



Article Effect of Vanadium Catalysts on Hydrogen Evolution from NaBH₄

Piotr Antoni Orłowski 1,2,* and Wojciech Grochala 1,*

- ¹ Centre of New Technologies, University of Warsaw, Żwirki i Wigury 93, 02-089 Warsaw, Poland
- ² Faculty of Chemistry, University of Warsaw, Pasteura 1, 02-093 Warsaw, Poland
- * Correspondence: p.orlowski@cent.uw.edu.pl (P.A.O.); w.grochala@cent.uw.edu.pl (W.G.)

Abstract: NaBH₄ is a very cheap and hydrogen-rich material, as well as a potential hydrogen store. However, the high temperature of its thermal decomposition (above 530 °C) renders it inapplicable in practical use. Here, we studied the effect of addition of diverse V-containing catalysts on thermal hydrogen desorption. It turns out that mechanochemical doping of NaBH₄ with vanadium metal, its oxides, or nanoparticles lowers the temperature of pyrolysis significantly. Notably, NaBH₄ milled for 3 h with 25 wt.% V₂O₅ or VO₂ releases ca. 70% of stored hydrogen in the temperature range of ca. 370–450 °C. On the other hand, precursors and solvents used to prepare rather uniform vanadium nanoparticles (~4 nm) suspended in THF or less uniform and larger ones (~15 nm) in odifluorobenzene have adverse effect on the purity of hydrogen evolved.

Keywords: sodium borohydride; vanadium; thermal decomposition; hydrogen storage materials; mechanochemical synthesis



Citation: Orłowski, P.A.; Grochala, W. Effect of Vanadium Catalysts on Hydrogen Evolution from NaBH₄. *Solids* **2022**, *3*, 295–310. https:// doi.org/10.3390/solids3020021

Academic Editors: Manickam Minakshi and Andrei Kovalevsky

Received: 20 January 2022 Accepted: 16 May 2022 Published: 18 May 2022

Publisher's Note: MDPI stays neutral with regard to jurisdictional claims in published maps and institutional affiliations.



Copyright: © 2022 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (https:// creativecommons.org/licenses/by/ 4.0/).

1. Introduction

Fossil fuels have been widely used as an energy source all over the world for centuries. Their intense usage has led to environmental pollution and climate change, and this has forced humanity to seek alternative, green energy sources and carriers. Hydrogen, next to none in its high gravimetric energy density, is a clean source of energy, with its combustion resulting only in water. This makes it a promising alternative to both fossil energy carriers and electric energy accumulators [1–5].

Sodium borohydride is one of the cheapest and most hydrogen-rich compounds known, having highly competitive volumetric hydrogen density [6]. Therefore, it is not surprising that much effort has been devoted to the possibility of using it as a hydrogen storage material. Hydrogen can be released from NaBH₄ either during its hydrolysis or upon thermal decomposition. Hydrolysis reactions in alkaline aqueous solutions take place at room temperature upon contact with a catalyst (so called Hydrogen-on-demand[®] technology [7]). However, the reversibility of this process is poor, as it is associated with the necessity to recycle very stable oxoborates(III) back to BH_4^- species. On the other hand, the pyrolysis profile has a maximum desorption peak above 500 °C [8] (values up to 534 \pm 10 °C at 1 bar of hydrogen [9] are given in the literature), which is quite high for mobile applications. Three main approaches taken to lower the decomposition temperature are catalytic enhancement of pyrolysis, tuning it via hydride mixing, and nanosizing of hydrogen-containing species [10–12]. Various dopants have been studied by numerous teams, and we can group them for convenience into four main categories (Tables 1-4): (I) first-period transition metal (TM) elements and their compounds, (II) second-period TM elements and their compounds, (III) lanthanides and their compounds, and (IV) other hydrides. Additionally, composites of NaBH₄ with diverse "inert" materials such as graphene and zeolites have been prepared, and their thermal profiles have been studied (Table 5). Last but not the least, attempts to prepare NaBH₄ nanoparticles to decrease the

| Sc [13] | Ti | V | Cr [13] | Mn [13] |
|--------------------------|--|---|--------------------------|---|
| ScF ₃ —501 °C | $\begin{array}{c} \text{Nano-493 °C [14]} \\ \text{TiF}_3 &300 °C [15] \\ 5\%_{\text{mol}} \text{TiF}_3 &300 °C [16] \\ \text{TiF}_4 & -522 °C [13] \\ \text{TiCl}_3 1:6 & -100 °C * [17] \\ \text{TiB}_2 & -503 °C [14] \\ \text{TiSiO}_4 & -489 °C [14] \end{array}$ | VF ₄ —499 °C [13] NaBH ₄ + PrF ₃ + VF ₃ 3:1:0.2—417 °C [18] V ₃ B—478 °C [14] | CrF ₃ —500 °C | MnF ₃ —483 °C |
| Fe [13] | Со | Ni | Cu [13] | Zn |
| FeF ₃ —498 °C | CoF ₃ —501 °C [13] Co ₃ B—480 °C [14] | Nano—483 °C [14] NiF2—452 °C [13] NiF2—453 °C [14] wt.10% Ni on Si/Al2O3—449 °C [14] NiCl2—460 °C [14] Ni3B—462 °C [14] | CuF ₂ —476 °C | ZnF ₂ —504 °C [13] ZnF ₂ 1:2—95 °C ** [19] |

thermal decomposition temperature of the pristine material are gathered in the last group (Table 6).

Table 1. Influence of the first-period transition metal-based dopants on thermal decompositiontemperature of NaBH4 (5%mol doping if not specified differently).

* polluted with B_2H_6 and diglyme; ** polluted with $B_2H_{6.}$

Table 2. Influence of the second-period transition metal-based dopants on thermal decomposition temperature of NaBH₄ ($5\%_{mol}$ doping if not specified differently).

| Y | Zr | Nb [13] | Rh [14] | Pd [14] | Ag [13] | Cd [13] |
|--|--------------------------------------|--|--|-------------|------------|--------------------------|
| $\begin{array}{c} YF_3 - 513 \ ^\circ C \ [13] \\ YF_3 \ 3:1 - 423 \ ^\circ C \ [20] \\ (x)YF_3 + (1 - x)GdF_3 \\ 3:1 \ [22]: \\ x = 2/3 - 449 \ ^\circ C \\ x = 1/2 - 446 \ ^\circ C \\ x = 1/3 - 440 \ ^\circ C \end{array}$ | ZrF4—503°C [13] ZrCl4—503 °C [21] | NbF5: 2% _{mol} —442 °C 10% _{mol} —379 °C 15% _{mol} —379 °C | Rh (5 wt.%) on Al ₂ O ₃ —476 °C | Nano—420 °C | AgF—498 °C | CdF ₂ —512 °C |

Table 3. Influence of lanthanide series metal-based dopants on thermal decomposition temperature of NaBH₄ ($5\%_{mol}$ doping if not specified differently).

| La [23] | Ce [13] | Pr [18] | Nd [24] | Ho [25] |
|--|--|-----------------------------|-----------------------------|-----------------------------|
| LaF ₃ 3:1—396 °C La 3:1—442 °C | CeF ₃ —506 °C CeF ₄ —502 °C | PrF ₃ 3:1—439 °C | NdF ₃ 3:1—413 °C | HoF ₃ 3:1—443 °C |

Table 4. Influence of co-milling of other hydrogen-rich compounds with NaBH₄ on its thermal decomposition temperature (molar ratio was used if not described differently).

| MH ₂ | Mg ₂ NiH ₄ [26] | NaNH ₂ | M(AlH ₄) _x | Li ₃ AlH ₆ [27] | MBH ₄ |
|---|---------------------------------------|--|---|---|---|
| M = Mg: 1:2-420 °C [28] 1:2-490 °C [29] 1:2 with 5% _{mol} of [30]: TiF ₃ 470 °C TiO ₂ 470 °C Zr470 °C Si470 °C BCC470 °C M = Ca: 1:6390 °C [31] | 5:4—~350 °C | 1:1—330 °C * [32] 2:1 with Co–Ni–B catalyst [33]: 1 wt.%—~300 °C 3 wt.%—~285 °C 5 wt.%—285 °C 7 wt.%—~285 °C | M = Li: 1:1 [16]: No catalyst—446 °C 5% TiF ₃ —~300 °C M = Ca: 2NaAlH ₄ + Ca(BH ₄) ₂ with 5 wt.% TiF ₃ —400 °C [34] | 1:1 (1 h)—400 °C 1:1 (24 h)—392 °C 1:2—430 °C 1:3—430 °C | M = Li 0.38:0.62: pure—350 °C [35] pure—420 °C [36] 60% _{vol} in carbon areogel—333 °C [35] M = K—472 °C [37] M = Mg—205 °C [38] M = Li, K, Mg, and Ca (equimolar)—330 °C [39] |

* polluted with ammonia.

| Ionic Liquids [40] | Carbon | Carbon Based | Zeolites [41] | Ah-BN [42] | NaBF ₄ ** [34] |
|--|---|---|---|------------|-----------------------------------|
| 1% _{mol} solution in: bmimBr—~165 °C bmimNTf ₂ —104 °C | 20% of scaffolds CMK-3 —235 °C and 380 °C * [43] ~25% of HSAG-500 [44]: infiltrated—~270 °C melted—~300 °C mixed—~320 °C | 45% fluorographite— 141 °C [45] graphene: 10%—370 °C [46] ?—426 °C [47] | MCM-22: 1:1—490 °C 1:2—503 °C 1:3—507 °C 1:4—508 °C SAPO-34: 1:1—483 °C 1:2—491 °C 1:3—493 °C 1:4—495 °C | 1:1—399 °C | 1:10 mol—468 °C 1:2 mol—305 °C |

Table 5. Thermal decomposition of NaBH₄ in its composite materials (mass ratio was used if not described differently).

* polluted with ammonia; ** polluted with BF_3 and $B_2H_{6\cdot}$

| Table 6. In | nfluence | of nanosiz | ing of NaE | BH₄ on its | thermal | decom | position | temperatu | re |
|-------------|----------|------------|------------|------------|---------|-------|----------|-----------|----|
| | | | | | | | | | |

| Solvented Ion Stabilization * [48] | Evaporation with 10% _{mol} of Ligands or Solvents [49] | Anti-Solvent Precipitation | Milled LiBH ₄ + NaCl |
|--|--|--|---|
| LiCl—495 °C MgCl ₂ —445 °C NaI—485 °C | Hexyloamine—489 °C dodecyloamine—476 °C octodecyloamine—473 °C tertabuthylamonium bromide—464 and 482 °C tetraoctylamonium bromide—484 °C tetradecyloamonium bromide—~500 °C dodecane—478 °C dodecanothiol—464 °C tri-decylic acid—~400 and 474 °C tetrabutylphosphonium bromide—471 °C | Bare—460 and 535 °C [50] Coated with: Ni—418 °C [50] Co—350 °C [51] Cu—400 °C [51] Fe—380 °C [51] Sn—450 °C [51] | Graphene coated (ultrasonicated and dried)—400 °C [47] Milled with graphene nanoflakes—~300 °C [52] Milled 1:10 mass with [53]: graphite—109 °C graphene oxide—114 °C carbon nanotubes—116 °C |
| | | | |

* polluted with buthylamine.

Some of the most spectacular results achieved via doping with the first-period TM species (Table 1) were seen for zinc(II) fluoride and titanium(III) chloride, which evolve hydrogen around 95 and 100 °C, respectively. However, as typical for the rather low temperature of thermal decomposition, H₂ gas is, in these cases, severely polluted with B₂H₆ or B₂H₆ and diglyme. For metals from the second TM period (Table 2), the lowest temperature of thermal decomposition of 379 °C was achieved for 10%_{mol} and 15%_{mol} doping with NbF₅. The third-period TM catalysts were also tested but the decrease in thermal decomposition temperature was not impressive (TaCl₅—460 °C and ReCl₃—465 °C [14]). In lanthanide series (Table 3), the best result was achieved for neodymium fluoride doping (413 °C).

Co-milling NaBH₄ with other hydrogen storage materials (Table 4), particularly protic ones, often leads to facile evolution of H₂ from a composite system. As for NaBH₄, particularly promising results were achieved for 5 wt.% Co-Ni-B doped 2NaNH₂/NaBH₄ mixture, milled in hexane environment, for which the temperature of pyrolysis with H₂ evolution dropped to a value as low as 285 °C. However, hydridic–protic stores rarely show sufficient reversibility [54,55].

If composites with diverse "inert" materials are considered (Table 5), substantial (45 wt.%) fluorographite addition resulted in the thermal decomposition point of 141 °C; an also interesting approach with the use of ionic liquid led to pure hydrogen desorption starting at 104 °C. Other composites usually yielded less appealing results.

The last group of proposed NaBH₄ modifications involves either nanostructurization or coating it with metal or graphene layers (Table 6) which could lead to a decomposition temperature as low as 350 $^{\circ}$ C for NaBH4 nanoparticles coated with cobalt.

It may be seen from the literature screening that vanadium compounds have rather seldom been used to modify the H₂-release properties NaBH₄, and only moderate results were achieved when using VF₃, VF₄, or V₃B as catalysts. This is quite disappointing in view of the fact that, from 40 to 100 °C, the γ phase of vanadium(II) hydride is known to exist in equilibrium with hydrogen gas and its metallic β form [56]. This implies a rather low temperature of H₂ release from VH₂, especially in an H₂-free atmosphere. Moreover, the process of H₂ release from VH₂ must have a rather low activation barrier, as it tends to be fast. Consequently, vanadium metal or its compounds (reduced in situ to VNPs) could act as catalysts and destabilize [BH₄]⁻ anions present in NaBH₄, thus decreasing the temperature of thermal decomposition of this material and leading to facile H₂ evolution at low temperature. Therefore, in this study, we researched doping of sodium borohydride with vanadium, vanadium oxides (V₂O₃, VO₂, V₂O₅), or vanadium nanoparticles and their effects on thermal stability of NaBH₄ hydrogen storage material.

2. Experimental

2.1. Materials

NaBH₄ (\geq 98%), LiAlH₄ 2.0 M solution in THF and catalysts V₂O₅ (\geq 99.6%), VO₂ (\geq 99%), and V₂O₃ (99.99%) were purchased from Sigma Aldrich (St. Louis, MO, USA). Ph₄PCl (98%) used in Ph₄PBH₄ synthesis was delivered by abcr GmbH (Karlsruhe, Germany). Solvents dichloromethane (DCM) (\geq 99.8% \leq 50 ppm H₂O) and tetrahydrofuran (THF) (\geq 99.8%, \leq 50 ppm H₂O) were purchased from ROTH (Karlsruhe, Germany), while o-difluorobenzene (o-DFB) (98%) was obtained from Fluorochem (Hadfield, UK). Before synthesis, DCM and THF were dried with P₂O₅ and distilled; o-DFB was degassed using a Schlenk line and LN₂. All solvents were then sealed in containers with 4 Å molecular sieves.

2.2. Equipment

A Vigor SG1200/750TS-F glovebox (Houston, TX, USA) was used for storing and preparing the samples; all reactions were performed in an inert gas (Ar) atmosphere (<10 ppm O_2 , <0.05 ppm H₂O) or using a Schlenk line. Mechanochemical doping was conducted in a stainless-steel disc bowl using a Testchem vibration mill (1400 RPM). Suspensions of VNPs were firstly sonicated using Polsonic Sonic-6D in an ice-cooled water bath. Thermal decomposition analysis of the samples was investigated using a thermogravimeter (TGA) combined with differential scanning calorimeter (DSC) from Netzsch STA 409 PG (NETZSCH-Gerätebau GmbH, Selb, Germany) using Al₂O₃ crucibles. TGA/DSC chamber was constantly purged at a constant Ar (99.9999%) flow rate of 80 mL·min⁻¹. The evolved gases were analyzed with a quadrupole mass spectrometer (MS) QMS 403 C (Pfeiffer Vacuum, A β lar, Germany), connected to the TGA/DSC device by a quartz capillary preheated to 200 °C to avoid condensation of low-boiling volatiles. Fourier-transform infrared spectroscopy (FTIR) of all solid products of doping was measured using a Vertex 80v FT-IR spectrometer (Bruker, Billerica, MA, USA). Anhydrous KBr was used as a pellet material.

2.3. Synthesis and Doping

Vanadium nanoparticles (VNPs) were synthesized via reduction of vanadium(III) compounds. The THF suspension was prepared using vanadium (III) chloride and LiAlH₄ solutions in THF. Then, 10 mL of a stoichiometric amount of reducer solution was added dropwise to 30 mL of 0.05 M solution of VCl₃ under intense stirring. In the case of VNPs suspended in o-DFB, acetonitrile-coordinated vanadium(III) bis(tetra(nonafluoro-tert-butoxy)aluminate) monochloride (VCl(Al(OC(CF₃)₃)₄)₂·5ACN) was synthesized according to [57] and used as source of vanadium and tetraphenylphosphonium borohydride (Ph₄PBH₄) as a reducer and dissolved in o-DFB. Next, 20 mL of 0.015 M reducer solution was added dropwise to 20 mL of 0.005 M solution of vanadium salt, under intense stirring. Excess of the reducer was used to ensure complete reduction of vanadium cation. Both suspensions were stirred for 24 h before use and denoted in dependence of solvent used as VNPs_{THF} and VNPs_{O-DFB}. Attempts of purification by centrifuging brought no results

since VNPs could not be separated from their suspension that way and were used without further purification. The rationale behind the use of VNs is in their large specific area, which could imply fast and uniform catalysis of H_2 evolution within the entire bulk of the hydrogen store.

Doping was carried out by mixing 5 or 25 wt.% of powder catalysts (V, V₂O₃, VO₂, or V₂O₅) with NaBH₄ and milling in 100 g batches for 5 or 30 min in milling periods of 1 and 5 min respectively, altered with liquid nitrogen (LN₂) cooling to avoid overheating of samples. In addition, one V₂O₅ sample was also milled for 3 h in 20 min periods. The samples were then denoted using the Na:XY T pattern, where X stands for the catalyst used, Y is its wt.% amount, and T is the milling time; the samples were tested with TGA/DSC in 20–450 or 20–600 °C range with 5 K/min heating rate together with MS of evolved gases and compared with milled pure NaBH₄ as reference. For activation energy studies of Na:V₂O₅25%_180 min, three additional heating rates were used: 10, 1, and 0.5 K/min.

In the case of VNP doping (100 mg) of NaBH₄, 2 or 10 mL of VNPs_{THF} or VNPs_{O-DFB}, respectively, were added to the glass ampoule, which was firstly sonicated for 20 min in ice-cold bath, and then dried under a dynamic vacuum using a Schlenk line until the pressure dropped to 5×10^{-2} mbar and for 30 min after. Samples were then transferred to a milling bowl, further milled for 30 min in the same way as powder-doped samples, and denoted Na:VNPs_{THF} and Na:VNPs_{O-DFB}, respectively.

3. Results

3.1. Synthesis of VNPs

TEM analysis of synthesized VNPs (Figure 1) showed that nanoparticles prepared in THF using LiAlH₄ are smaller and more uniform than those synthesized in o-DFB.



Figure 1. TEM images of VNPs prepared in THF and o-DFB solutions.

The particle radius distribution based on several TEM images (Figure 2) was prepared in order to estimate size and standard deviation of their size. As calculated, mean sizes of VNPs were 14.86 \pm 7.71 nm and 3.57 \pm 0.93 nm for o-DFB and THF suspensions, respectively. The VNPs_{THF} size histogram could be described with a normal distribution, being more uniform in size and smaller than VNPs_{O-DFB} which had various, aspherical shapes and a size histogram looking more like a lognormal distribution. Since LiAlH₄ is a much stronger reducer than Ph₄PBH₄, vanadium is reduced more quickly; therefore, nanoparticles grow to a more uniform, smaller size. Unstirred VNPs are stable and stay suspended without any sign of agglomeration for months, despite no surfactant being used.



Figure 2. VNPs size distribution depending on route of synthesis.

3.2. Thermogravimetric and Spectroscopic Analysis of Doped Samples

To screen the behavior of diverse V dopants, samples with 5 wt.% of catalyst milled in five short periods of 1 min each were preliminarily studied. The TG–DSC profiles for these samples, as well as a reference sample of pristine NaBH₄ (milled in a similar way), together with the ion current for diverse mass peaks in the MS of the evolved gas, are shown jointly in Figure 3. The picked masses in MS correspond to hydrogen, water, and diborane fragmentation patterns.

There was a relatively minor effect of these short-milled dopants on the thermal decomposition of NaBH₄, with a noticeable effect seen only for VO₂ (inflection of the TG curve at 402 °C associated with mass loss of 0.6 wt.% up to 450 °C) and a more pronounced one for V₂O₅ (clear mass decrease above 398 °C, associated with the total mass loss of 1.0 wt.% up to 450 °C). At the same time, there was no visible decomposition in the milled pristine NaBH₄ sample. MS clearly indicated that these events corresponded to endothermic H₂ evolution but not associated with water or diborane.

It is worth mentioning that the small mass drift observable on a few TGA curves is a phenomenon resulting from apparatus imperfection and cannot always be avoided (despite hours-long weight stabilization). However, the sudden mass drop resulting from the decomposition reaction can be clearly distinguished; thus, it does not result in data misinterpretation in qualitative studies. Encouraged by this result, we further focused on V₂O₅-doped samples. Another three samples with increased content of vanadium pentoxide of 25 wt.% were prepared via 5, 30, and 180 min milling. As-obtained samples were inspected with FTIR, and the results were compared to those for pristine NaBH₄ and V₂O₅ (Figure 4).

No change in wavenumber at peak or in the relative intensities of diverse absorption bands characteristic for NaBH₄ (2400, 2295, 2223, and 1120 cm⁻¹) was observed upon doping with V₂O₅, independent of the milling time. However, bands at 1018, 838, 621, and 482 cm⁻¹ which are characteristic for V₂O₅ clearly decreased their intensity when the sample was milled for 30 instead of 5 min, while the band at 514 cm⁻¹ could be barely seen in the 5 min milled sample. Noticeable shifts in the 838 and 621 cm⁻¹ peaks could be observed as a function of milling time. When milled for 3 h, these bands disappeared almost completely, and a few new bands could be described: a very weak band at 732 cm⁻¹, two weak bands at 882 and 816 cm⁻¹, a moderate band at 602 cm⁻¹, and a very strong band at 436 cm⁻¹ (off the scale), together with bands characteristic for water in the range of 3000–3600 cm⁻¹. This result indicates that V₂O₅ slowly reacted with milled borohydride and underwent a progressive reduction, associated with the formation of unknown species. These bands did not originate from any known compound of vanadium, as revealed by our scrutiny. Simultaneously, X-ray diffraction patterns for the 3 h milled sample did not show the presence of any new crystalline moiety. In each case, however, there remained a



substantial amount of bulk NaBH₄ in these samples as evidenced by stable B–H stretching and H–B–H bending regions, as also evidenced in X-ray diffraction patterns (not shown).

Figure 3. TGA/DSC + MS curves of pristine NaBH₄ and NaBH₄ doped for 5 min with 5 wt.% of catalyst. DCS and MS curves are stacked in each section with an offset applied for their better distinction, but without distortion of the quantitative proportion between them. The fact that the TGA profiles are not flat for the doped samples may be associated with the absorption of a very small amount of moisture during milling; water vapor was then released during heating. Note that the TGA scale comprises 3 wt.% only; hence, the noise is more pronounced than in all forthcoming figures.



Figure 4. FTIR spectra of Na:V₂O₅25%_5 min and Na:V₂O₅25%_30 min in comparison to pure NaBH₄ and V₂O₅. Spectra of NaBH₄-containing species were normalized to the most intense peak originating from B–H stretching. Spectra were shifted in vertical scale for clarity. Inset shows a blow-up of the 400–1000 cm⁻¹ range.

All three samples were studied with TGA–DSC–MS, and the results were compared to those for $Na:V_2O_55\%_5$ min obtained with a very short milling time (5 min) and low catalyst load of 5 wt.% (Figure 5).

There was a clear effect of both catalyst load and milling time on the thermal decomposition of NaBH₄/V₂O₅ conglomerates, as seen in TG–DSC–MS profiles. The weak effect seen for the Na:V₂O₅5%_5 min sample at 398 °C was enhanced and shifted to lower temperature of 390 °C for the sample Na:V₂O₅25%_5 min and further shifted to 383 °C for the sample Na:V₂O₅25%_30 min. The lowest onset of thermal decomposition was seen for the 3 h milled sample (369 °C). All these events corresponded to the sharp and complex endothermic peaks of hydrogen desorption and were adjoined by sharp H₂ release in the temperature range of 380 to 410 °C as seen in the MS. Hydrogen was free from major contamination, as additionally evidenced by the MS.

The total mass loss between the onset of thermal decomposition and 450 °C was 4.0%, 4.1%, and 5.4% for 25 wt.% doped samples milled for 5, 30, and 180 min, respectively (Figure 6). The latter value corresponds to ca. 70% of total hydrogen stored by the sample. Importantly, as indicated by MS, hydrogen was not contaminated by common impurities such as B_2H_6 , other boron hydrides, and water.

The onset of thermal decomposition for doped samples (368–388 °C) was quite low as compared to the temperature of thermal decomposition for pristine NaBH₄ and even to that for the best catalyzed samples described in the literature. Actually, only TiF₃ was proven to provide an even lower decomposition onset than catalysts studied here (300 °C) [15].



Figure 5. TGA/DSC + MS curves of Na:V₂O₅5%_5 min, Na:V₂O₅25%_5 min, Na:V₂O₅25%_30 min, and Na:V₂O₅25%_180 min samples. DCS and MS curves are stacked in each section with an offset for visual improvement, without proportion distortion.

The Kissinger method [58,59] was used to determine the activation energy of decomposition for NaV₂O₅25%_180 min. Three additional experiments were conducted using heating rates of 0.5, 1, and 10 K/min in addition to the default 5 K/min used before (Figure 7). The clearly observable intermediate decomposition step for 10 and 5 K/min heating rates could not be detected at lower heating rates due to its size compared to neighboring ones; thus, only the first and last (strong) peaks were taken into activation energy calculations (Figure 8).



Figure 6. Mass loss up to 450 °C observed for Na:V₂O₅25%_5 min, Na:V₂O₅25%_30 min and Na:V₂O₅25%_180 min with respect to the milling time together with the onset of the thermal decomposition temperature.



Figure 7. DSC measurement for Na:V₂O₅25%_180 min sample using four different heating rates. Values of peaks and onsets are marked with symbols; onset values are additionally described with their value in $^{\circ}$ C.



Figure 8. Kissinger plot of Na:V₂O₅25%_180 min sample for first and last peaks of decomposition onsets and maxima together with associated by color tables containing the activation energy calculated and a description of fitted lines.

The activation energy of the first decomposition step for doped sample decreased drastically to 65.9 ± 3 kJ/mol (peak) or 69.0 ± 2 kJ/mol (onset) in comparison with 275 kJ/mol for pristine NaBH₄ [21]. This implies a fourfold reduction of the activation energy; our result may also be compared to that of $ZrCl_4$ -doped NaBH₄, which is characterized by an E_a of 180 kJ/mol [21]. On the other hand, the E_a value for the last decomposition step varied when calculated for onset or peak value (120.3 \pm 1 and 169 \pm 18 kJ/mol respectively); nevertheless, it was still remarkably smaller than the literature value for NaBH₄. It is worth noticing, however, that the first decomposition step, characterized by very small activation energy, corresponded to the vast majority of hydrogen desorbed. Interestingly, the activation energies obtained for undoped but long-milled NaBH₄ were as follows: 143.0 ± 1.6 kJ/mol (first peak) and 70.0 ± 0.9 kJ/mol (second peak). Therefore, the reduction in the activation barrier at the first stage of decomposition observed in V_2O_5 -catalyzed samples was partially due to nano-amorphization of NaBH₄ and partially due to the presence of a catalyst. On the other hand, the processes taking place at the second stage of decomposition were supposedly entirely different for the V₂O₅-free and V₂O₅-rich samples, as indicated by the counterintuitive behavior of the activation energies at that stage.

The fact that two main peaks were observed in the thermal profile means that two different species were decomposing at each of these steps. We attempted to gain insight into the nature of intermediate decomposing species and reaction products by performing additional experiments. The initial surmise was that the last step of decomposition could originate from the part of NaBH₄ not in contact with catalyst, but where H₂ release was easier than for pristine NaBH₄ due to pronounced milling and non-amorphization of the sample. Indeed, as already mentioned, milled NaBH₄ showed two major distinct decomposition steps, similarly to the catalyzed samples. However, none of those occurred at temperatures as low as 335–425 °C since the onset of thermal decomposition for milled NaBH₄ was as high as 461 °C (not shown) and extended to over 600 °C (in agreement with literature data). Additional X-ray diffraction experiments for samples heated up to diverse

temperatures failed to observe any crystalline species beyond traces of the bulk NaBH₄. Moreover, while both thermal peaks coincided with H₂ evolution, the evolved gas analysis failed to detect any impurity species such as B_2H_6 and higher boron hydrides. Therefore, at the current stage, the genuine nature of a (probably in situ formed) catalyst and that of the hydride intermediate undergoing the second stage of decomposition must remain an open question. We notice that the unequivocal detection of the catalyst nature is often nontrivial, as documented by many cases including that of Ti species-catalyzed NaAlH₄, which stands today as one of reference materials in hydrogen storage. One cannot exclude even a scenario that the presence of V_2O_5 modifies the path of the decomposition but remains in the solid residue (e.g., as some sort of vanadate salt). All these issues go beyond the scope of the current preliminary work and remain to be thoroughly studied in the future.

Having achieved a marked reduction in the thermal decomposition temperature of NaBH₄ by the high load of V_2O_5 and a prolonged milling time, we applied the same procedure to the remaining vanadium oxides. The TG–DSC–MS profiles for all samples are jointly shown in Figure 9.



Figure 9. TGA/DSC + MS curves of pristine NaBH₄ and sampled doped for 30 min with 25 wt.% of diverse vanadium catalysts. DCS and MS curves are stacked in each section with an offset for better distinction, without distortion of the quantitative proportions.

A substantial effect (and comparable to that for V_2O_5) on TG and DSC profiles can only be seen for VO_2 ; here, the onset of thermal decomposition was around 377 °C, but the amount of hydrogen evolved up to 450 °C was smaller than that for the V_2O_5 additive. The effects seen for V_2O_3 and V were the least pronounced.

It is important to note that the total mass loss up to 600 °C in almost all samples exceeded the total H content of the samples. This is because sodium vapor is partly released at high temperatures [17,50,60]. It is uncertain at this time what amount of sodium remained in the doped samples, as well as the chemical identity of the phase(s) containing this metal.

Having studied vanadium- and vanadium oxide-doped samples, our attention turned to vanadium nanoparticles. Samples doped with vanadium nanoparticles were denoted Na:VNPs_{THF} and Na:VNPs_{O-DFB}, and they were studied with TGA–DSC–MS analogously to previous samples (Figure 10). Reference curves for milled NaBH₄ were added for comparison.



Figure 10. TGA/DSC + MS curves of milled NaBH₄ and both VNP-doped samples. DCS and MS curves are stacked in each section with an offset for better distinction, but without distortion of quantitative proportions. Values of m/z = 42 and 114 correspond to the THF and o-DFB MS main peaks, respectively.

Both VNP-doped samples seemingly released H_2 at a lower temperature than the reference sample, as can be judged from the MS profiles. However, the doped samples also released copious amounts of CO₂, B_2H_6 , and solvent residues (only in the case of Na:VNPs_{THF}) at even lower temperatures, as seen in the MS and TGA profiles. These contaminations most probably came from byproducts of VNP synthesis and are certainly highly undesired for any practical application.

4. Conclusions

We studied the effect of vanadium and its oxides and nanoparticles (VNPs) on the thermal decomposition of NaBH₄. It was revealed that 3 h milling of NaBH₄ with 25 wt.% of V₂O₅ decreased the temperature of NaBH₄ decomposition by as much as 165 °C with respect to pristine sodium borohydride. VO₂ doping also decreased the temperature of NaBH₄ pyrolysis, but to a lesser degree; moreover, the hydrogen release peak was much broader than for V₂O₅ doping. The hydrogen released up to 450 °C was free from B₂H₆, other boron hydrides, and water. In contrast to expectations, vanadium metal provided nearly no improvement in the hydrogen desorption temperature of sodium borohydride. Doping with VNPs resulted in contamination of the evolved H₂ with some precursors used for their synthesis, which is a highly undesirable effect.

Extension of these studies may focus on the chemical nature of vanadium in the extensively milled and thermally decomposed samples, attempts to achieve at least partial reversibility of H_2 storage, understanding the nature of the hydride intermediate and of the fate of sodium in the catalyzed samples, and broadening of the study toward other light metal borohydrides.

Author Contributions: Conceptualization, W.G.; Data curation, P.A.O.; Formal analysis, P.A.O.; Funding acquisition, P.A.O.; Investigation, P.A.O.; Methodology, P.A.O.; Project administration, P.A.O.; Resources, P.A.O.; Validation, P.A.O.; Visualization, P.A.O.; Writing–original draft, P.A.O.; Writing–review & editing, W.G. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by Ministry of Science and Higher Education of Poland, grant number 501-D313-59-0557788.

Data Availability Statement: The data presented in this study are available on request from the P.A.O. The data are not publicly available.

Acknowledgments: Piotr Antoni Orłowski acknowledges the Ministry of Science and Higher Education for the scholarship awarded by the Diamond Grant competition.

Conflicts of Interest: The authors declare no conflict of interest.

References

- 1. Grochala, W.; Edwards, P.P. Thermal decomposition of the non-interstitial hydrides for the storage and production of hydrogen. *Chem. Rev.* **2004**, *104*, 1283–1316. [CrossRef]
- 2. Züttel, A. Hydrogen storage methods. Sci. Nat. 2004, 91, 157–172. [CrossRef] [PubMed]
- Bannenberg, L.J.; Heere, M.; Benzidi, H.; Montero, J.; Dematteis, E.M.; Suwarno, S.; Jaroń, T.; Winny, M.; Orłowski, P.A.; Wegner, W.; et al. Metal (boro-) hydrides for high energy density storage and relevant emerging technologies. *Int. J. Hydrogen Energy* 2020, 45, 33687–33730. [CrossRef]
- Schlapbach, L.; Züttel, A. Hydrogen-storage materials for mobile applications. In *Materials for Sustainable Energy: A Collection of Peer-Reviewed Research and Review Articles from Nature Publishing Group*; World Scientific: Singapore, 2011; Volume 414, pp. 265–270.
 Graetz, J. New approaches to hydrogen storage. *Chem. Soc. Rev.* 2009, *38*, 73–82. [CrossRef]
- Li, H.-W.; Zhu, M.; Buckley, C.; Jensen, T.R. Functional materials based on metal hydrides. *Inorganics* 2018, 6, 91. [CrossRef]
- Mohring, R.M.; Eason, I.A.; Fennimore, K.A. Performance Bench Testing of Auotive-Scale Hydrogen on Demand[™] Hydrogen Generation Technology; SAE Technical Paper: Warrendale, PA, USA, 2002.
- Huang, Y.; Cheng, Y.; Zhang, J. A Review of High Density Solid Hydrogen Storage Materials by Pyrolysis for Promising Mobile Applications. *Ind. Eng. Chem. Res.* 2021, 60, 2737–2771. [CrossRef]
- Martelli, P.; Caputo, R.; Remhof, A.; Mauron, P.; Borgschulte, A.; Zuttel, A. Stability and decomposition of NaBH₄. J. Phys. Chem. C 2010, 114, 7173–7177. [CrossRef]

- 10. Puszkiel, J.; Garroni, S.; Milanese, C.; Gennari, F.; Klassen, T.; Dornheim, M.; Pistidda, C. Tetrahydroborates: Development and potential as hydrogen storage medium. *Inorganics* **2017**, *5*, 74. [CrossRef]
- 11. Milanese, C.; Jensen, T.R.; Hauback, B.C.; Pistidda, C.; Dornheim, M.; Yang, H.; Lombardo, L.; Zuettel, A.; Filinchuk, Y.; Ngene, P.; et al. Complex hydrides for energy storage. *Int. J. Hydrogen Energy* **2019**, *44*, 7860–7874. [CrossRef]
- 12. Andersson, J.; Grönkvist, S. Large-scale storage of hydrogen. Int. J. Hydrogen Energy 2019, 44, 11901–11919. [CrossRef]
- Llamas, J.I.; Kalantzopoulos, G.N.; Nordholm, K.; Hauback, B.C. Destabilization of NaBH₄ by transition metal fluorides. *Molecules* 2020, 25, 780. [CrossRef]
- Humphries, T.D.; Kalantzopoulos, G.N.; Llamas-Jansa, I.; Olsen, J.E.; Hauback, B.C. Reversible hydrogenation studies of NaBH₄ milled with Ni-containing additives. J. Phys. Chem. C 2013, 117, 6060–6065. [CrossRef]
- 15. Mao, J.; Guo, Z.; Nevirkovets, I.P.; Liu, H.K.; Dou, S.X. Hydrogen de-/absorption improvement of NaBH₄ catalyzed by titaniumbased additives. *J. Phys. Chem. C* 2012, *116*, 1596–1604. [CrossRef]
- Mao, J.F.; Yu, X.B.; Guo, Z.P.; Poh, C.K.; Liu, H.K.; Wu, Z.; Ni, J. Improvement of the LiAlH₄–NaBH₄ system for reversible hydrogen storage. J. Phys. Chem. C 2009, 113, 10813–10818. [CrossRef]
- Lai, Q.; Milanese, C.; Aguey-Zinsou, K.F. Stabilization of nanosized borohydrides for hydrogen storage: Suppressing the melting with TiCl₃ doping. ACS Appl. Energy Mater. 2018, 1, 421–430. [CrossRef]
- Chong, L.; Zou, J.; Zeng, X.; Ding, W. Reversible hydrogen sorption in NaBH₄ at lower temperatures. *J. Mater. Chem. A* 2013, *1*, 13510–13523. [CrossRef]
- Zhang, Z.G.; Wang, H.; Zhu, M. Hydrogen release from sodium borohydrides at low temperature by the addition of zinc fluoride. *Int. J. Hydrogen Energy* 2011, 36, 8203–8208. [CrossRef]
- 20. Zou, J.; Li, L.; Zeng, X.; Ding, W. Reversible hydrogen storage in a 3NaBH₄/YF₃ composite. *Int. J. Hydrogen Energy* **2012**, 37, 17118–17125. [CrossRef]
- 21. Kumar, S.; Jaina, J.; Miyaoka, H.; Ichikawa, T.; Kojima, Y. Study on the thermal decomposition of NaBH₄ catalyzed by ZrCl₄. *Int. J. Hydrogen. Energy* **2017**, *42*, 22432–22437. [CrossRef]
- 22. Huang, T.; Zou, J.; Zeng, X.; Wang, J.; Liu, H.; Ding, W. Reversible hydrogen sorption behaviors of the 3NaBH_{4-(x)}YF_{3-(1-x)}GdF₃ system: The effect of double rare earth metal cations. *Int. J. Hydrogen Energy* **2019**, *44*, 4868–4877. [CrossRef]
- Chong, L.; Zou, J.; Zeng, X.; Ding, W. Effects of La fluoride and La hydride on the reversible hydrogen sorption behaviors of NaBH₄: A comparative study. J. Mater. Chem. A 2014, 2, 8557–8570. [CrossRef]
- 24. Chong, L.; Zou, J.; Zeng, X.; Ding, W. Mechanisms of reversible hydrogen storage in NaBH₄ through NdF₃ addition. *J. Mater. Chem. A* **2013**, *1*, 3983–3991. [CrossRef]
- 25. Chong, L.; Zou, J.; Zeng, X.; Ding, W. Study on reversible hydrogen sorption behaviors of a 3NaBH₄/HoF₃ composite. *Int. J. Hydrogen Energy* **2014**, *39*, 14275–14281. [CrossRef]
- Afonso, G.; Bonakdarpour, A.; Wilkinson, D.P. Hydrogen storage properties of the destabilized 4NaBH₄/5Mg₂NiH₄ composite system. J. Phys. Chem. C 2013, 117, 21105–21111. [CrossRef]
- Yahya, M.S.; Ali, N.A.; Sazelee, N.A.; Mustafa, N.S.; Yap, F.A.H.; Ismail, M. Intensive investigation on hydrogen storage properties and reaction mechanism of the NaBH₄-Li₃AlH₆ destabilized system. *Int. J. Hydrogen Energy* 2019, 44, 21965–21978. [CrossRef]
- Nwakwuo, C.C.; Pistidda, C.; Dornheim, M.; Hutchison, J.L.; Sykes, J.M. Microstructural study of hydrogen desorption in 2NaBH₄+MgH₂ reactive hydride composite. *Int. J. Hydrogen Energy* 2012, *37*, 2382–2387. [CrossRef]
- Garroni, S.; Pistidda, C.; Brunelli, M.; Vaughan, G.B.M.; Surinach, S.; Baro, M.D. Hydrogen desorption mechanism of 2NaBH₄+MgH₂ composite prepared by high-energy ball milling. *Scr. Mater.* 2009, 60, 1129–1132. [CrossRef]
- Mao, J.F.; Yu, X.B.; Guo, Z.P.; Liu, H.K.; Wu, Z.; Ni, J. Enhanced hydrogen storage performances of NaBH₄–MgH₂ system. J. Alloys Compd. 2009, 479, 619–623. [CrossRef]
- 31. Mao, J.; Guo, Z.; Yu, X.; Liu, H. Improved hydrogen storage properties of NaBH₄ destabilized by CaH₂ and Ca(BH₄)₂. *J. Phys. Chem. C* 2011, *115*, 9283–9290. [CrossRef]
- Somer, M.; Acar, S.; Koz, C.; Kokal, I.; Höhn, P.; Cardoso-Gil, R.; Aydemir, U.; Akselrud, L. Alpha-and beta-Na₂[BH₄][NH₂]: Two modifications of a complex hydride in the system NaNH₂–NaBH₄; syntheses, crystal structures, thermal analyses, mass and vibrational spectra. *J. Alloys Compd.* 2010, 491, 98–105. [CrossRef]
- Pei, Z.; Wu, C.; Bai, Y.; Liu, X.; Wu, F. NaNH₂–NaBH₄ hydrogen storage composite materials synthesized via liquid phase ball-milling: Influence of Co–Ni–B catalyst on the dehydrogenation performances. *Int. J. Hydrogen Energy* 2017, 42, 14725–14733. [CrossRef]
- 34. Mustafa, N.S.; Ismail, M. Significant effect of TiF₃ on the performance of 2NaAlH₄+ Ca(BH₄)₂ hydrogen storage properties. *Int. J. Hydrogen Energy* **2019**, *44*, 21979–21987. [CrossRef]
- Javadian, P.; Sheppard, D.A.; Buckley, C.E.; Jensen, T.R. Hydrogen storage properties of nanoconfined LiBH₄–NaBH₄. *Int. J. Hydrogen Energy* 2015, 40, 14916–14924. [CrossRef]
- Liu, Y.; Reed, D.; Paterakis, C.; Vasquez, L.C.; Baricco, M.; Book, D. Study of the decomposition of a 0.62LiBH₄-0.38NaBH₄ mixture. *Int. J. Hydrogen Energy* 2017, 42, 22480–22488. [CrossRef]
- Jensen, S.R.H.; Jepsen, L.H.; Skibsted, J.; Jensen, T.R. Phase Diagram for the NaBH₄–KBH₄ System and the Stability of a Na_{1-x}K_xBH₄ Solid Solution. J. Phys. Chem. C 2015, 119, 27919–27929. [CrossRef]
- 38. Ley, M.B.; Roedern, E.; Thygesen, P.M.M.; Jensen, T.R. Melting behavior and thermolysis of NaBH₄-Mg(BH₄)₂ and NaBH₄-Ca(BH₄)₂ composites. *Energies* **2015**, *8*, 2701–2713. [CrossRef]

- Dematteis, E.M.; Santoru, A.; Poletti, M.G.; Pistidda, C.; Klassen, T.; Dornheim, M.; Baricco, M. Phase stability and hydrogen desorption in a quinary equimolar mixture of light-metals borohydrides. *Int. J. Hydrogen Energy* 2018, 43, 16793–16803. [CrossRef]
- 40. Fu, H.; Wu, Y.; Chen, J.; Wang, X.; Zheng, J.; Li, X. Promoted hydrogen release from alkali metal borohydrides in ionic liquids. *Inorg. Chem. Front.* 2016, *3*, 1137–1145. [CrossRef]
 41. Yi, S.; Zhang, B. Fu, Y.; Tang, K. C.; Zhang, T.; Zhang, Y.; Yu, H. Hadragen, Balazza, Therma demonstrated in a fillentia etail and fillentia etail etail and fillentia etail etail
- Xi, S.; Zhang, P.; Fu, Y.; Tome, K.C.; Zhang, T.; Zhou, S.; Guo, Y.; Yu, H. Hydrogen Release: Thermodynamic and kinetic studies of NaBH₄ activated by different zeolite nanoparticles. *Energy Fuels* 2020, *34*, 10218–10224. [CrossRef]
- Manoharan, K.; Palaniswamy, V.K.; Raman, K.; Sundaram, R. Investigation of solid state hydrogen storage performances of novel NaBH₄/Ah-BN nanocomposite as hydrogen storage medium for fuel cell applications. *J. Alloys Compd.* 2021, 860, 158444. [CrossRef]
- 43. Ampoumogli, A.; Steriotis, T.; Trikalitis, P.; Giasafaki, D.; Bardaji, E.G.; Fichtner, M.; Charalambopoulou, G. Nanostructured composites of mesoporous carbons and boranates as hydrogen storage materials. J. Alloys Compd. 2011, 509, S705–S708. [CrossRef]
- 44. Ngene, P.; van den Berg, R.; Verkuijlen, M.H.W.; de Jong, K.P.; de Jongh, P.E. Reversibility of the hydrogen desorption from NaBH₄ by confinement in nanoporous carbon. *Energy Environ. Sci.* **2011**, *4*, 4108–4115. [CrossRef]
- Zhang, L.; Xiao, X.; Fan, X.; Li, S.; Ge, H.; Wang, Q.; Chen, L. Fast hydrogen release under moderate conditions from NaBH₄ destabilized by fluorographite. *RSC Adv.* 2014, *4*, 2550–2556. [CrossRef]
- Fang, Y.; Zhang, J.; Hua, M.Y.; Zhou, D.W. Modifying effects and mechanisms of graphene on dehydrogenation properties of sodium borohydride. *J. Mater. Sci.* 2020, 55, 1959–1972. [CrossRef]
- 47. Chong, L.; Zeng, X.; Ding, W.; Liu, D.; Zou, J. NaBH4 in "graphene wrapper:" Significantly enhanced hydrogen storage capacity and regenerability through nanoencapsulation. *Adv. Mater.* **2015**, *27*, 5070–5074. [CrossRef]
- Wang, T.; Aguey-Zinsou, K.F. "Surfactant-free" sodium borohydride nanoparticles with enhanced hydrogen desorption properties. ACS Appl. Energy Mater. 2020, 3, 9940–9949. [CrossRef]
- 49. Wang, T.; Aguey-Zinsou, K.F. Controlling the growth of NaBH4 nanoparticles for hydrogen storage. *Int. J. Hydrogen Energy* **2020**, 45, 2054–2067. [CrossRef]
- 50. Christian, M.L.; Aguey-Zinsou, K.F. Core–shell strategy leading to high reversible hydrogen storage capacity for NaBH₄. ACS Nano 2012, 6, 7739–7751. [CrossRef]
- 51. Christian, M.; Aguey-Zinsou, K.F. Synthesis of core-shell NaBH₄@M (M = Co, Cu, Fe, Ni, Sn) nanoparticles leading to various morphologies and hydrogen storage properties. *Chem. Comm.* **2013**, *49*, 6794–6796. [CrossRef]
- Li, Y.; Ding, X.; Zhang, Q. Self-printing on graphitic nanosheets with metal borohydride nanodots for hydrogen storage. *Sci. Rep.* 2016, *6*, 31144. [CrossRef]
- 53. Yang, H.; Lombardo, L.; Luo, W.; Kim, W.; Zuttel, A. Hydrogen storage properties of various carbon supported NaBH₄ prepared via metathesis. *Int. J. Hydrogen Energy* **2018**, *43*, 7108–7116. [CrossRef]
- 54. Maj, Ł.; Grochala, W. Theoretical design of catalysts for the heterolytic splitting of H₂. *Adv. Funct. Mater.* **2006**, *16*, 2061–2076. [CrossRef]
- Hamilton, C.W.; Baker, R.T.; Staubitz, A.; Manners, I. B-N compounds for chemical hydrogen storage. *Chem. Soc. Rev.* 2009, 38, 279–293. [CrossRef] [PubMed]
- 56. Reilly, J.J.; Wiswall, R.H. Higher hydrides of vanadium and niobium. Inorg. Chem. 1970, 9, 1678–1682. [CrossRef]
- 57. Koteras, K. Synteza i właściwości fizykochemiczne nowych, wysoce reaktywnych soli wapnia, tytanu i wanadu z anionami słabo koordynującymi. Master's Thesis, Warsaw University of Technology, Warsaw, Poland, 2018.
- 58. Kissinger, H.E. Variation of peak temperature with heating rate in differential thermal analysis. *J. Res. Natl. Bur. Stand.* **1956**, *57*, 217–221. [CrossRef]
- 59. Kissinger, H.E. Reaction kinetics in differential thermal analysis. Anal. Chem. 1957, 29, 1702–1706. [CrossRef]
- Wang, T.; Aguey-Zinsou, K.-F. Direct Synthesis of NaBH₄ Nanoparticles from NaOCH₃ for Hydrogen Storage. *Energies* 2019, 12, 4428. [CrossRef]