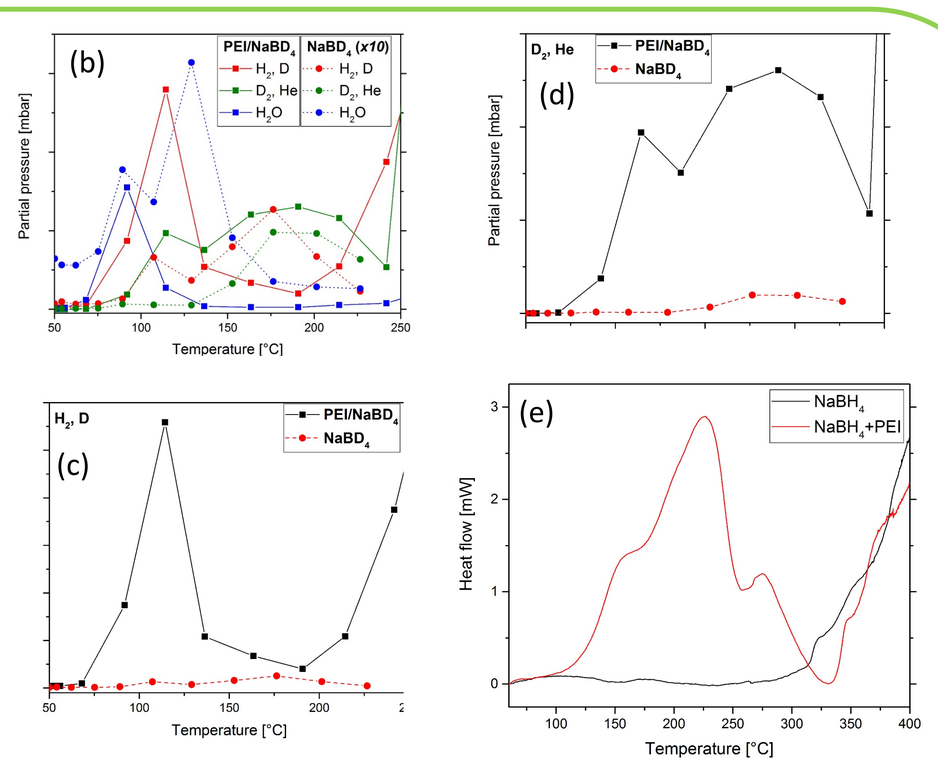
PEI affects the temperature behavior of $NaBD_4$ [1]:

- Significant increase of deuterium release
- Stabilization of $NaBD_4$ by PEI coverage
- Deuterium release sets in at lower temperature:
  - Desorption maximum of D at 120°C
  - Broad desorption maximum of D_2
- PEI coating enhances deuterium release

- PEI induced H-transport by vacancy creation in $NaBH_4$?
- Promising material for hydrogen storage.



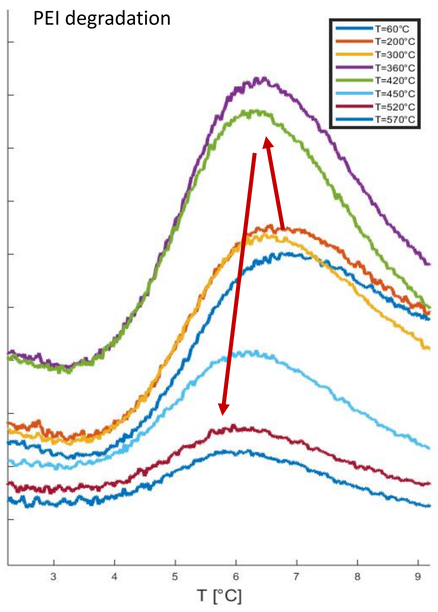
(a) QMS: Deuterium release rates and degradation temperatures



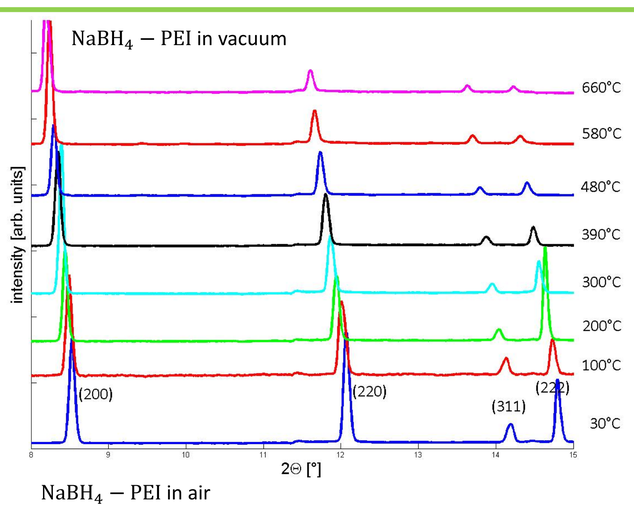
(b), (c), (d): QMS: Desorption rates from $NaBD_4$ – PEI compared to $NaBD_4$

(e) DSC measurements of $NaBH_4$and $NaBH_4$ – PEI

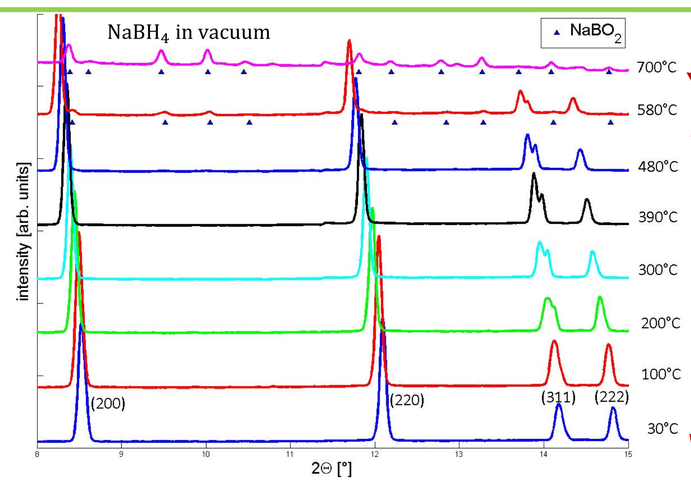
Experimental results

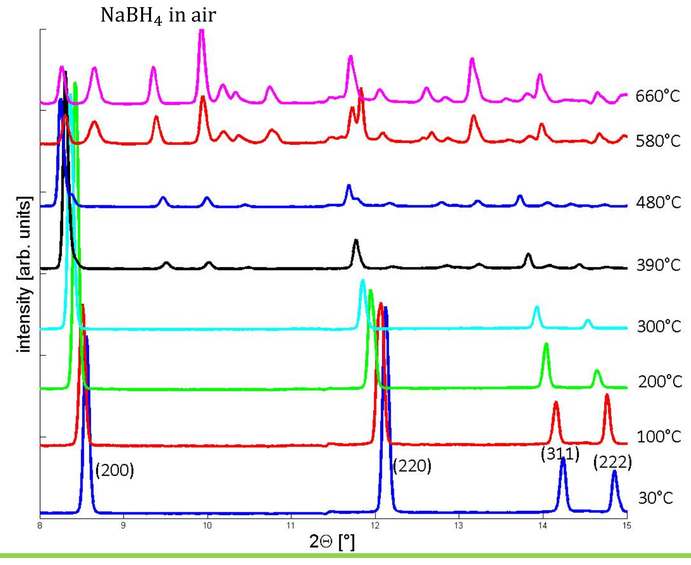


	$NaBH_4$	$NaBH_4$-PEI	Atmosphere
$NaBH_4$ decomposition	700°C 580°C	700°C 580°C	vacuum air
PEI degradation	- -	>420°C -	vacuum air
$NaBO_2$ detected	580°C 390°C	-	vacuum air

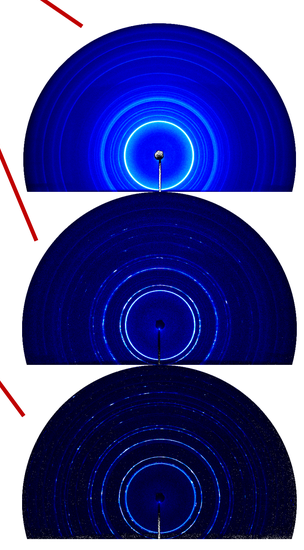


$NaBH_4$ – PEI in air





Picture to be added



MAR images of $NaBH_4$ in vacuum

Conclusion

- PEI coverage does not effect the decomposition temperature of $NaBH_4$
- Decomposition temperature strongly depends on reaction atmospehre
- PEI coverage hinders / reduces sample oxidation. Macroscopic degradation of PEI above 420°C
- Peak splitting observed for $NaBH_4$ in vacuum (H-vacancy creation at higher temperature?)

Outlook

- Rietveld analysis of structures and temperature dependence of lattice constants
- Study of the temperature regime up to 300°C to focus on initial hydrogen release
- Therefore, use sample rotation and annealing via nitrogen jet
- Study of different reaction atmosphere and possibly neutron diffraction experiments

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