Catalyzed KSiH₃ as a reversible hydrogen storage material†

R. Janot,*a W. S. Tang,b,c D. Clémençon,a and J.-N. Chotard,a

Solid-state hydrogen storage through the reversible formation of metallic hydrides is a key issue for the development of hydrogen as an energy vector. Herein we report the hydrogen storage performances of the KSiH₃ phase ball-milled with NbF₅ as a catalyst. The kinetics of hydrogen absorption/desorption are strongly enhanced by the addition of a catalyst as revealed by the large decrease of activation energies for both the absorption and desorption reactions. No disproportionation phenomenon is observed, indicating that the reaction between KSiH₃ and KSi is perfectly reversible with a hydrogen storage capacity of 4.1 wt% H₂. The thermodynamic properties of this KSi/KSiH₃ equilbrium were investigated by plotting PCI curves from 90 °C to 130 °C: an enthalpy of 24.3 kJ mol⁻¹ H₂ and a low entropy change of 59.5 J K⁻¹ mol⁻¹ H₂ are found. This low entropy variation is related to the high mobility of the H atoms in the α-KSiH₃ phase as recently demonstrated by Quasi-elastic Neutron Scattering (QENS) experiments.

Introduction

In recent years, there has been an increasing interest in the study of different hydrogen storage compounds, particularly for complex hydrides because of their high theoretical gravimetric capacities.1–3 Various materials comprising light weight elements, like amides M(NH₂)ₓ/imides M(NH)ₓ/C₃,4–12 alanates M(AlH₄)ₓ, or Mn(AlH₄)ₓ13–21 borohydrides M(BH₄)ₓ2 are some examples that have been well investigated. A recent review on the hydrogen storage properties of the different families of complex hydrides was recently published.3

Looking back in the literature, another notable class of hydrides is the alkali silanide MSiH₃ family. KSiH₃ was the first alkali silanide synthesized by Ring et al. in 1961 through a wet chemistry method;3 excess potassium was mixed with silane gas (SiH₄) in monoglyme at –78 °C. Subsequently in 1968, the potassium to cesium analogues were successfully synthesized by Amberger et al.14 using a similar wet chemistry method of mixing the alkali metal with SiH₄ in monoglyme/diglyme at 20 °C. All three silanides crystallize in the same cubic Pm̅3m space group with cell parameter values of a = 7.23(1), 7.52(1), and 7.86(1) Å for KSiH₃, RbSiH₃, and CsSiH₃, respectively.15

Finally in 1989, during differential thermal analysis performed on KSiH₃, Mundt et al. observed a reversible phase transition between the high-temperature cubic α-phase and a low-temperature β-phase.40 X-ray diffraction performed at –110 °C confirmed a different phase at low temperature: β-KSiH₃ crystallizes in the Pm̅a orthorhombic space group with no apparent disorder, consisting of isolated potassium cations and the pyramidal silanide [SiH₄]⁻ anionic group. A short silicon–hydrogen bond distance of 1.44 Å was found, comparable to the value in gaseous SiH₄ (dSi–H = 1.40 Å). The MSiH₃ silanides can be therefore considered as complex hydrides with a SiH₄⁻ covalent group, similar to AlH₄⁻ in MAH₄ alanates and BH₄⁻ in MBH₄ borohydrides.

Recently, we have reported the hydrogenation properties of the MSi Zintl phases.37–40 Zintl phases possess chemical properties in between the intermetallic and ionic compounds with extended polyanions matching the Zintl–Klemm concept, i.e. the polyanion structure is similar to a neighbouring isoelectronic element.41–43 The heavier alkali congeners {MSi, M = Na, K, Rb, Cs} contain isolated [Si₄]⁻ tetrahedra (isoelectronic with white phosphorus P₄); NaSi is found in the C2/c monoclinic unit cell and the others in cubic P43n ones.44 These alkali silicides are extremely air and moisture sensitive. On the other hand, LiSi does not possess the same Zintl phase structure and crystallizes in the I₄/a tetragonal unit cell with a three-dimensional silicon network (analogous to black phosphorus).45,46 This LiSi phase is usually obtained by high temperature and pressure synthesis methods [600 °C, 4 GPa],46 but we have since demonstrated that it can be alternatively obtained by a much more convenient method i.e. simple ball-milling of elemental Li and Si under argon.49
The hydrogenation of the monosilicide MSi Zintl phases with heavy alkali metals (M = K, Rb, Cs) into their corresponding silicane complex hydrides z-MSiH3 shows reversible hydrogen absorption–desorption equilibrium within a good temperature-pressure window.\(^\text{48}\) In all three systems, pristine MSi absorbs 3 H\(_2\)/fu to form z-KSiH3, z-RbSiH3, and z-CsSiH3, with capacities of 4.3, 2.6, and 1.85 wt\% H\(_2\), respectively, and the corresponding alloy is re-obtained upon desorption. The systems undergo huge volume expansion upon hydrogenation, with the CsSi/z-CsSiH3 equilibrium having a value of 56%, the highest ever reported for hydrogenation reactions in the literature.\(^\text{48}\) We have also shown an enthalpy–entropy compensation effect for the MSi/z-MSiH3 equilibrium: a concomitant linear increase in the enthalpy (more stable silicane) and entropy change (more localized H atoms in the crystal structure) for the larger cation (Cs+). Because of this linear thermodynamic increment, a desorption temperature of ca. 136 °C at 1 bar hydrogen equilibrium pressure is obtained for all three alkali monosilicide–silicane systems, re-emphasizing their reversibility under near ambient conditions. From this investigation, alkali silanides M+\([\text{SiH}_3]\) appear to be an interesting new class of compounds for solid-state hydrogen storage.

From an application point of view, KSi/KSiH3 remains the most interesting due to its higher storage capacity of 4.3 wt\% H\(_2\).\(^\text{37,48}\) Unfortunately, the kinetics of this system are quite slow for the as-prepared KSi powder, taking several hours for complete absorption at 100 °C and complete desorption at 200 °C.\(^\text{27}\) In our previous study, the absorption kinetics were strongly enhanced by ball-milling KSi with 10 wt% carbon black with the initial rate of absorption increased by an order of magnitude. However, without proper control of the exothermicity during hydrogenation, we were otherwise confronted with a disproportionation phenomenon,\(^\text{39}\) i.e. the formation of KH and the K\(_x\)Si\(_{1-x}\) clathrate phase instead of KSiH\(_3\). Definitively, for fast hydrogenation, good heat management is required to make the KSi/z-KSiH3 system fully reversible. More recently, a Japanese group has shown that mesoporous Nb\(_2\)O\(_5\) is a very effective catalyst for enhancing the hydrogen release kinetics of KSiH\(_3\).\(^\text{40}\)

By ball-milling KSi with 5 mol\% (16 wt%) Nb\(_2\)O\(_5\), the KSiH\(_3\) desorption activation energy decreased from 142 kJ mol\(^{-1}\) for the pristine material to 63 kJ mol\(^{-1}\) for the catalyzed sample. In the same group also discussed the disproportionation issue during fast hydrogenation, under similar conditions but with different steps: one KSi sample was hydrogenated by first introducing hydrogen pressure at room temperature and then increasing the temperature to 100 °C; whereas another KSi sample was hydrogenated by first heating to 100 °C under vacuum and then an instant exposure to 50 bar H\(_2\). The latter disproportionates into unfavourable products of KH and Si due to the sudden drastic exothermic thermal release, while the sole KSiH\(_3\) product following the first pathway maintains the reversible characteristic of the KSi/KSiH\(_3\) transformation.\(^\text{49}\)

In this paper, we investigate the effects of Nb\(_2\)F\(_5\) addition on the absorption/desorption kinetics of the KSi/z-KSiH\(_3\) system. The thermodynamics of the KSi/z-KSiH\(_3\) equilibrium are also finely reinvestigated thanks to PCI (Pressure–Composition–Isotherm) curves obtained by thermogravimetry on the NbF\(_5\)-catalyzed KSiH\(_3\) material.

**Experimental**

As the KSi powders are extremely air and moisture sensitive, they were carefully handled in an argon-filled glovebox (O\(_2\) and H\(_2\)O levels below 10 ppm).

**Synthesis**

KSi alloys were synthesized by solid-state reactions between elemental alkali metal (potassium cubes 5 × 5 × 5 mm) and silicon powder (<40 μm) with a slight excess of silicon (3 mol%) into stainless steel sealed tubes. A silicon excess was used to avoid any traces of unreacted metallic K and thus to avoid any traces of KH after hydrogenation, which would be harmful for the precise determination of the hydrogen absorption/desorption properties of the KSi compound. The tubes were sealed by arc-welding in the glovebox and then placed in a resistance furnace. The samples were annealed at 500 °C for 3 days using a heating rate of 1 °C min\(^{-1}\) and then cooled down to room temperature for ca. 6 hours.

Commercial NbF\(_5\) powder (Sigma-Aldrich\(^\text{38}\)) was ball-milled with a SPEX 8000 mixer-mill using a 50 cc hardened steel milling jar and 10 mm steel balls. The balls-to-powder weight ratio was 40. After 6 hours of milling, the NbF\(_5\) particle size was typically in the 200–500 nm range as observed from scanning electron microscopy (cf. Fig. S1 in the ESI\(^\text{1}\)). KSi was then ball-milled under argon with 5 wt% of this premilled NbF\(_5\) using a Retsch PM100 planetary miller. As above, a 50 cc hardened steel milling jar and 10 mm milling balls were used and the balls-to-powder weight ratio was 40.

**Structure**

X-ray powder diffraction (XRPD) was performed using a Bruker D\(_8\) Advanced diffractometer with Cu radiation (\(\lambda_1 = 1.54056\) Å, \(\lambda_2 = 1.54439\) Å) equipped with a LynxEye detector. Airtight X-ray sample holders with Be windows were used for keeping the samples out of air and moisture. To obtain the composition of the samples (e.g. the amount of the different phases), XRPD data were refined using the Fullprof software.

**Morphology**

Scanning Electron Microscopy (SEM) was performed using a FEI Quanta 200F microscope equipped with an Oxford EDX spectrometer. Sample powders were deposited onto carbon stickers in the glovebox and then introduced into the microscope through the use of a specifically developed transfer chamber. EDX spectroscopy was used to check the K to Si ratio of the KSi phases and to get a chemical mapping of the dispersion of Nb throughout the samples after milling.

**Thermal analysis**

Differential Scanning Calorimetry (DSC) measurements were carried out under an argon flow by using a Netzsch DSC204
calorimeter. Aluminium crucibles were sealed in the glovebox and put on the DSC calorimeter under argon flow. The cap of the crucible was holed just before the experiment in order to allow gas release upon heating. Different heating rates (1 to 20 °C min⁻¹) were used in order to determine the activation energy of the desorption process using the Kissinger method.

### Hydrogenation properties

The absorption/desorption PCI (Pressure-Composition-Isotherm) curves were recorded by the gravimetric method using a Hiden IGA001 gravimetric analyzer. The working pressure of this apparatus can vary from secondary vacuum to 20 bar of hydrogen (Air Liquide Alphagaz 1, a purity of 99.999%). The sample weight was typically of the order of 100 mg and the powder was loaded in a stainless steel bucket in the glovebox. The bucket was hung to the thermobalance under argon using a specially designed transfer chamber. The gravimetric method was used here, instead of the volumetric one, as it allows a precise kinetic analysis under perfectly isobaric conditions (i.e. for the volumetric method, the quantity of hydrogen is calculated from pressure changes and therefore the kinetics investigations are not isobaric). The kinetics of the NbF₅-catalyzed KSi powders were determined at 4 different temperatures (90, 110, 130 and 150 °C) with 10 bar of hydrogen for the absorption and 0.1 mbar for desorption.

### Results and discussion

After 3 days of annealing at 500 °C, the KSi compound is pure as determined from X-ray diffraction (cf. Fig. S2 in the ESI† XRD diagram labelled (a)), and its particle size is in the 10–100 μm range as observed in the SEM micrograph shown in Fig. 1a. After ball-milling with NbF₅ for one hour, the size is drastically reduced with the larger particles having a 5 μm diameter and most of the particles around 1–2 μm (cf. Fig. 1b). Thanks to EDX mapping, it has been checked that the K/Si ratio is very close to one over the whole sample and that Nb is homogeneously dispersed in the ball-milled material. We notice that the surface of the particles remained “clean” without any bubble-like shapes as previously observed for slightly oxidized KSi powders. This highlights that this ball-milled KSi sample is free from oxidation. The XRD diagram obtained on the ball-milled NbF₅-catalyzed sample (cf. Fig. S2,† diagram (b)) reveals a strong KSi amorphization with very broad reflections. No other reflection is observed indicating the high dispersion/small particle size of the Nb-containing species. Actually, the amount of added NbF₅ is low in this material (5 wt% i.e. 1.8 mol%) and the identification of the exact nature of the Nb-containing species obtained after ball-milling is impossible here by X-ray diffraction. The ball-milling of KSi with NbF₅ leads probably to the formation of KF and Nb or Nb-based compounds with a low Nb oxidation state. As a matter of fact, KSi is a strong reducing agent: this is a Zintl phase consisting of K⁺ cations and very reducing [Si₄]³⁻ tetrahedral polyanions. KSi is therefore able to easily reduce Nb⁵⁺ to lower oxidation states or even metallic niobium. In addition, we have shown in previous studies that potassium can be easily extracted from KSi, either electrochemically,⁵¹ or by ball-milling.²⁹ In the latter case, for instance, the ball-milling of KSi with LiF leads to the formation of LiSi and KF. Owing to these previous results, it is strongly plausible that the ball-milling of KSi with NbF₅ leads to the formation of KF and Nb or Nb-based compounds, but their existence cannot be demonstrated by X-ray diffraction due to their too low concentrations in the present material. Further experiments, for instance Transmission Electron Microscopy (TEM)/electron diffraction for KF detection and X-ray Photoelectron Spectroscopy (XPS) for Nb oxidation state determination, are needed.

There are many reports in the literature about the nature of Nb-based catalysts when used for the MgH₂ kinetics enhancement.²³⁻²⁴ For sure, Nb⁵⁺ is reduced upon ball-milling to lower oxidation states (+2 or even the metallic state) and the possible formation of NbH₄ hydrides is also reported. The nature of the Nb-containing phase acting as the effective catalyst is still discussed in the hydrogen storage community. About the Japanese report on the use of Nb₂O₃ as a catalyst for KSiH₃, XPS experiments showed the formation of NOB after milling and it is assumed that this phase is actually responsible for the kinetics enhancement.⁴⁹

Both pristine KSi and catalyzed KSi were exposed to 10 bar of H₂ and then heated at 150 °C for 10 hours. In both cases, the XRD patterns measured on the hydrogenated powders reveal that all the XRD reflections can be indexed to the Fm3m cubic unit cell of the α-KSiH₃ polymorph (cf. Fig. S2,† diagrams (c and d)). Unreacted KSi is not present and no disproportionation process has occurred upon hydrogenation. The hydrogen release behaviour of these two hydrogenated powders was then investigated by DSC calorimetry as displayed in Fig. 2. A single sharp endothermic peak is observed at 168 °C for the catalyzed material (at a heating rate of 10 °C min⁻¹), whereas the hydrogen release occurs above 200 °C for the pristine KSiH₃ powder (cf. Fig. 2). For non-catalyzed hydrogenated KSi, the hydrogen release actually exhibits two broad endothermic peaks at about 215 and 265 °C, probably due to different particle sizes of KSiH₃. Clearly, the NbF₅ addition by ball-milling strongly decreased the hydrogen desorption temperature of KSiH₃. It is worth mentioning that, in our case, longer milling time does not lead to a further decrease of the hydrogen release.
where $K$ is the hydrogen release reaction ($\alpha$ faster heating rate leads to a higher peak maximum related to singer plot ($\beta$ energy of the desorption process. From the slope of the Kissinger plot obtained for NbF$_5$-catalyzed KSiH$_3$, which is a value largely $1$ for KSiH$_3$ and $1$ is measured for 20 h-milled KSi with $5 \text{ mol}\%$ Nb$_2$O$_5$ (corresponding to $16 \text{ wt}\%$ Nb$_2$O$_5$), a value similar to the activation energy obtained in our case with only $5 \text{ wt}\%$ NbF$_5$. From previous studies made in our laboratory about the effects of catalyst addition on the hydrogen release kinetics of MgH$_2$, the superior effect of NbF$_5$ compared to Nb$_2$O$_5$ was already noticed. This better catalytic effect could be nested in the formation of a Nb$^{5+}$--H$^+$ bond favoured by the large electronic delocalization of the Nb--F bond (i.e. higher electronegativity of F than O in the Nb$_x$X$_y$ compound) leading to a further weakening of the surface metal--H bond in the hydride as already discussed in the literature.

In order to confirm the kinetic enhancement observed by DSC, thermogravimetric experiments were performed on the NbF$_5$-catalyzed KSi sample for both absorption (10 bar H$_2$) and desorption (0.1 mbar H$_2$). Fig. 4a shows the curves of hydrogen release at 90, 110, 130 and 150 °C. An experimental hydrogen storage capacity of around $4.1 \text{ wt}\%$ is measured which is in very good agreement with the theoretical capacity based on the formation of KSiH$_3$ (4.3 wt% hydrogen storage capacity) and the weight of inactive catalyst (5 wt%). The hydrogen release is particularly fast above $130 \text{ °C}$ with less than one hour to obtain a complete desorption. The activation energy was calculated using the Arrhenius equation:

$$\ln K = -E_a/RT_m + \ln(RK_0/E_a)$$

where $K = \beta/T_m^2$, $\beta$ is the heating rate, $T_m$ is the peak maximum temperature, $R$ is the gas constant and $E_a$ is the activation energy of the desorption process. From the slope of the Kissinger plot (cf. inset of Fig. 3), an energy of $66.1 \text{ kJ mol}^{-1}$ is obtained for NbF$_5$-catalyzed KSiH$_3$, which is a value largely below the one previously obtained for non-catalyzed KSiH$_3$ ($121 \text{ kJ mol}^{-1}$) from isothermal experiments (i.e. weight loss as a function of time for a given temperature) using the Arrhenius equation.$^{38}$ In a previous attempt to decrease the KSiH$_3$ desorption activation energy, KSi was ball-milled with carbon black,$^{28}$ but a disproportionation phenomenon was observed upon hydrogenation with the formation of KH and the clathrate K$_8$Si$_{46}$ phase instead, probably due to a bad management of the heat generated upon hydrogenation. In the present study, there was no disproportionation reaction as only $\alpha$-KSiH$_3$ was always detected by X-ray diffraction performed on all the hydrogenated powders.

A Japanese group has investigated the effects of different catalysts such as nano-metals (Ni, Co, Nb), TiO$_2$, TiCl$_3$ and Nb$_2$O$_5$ on the hydrogen release kinetics of KSiH$_3$. Although the effect of metal additions appears limited, with the lowest activation energy of $106 \text{ kJ mol}^{-1}$ using Ni,$^{55}$ a more significant decrease of activation energy was reported with mesoporous Nb$_2$O$_5$. A value of $63 \text{ kJ mol}^{-1}$ was measured for 20 h-milled KSi with $5 \text{ mol}\%$ Nb$_2$O$_5$ (corresponding to $16 \text{ wt}\%$ Nb$_2$O$_5$), a value similar to the activation energy obtained in our case with only $5 \text{ wt}\%$ NbF$_5$. From previous studies made in our laboratory about the effects of catalyst addition on the hydrogen release kinetics of MgH$_2$, the superior effect of NbF$_5$ compared to Nb$_2$O$_5$ was already noticed. This better catalytic effect could be nested in the formation of a Nb$^{5+}$--H$^+$ bond favoured by the large electronic delocalization of the Nb--F bond (i.e. higher electronegativity of F than O in the Nb$_x$X$_y$ compound) leading to a further weakening of the surface metal--H bond in the hydride as already discussed in the literature.

In order to determine the activation energy of the hydrogen desorption reaction, DSC calorimetry was performed at different heating rates (2, 5, 10 and 20 °C min$^{-1}$). As expected, a faster heating rate leads to a higher peak maximum related to the hydrogen release reaction (cf. Fig. 3). The activation energy was then calculated using the Kissinger equation:

$$\ln K = -E_a/RT_m + \ln(RK_0/E_a)$$

where $K = \beta/T_m^2$, $\beta$ is the heating rate, $T_m$ is the peak maximum temperature, $R$ is the gas constant and $E_a$ is the activation energy of the desorption process. From the slope of the Kissinger plot (cf. inset of Fig. 3), an energy of $66.1 \text{ kJ mol}^{-1}$ is obtained for NbF$_5$-catalyzed KSiH$_3$, which is a value largely below the one previously obtained for non-catalyzed KSiH$_3$ ($121 \text{ kJ mol}^{-1}$) from isothermal experiments (i.e. weight loss as a function of time for a given temperature) using the Arrhenius equation.$^{38}$ In a previous attempt to decrease the KSiH$_3$ desorption activation energy, KSi was ball-milled with carbon black,$^{28}$ but a disproportionation phenomenon was observed upon hydrogenation with the formation of KH and the clathrate K$_8$Si$_{46}$ phase instead, probably due to a bad management of the heat generated upon hydrogenation. In the present study, there was no disproportionation reaction as only $\alpha$-KSiH$_3$ was always detected by X-ray diffraction performed on all the hydrogenated powders.

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In order to confirm the kinetic enhancement observed by DSC, thermogravimetric experiments were performed on the NbF$_5$-catalyzed KSi sample for both absorption (10 bar H$_2$) and desorption (0.1 mbar H$_2$). Fig. 4a shows the curves of hydrogen release at 90, 110, 130 and 150 °C. An experimental hydrogen storage capacity of around $4.1 \text{ wt}\%$ is measured which is in very good agreement with the theoretical capacity based on the formation of KSiH$_3$ (4.3 wt% hydrogen storage capacity) and the weight of inactive catalyst (5 wt%). The hydrogen release is particularly fast above $130 \text{ °C}$ with less than one hour to obtain a complete desorption. The activation energy was calculated using the Arrhenius equation:

$$\ln K = A \exp(-E_a/RT)$$

where $K$ is the reaction rate, $R$ is the gas constant and $A$ is the pre-exponential factor. A value of $61.0 \text{ kJ mol}^{-1}$ is obtained (cf. inset of Fig. 4a), in good agreement with the energy obtained from the DSC curves and the Kissinger method ($66.1 \text{ kJ mol}^{-1}$).

The kinetic investigation upon absorption (10 bar H$_2$) by the same thermogravimetric method is shown in Fig. 4b. The hydrogenation is fast, taking less than one hour to perform a full absorption at temperatures above $100 \text{ °C}$. The inset of Fig. 4b shows the Arrhenius plot ($\ln K$ as a function of $1/T$) corresponding to the absorption reaction. A low activation energy of $33.2 \text{ kJ mol}^{-1}$ is obtained, whereas an energy of $56.0 \text{ kJ mol}^{-1}$ was previously determined for pristine KSi.$^{38}$ A comparison with the Nb$_2$O$_5$-catalyzed KSi material reported in

![Fig. 2] Differential scanning calorimetry at 10 °C min$^{-1}$ for KSiH$_3$ and NbF$_5$-catalyzed KSiH$_3$. Temperature as recorded by DSC calorimetry and does not lead to faster hydrogen release kinetics.

**Fig. 3** Differential scanning calorimetry at 4 different heating rates for NbF$_5$-catalyzed KSiH$_3$. Inset: Kissinger plot allowing the calculation of the activation energy of the desorption reaction.

![Fig. 4a] Differential scanning calorimetry at 10 °C min$^{-1}$ for KSiH$_3$ and NbF$_5$-catalyzed KSiH$_3$. Temperature as recorded by DSC calorimetry and does not lead to faster hydrogen release kinetics.

**Fig. 4a** Differential scanning calorimetry at 10 °C min$^{-1}$ for KSiH$_3$ and NbF$_5$-catalyzed KSiH$_3$. Temperature as recorded by DSC calorimetry and does not lead to faster hydrogen release kinetics.

![Fig. 4b] Differential scanning calorimetry at 10 °C min$^{-1}$ for KSiH$_3$ and NbF$_5$-catalyzed KSiH$_3$. Temperature as recorded by DSC calorimetry and does not lead to faster hydrogen release kinetics.

**Fig. 4b** Differential scanning calorimetry at 10 °C min$^{-1}$ for KSiH$_3$ and NbF$_5$-catalyzed KSiH$_3$. Temperature as recorded by DSC calorimetry and does not lead to faster hydrogen release kinetics.

![Fig. 5] Differential scanning calorimetry at 10 °C min$^{-1}$ for KSiH$_3$ and NbF$_5$-catalyzed KSiH$_3$. Temperature as recorded by DSC calorimetry and does not lead to faster hydrogen release kinetics.
the literature is unfortunately not possible since the activation energy upon absorption was not reported for this material.

The cycling stability of the NbF5-catalyzed KSi sample was then investigated at 150 °C on the same thermogravimetric analyzer (absorption 10 bar H2 and desorption 0.1 mbar H2). A very good retention capacity is obtained since the storage capacity still exceeds 4.0 wt% after 10 absorption/desorption cycles as shown in Fig. 5. The shape of the hydrogen release kinetic curve has slightly changed after 10 cycles (cf. Fig. 5a), but the overall time needed to perform complete desorption remains the same: around 30 min. For the hydrogen absorption kinetics, a slight decline is noticed after 10 cycles (cf. Fig. 5b). It must be noted that a much faster hydrogenation reaction could be attained if the applied hydrogen pressure was increased above 10 bar, since the plateau pressure upon KSi hydrogenation at 150 °C is around 2.6 bar as discussed in the following section.

**Thermodynamic investigation**

Due to the particularly slow kinetics of the pristine KSi phase, full PCI curves were not plotted in our previous reports on the KSi/α-KSiH3 equilibrium. For the determination of the enthalpy and entropy of the absorption/desorption reaction, we have instead measured the equilibrium pressures at the mid-plateau when desorbing KSiH3 at different temperatures. Namely, α-KSiH3 was first desorbed at a certain temperature (T1) down onto its plateau pressure. To ensure that its corresponding equilibrium pressure was well determined, the value was taken at the mid-plateau of T1. The sample was then heated up to T2 and held until the equilibrium pressure was stable, before the temperature was increased to T3 and so on. In this way, a single PCI was performed on the desorption plateau, with temperature increments only after the equilibrium pressure was well established. At the end of the experiment, the total quantity of hydrogen gas which has been released during the measurement was calculated in order to check whether the measured equilibrium pressure still corresponded to the plateau (two-phase domain) pressure. Using the Van’t Hoff equation, enthalpy and entropy values of 22.6 kJ mol⁻¹ H2 and 54.4 J K⁻¹ mol⁻¹ H2 were obtained from the KSiH3 desorption, respectively. This very low entropy value was initially surprising, since it was much less than the classical entropy change of around 100–130 J K⁻¹ mol⁻¹ H2 usually obtained upon hydrogen desorption of intermetallics (i.e. the change between the low entropy of H atoms well located in interstitial sites and the large entropy of gaseous H2 molecules). This low entropy was supported by DFT calculations. Specifically, vibrational analysis and phonon calculations were made by the...
direct general approach to lattice dynamics as implemented in the Phonon-MedeA software. By DFT calculations, an enthalpy of 28.1 kJ mol\(^{-1}\) H\(_2\) was found in agreement with the value of 22.6 kJ mol\(^{-1}\) H\(_2\) found experimentally. About the entropy change, a value of 62.5 J K\(^{-1}\) mol\(^{-1}\) H\(_2\) or 52 J K\(^{-1}\) mol\(^{-1}\) H\(_2\) was found by DFT calculations taking into account the rotational entropy of SiH\(_3\) or the statistical distribution of H atoms in the 96k Wyckoff positions, respectively. These values correspond well with the entropy change of 54.4 J K\(^{-1}\) mol\(^{-1}\) H\(_2\) found experimentally for the uncatalyzed-KSiH\(_3\) material.

In the paper reporting the excellent catalytic effect of Nb\(_2\)O\(_5\) for enhancing the KSiH\(_3\) hydrogen release kinetics,\(^{49}\) a thermo-dynamic investigation was also performed. Full PCI curves were plotted upon desorption at 150, 175 and 200 °C using a volumetric Sievert apparatus. Significantly different enthalpy and entropy values were obtained: the desorption enthalpy was found to be 40.1 kJ mol\(^{-1}\) H\(_2\), while the entropy value was 106 J K\(^{-1}\) mol\(^{-1}\) H\(_2\). In order to understand this discrepancy between our previous reports and this recent Japanese article, we have also plotted full PCI curves on a catalyzed-KSiH\(_3\) sample.

Fig. 6 shows the PCI curves obtained upon absorption and desorption at 150 °C for the NbF\(_5\)-catalyzed KSiH\(_3\) material and then desorption at 130 °C, 110 °C and 90 °C. For each point observed on the PCI curves, holding durations of 12 hours were used to ensure a perfect equilibrium condition for each pressure step. A significant hysteresis is observed at 150 °C with plateau pressures upon absorption and desorption at about 2.6 and 1.29 bar, respectively. This hysteresis is usually attributed to the extra energy needed for the lattice expansion and resulting mechanical stresses upon hydrogenation. By decreasing the temperature from 150 °C to 90 °C, we observe that the desorption plateau pressure is only slightly shifted from 1.29 bar to 0.41 bar. The corresponding Van’t Hoff plot (ln P/P\(_0\) as a function of 1/T) is shown in the inset of Fig. 6. Using the Van’t Hoff equation, enthalpy and entropy values of 24.3 kJ mol\(^{-1}\) H\(_2\) and 59.5 J K\(^{-1}\) mol\(^{-1}\) H\(_2\) are obtained, respectively. These values are in good agreement with those we have previously reported for a non-catalyzed KSiH\(_3\) sample, either from experimental measurements, or from DFT calculations, as explained above.\(^{37,40}\)

Recent evidence for the high disorder in the \(\alpha\)-KSiH\(_3\) silanide comes from neutron scattering experiments. Initially, when neutron powder diffraction (NPD) was performed on the \(\alpha\)-MSiD\(_3\) compounds (M = K, Rb, Cs), the best refinements were obtained with the deuterium atoms in the 96k Wyckoff site with a low occupancy of 12%, but large thermal factors reflected significant movements within the cubic unit cell.\(^{37,40}\) However, the nature of the orientational disorder, static or dynamic, was still not yet fully understood. Subsequent strong evidence from spectroscopic analysis suggested that the disorder was dynamic.\(^{40}\) A Quasi-Elastic Neutron Scattering (QENS) study of \(\alpha\)-KSiH\(_3\) has confirmed this dynamic disorder.\(^{50}\) The QENS results show that the order–disorder (\(\beta\)–\(\alpha\)) phase transition leads to dynamical changes associated with rapid reorientational motions of the pyramidal SiH\(_3\) anions.

A study of the dynamical trends in the alkali metal silanides series (with K, Rb, and Cs but also the mixed M\(_{0.5}\)M\(_{0.5}\)SiH\(_3\) phases) was recently conducted by neutron scattering methods.\(^{62}\) Interestingly, the reorientational mobility of SiH\(_3\) decreased when increasing the cation size: \(\alpha\)-CsH\(_3\) is more ordered than \(\alpha\)-RbCsH\(_3\), which in turn is more ordered than \(\alpha\)-KSiH\(_3\). This experimental observation is in perfect agreement with the enthalpy/entropy compensation effect reported previously.\(^{60}\) A simultaneous linear increase in the enthalpy (more stable silanide) and entropy change (more localized H atoms in the crystal structure) with increasing cation size was determined from equilibrium pressure measurements. Clearly, the pronounced SiH\(_3\) dynamics is the reason for the high entropy observed in the disordered \(\alpha\)-KSiH\(_3\) phase. This leads to the low entropy variation for hydrogen absorption/desorption, which is the main cause of the favourable hydrogen storage properties of these materials.

**Conclusions**

We have investigated the effects of NbF\(_5\) as a catalyst for enhancing the hydrogen absorption/desorption kinetics of the KSi/\(\alpha\)-KSiH\(_3\) system. Through a ball-milling process with NbF\(_5\), the hydrogen release kinetics of \(\alpha\)-KSiH\(_3\) are strongly enhanced with a complete desorption in less than one hour at temperatures above 130 °C. The activation energy of the desorption reaction is decreased from 121 kJ mol\(^{-1}\) for the non-catalyzed material to 61–66 kJ mol\(^{-1}\) for the 1 hour NbF\(_5\)-milled KSi powder. The catalyzed material exhibits a 4.1 wt% experimental hydrogen storage capacity with a nice retention of its fast kinetics upon cycling. The thermodynamics of the KSi/\(\alpha\)-KSiH\(_3\) equilibrium were also reinvestigated by plotting PCI curves using a gravimetric analyzer. Enthalpy and entropy values of 24.3 kJ mol\(^{-1}\) H\(_2\) and 59.5 J K\(^{-1}\) mol\(^{-1}\) H\(_2\) were obtained, respectively, confirming our previous reports. In this study, we have therefore been able to strongly promote the hydrogen storage kinetics of the KSi/\(\alpha\)-KSiH\(_3\) system and to keep...
a perfectly reversible reaction near ambient conditions, without any disproportionation phenomenon.

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