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Catalytic Modification in Dehydrogenation Properties of KSiH_3

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Ankur Jain^{a#}, Takayuki Ichikawa^{a*}, Shotaro Yamaguchi^b, Hiroki Miyaoka^c, and Yoshitsugu Kojima^a

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A number of known catalysts, which are proven to be very effective for several hydrogen species, were attempted in order to see the effect on hydrogen ab/desorption properties of KSiH_3 . Among all the catalysts used in this work, mesoporous Nb_2O_5 is found to be quite effective with a reduction in activation energy from 142 kJ mol^{-1} for pristine KSi to 63 kJ mol^{-1} for mesoporous Nb_2O_5 added KSi , thus allowing desorption to be started at 100–120 °C. Any disproportionation is not observed in controlled hydrogenation process. The mechanism for this improvement is also proposed in details. The kinetic modifications on the ab/desorption properties of KSiH_3 provide an alternative to the well-known family of heavy BCC alloys which are capable to work in the same temperature range but with a lower gravimetric hydrogen content, almost half of KSi system.

Introduction

Search for new materials – capable for storing hydrogen has been very attractive field of research for material scientists. The standard requirements as practical storage material are: (1) high storage capacity, (2) high charging discharging rate, (3) ambient working temperature and pressure condition. Light hydrides like MgH_2 [1] and LiH [2] with high storage capacities of 7.6 wt.% and 12.7 wt.% respectively fulfils the first requirement but lacks on other two due to their high thermodynamic stability. Many efforts have been reported for the destabilisation of these hydrides using different additives [1–8]. As an example, with Si addition, the hydrogen desorption temperature of LiH could be reduced down to 500 °C from 900 °C [2, 3], but the temperature is still too high for practical applicability. Recent work on potassium silanide (KSiH_3) by a French group [9] have shown this innovative hydride material satisfies most of the required criteria. KSiH_3 first appeared in the literature in early 1960s, where it was synthesized by reaction between potassium and silane gas in presence of 1,2-dimethoxy ethane at 195 K [10]. However, it was not considered as potential hydrogen storage media due to insufficient availability of detailed crystallographic data and other properties until the recent report by French group.

† Electronic Supplementary Information (ESI) available: Supplementary figure 1–6; supplementary table 1; See DOI: 10.1039/b000000x/

KSi reveals cubic structure (space group $\text{P}\bar{4}3\text{n}$) which transformed to cubic structured (space group $\text{Fm}\bar{3}\text{m}$) KSiH_3 upon exposure to hydrogen.

The presence of very short Si-H bonds ($d_{\text{Si-H}} = 1.47\text{Å}$), as found in silanes ($d_{\text{Si-H}} = 1.40\text{Å}$) makes this complex hydride very special in contrast to other Si containing ternary hydride system such as Li-Si-H [11], SrAlSiH [12] etc. having longer Si-H bonds. Favourable thermodynamic parameter $\Delta H = -28\text{ kJ/molH}_2$ allows absorption reaction to be occurred at 100 °C under 5 MPa H_2 while the reaction proceeds in the reverse direction at 200 °C [9]. However, the higher activation energy slows down the ab/desorption processes; taking more than 5 h to ab/desorb its total hydrogen content. In order to improve the kinetics, milling with carbon powder was attempted by the same group [13]. However, in presence of carbon, KSiH_3 losses its reversibility and disproportionate into KH , Si , and K-Si intermetallic phases.

In this work, we have chosen TiO_2 , TiCl_3 and Nb_2O_5 as a catalyst owing to their effectiveness for several hydrogen species [14–16]. The ab/desorption isotherms for 1 h milled $\text{KSi} / \text{KSiH}_3$ systems are measured at different temperatures. The kinetic improvement is observed from reduced activation energy in catalysed $\text{KSi} / \text{KSiH}_3$ systems without disproportionation in controlled hydrogen sorption process. The mechanism for this improvement is proposed in details.

Experimental

KSi alloy was prepared by heat treatment of potassium (99.95%) and silicon (99%) together in a closed stainless steel chamber under Ar atmosphere. The chamber was heated up to 500 °C at a heating rate 1 °C/min and then keep it at the same temperature for 72 h.

^aInstitute for Advanced Materials Research, Hiroshima University, Higashi-Hiroshima 739-8530, Japan. Tel&Fax: +81-(0)82-424-5744. E-mail: #ankur.j.ankur@gmail.com (A. Jain); * tichi@hiroshima-u.ac.jp (T. Ichikawa)

^bGraduate school of Advanced Sciences of Matter, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

^cInstitute for Sustainable Sciences and Development, Hiroshima University, Higashi-Hiroshima 739-8530, Japan

Then the chamber was allowed to be cooled down to room temperature in 8 h. The catalysts i.e. TiO_2 (99.999%), TiCl_3 (99.99%), normal Nb_2O_5 (99.99%) and mesoporous Nb_2O_5 (99.9%, Pore size: 22Å, Specific surface area: 800m²/g) were added to KSi using Fritsch P7 ball milling apparatus. The amount of catalyst is expressed in mol% throughout the manuscript. The milling was performed at 370 rpm for 1 h and 20 h under 0.1 MPa Ar with 10 min work and 10 min rest pattern. 10 Cr steel balls (SUJ-2, 7mm in diameter) were used for 1 g sample. Since KSi is highly reactive and explode upon interaction with even small quantity of air and moisture, all the handlings of unmilled/milled samples were done in high purity Ar (99.9999%) filled glove box (Miwa MFG, MP-P60W). The oxygen and moisture contents were maintained at <0.01ppm. The structural characterization was performed using X-ray diffraction (XRD) technique (Rigaku, RINT-200) with $\text{CuK}\alpha$ radiation on the samples covered with polyimide sheet (Dupont-Toray co. Ltd., Kapton) to avoid direct interaction of samples with air and moisture. Scanning electron microscopy (SEM) technique (JEOL, JSM-6380A) was used for the morphological observations. The samples were spread on carbon tape and transferred to SEM chamber using specifically designed transfer device enabling us to transfer the samples without exposing to air and moisture. The thermal behaviour of KSi - KSiH_3 transformation was followed using differential scanning calorimetry (TA instruments, Q10PDSC) under 5 MPa H_2 and 0.1 MPa Ar for absorption and desorption processes, respectively. Pressure – composition isotherms (PCIs) were performed using Sievert type apparatus (Suzuki Shokan Co. Ltd.) in pressure and temperature range of 0.001 – 5.0 MPa and 85 – 200 °C. In this experiment, we applied 1 h waiting time for the pressure stabilization. In order to obtain the pressure value X-ray photoelectron spectroscopy (XPS; Thermo Fisher Scientific, ESCALAB 250Xi, Al-K α = 1486.6 eV) technique was used to understand the surface state of catalyst.

Results and discussion

The samples of pristine and milled KSi with or without catalysts show no traces of unreacted potassium or silicon (supplementary figure 1). The samples milled KSi with catalysts

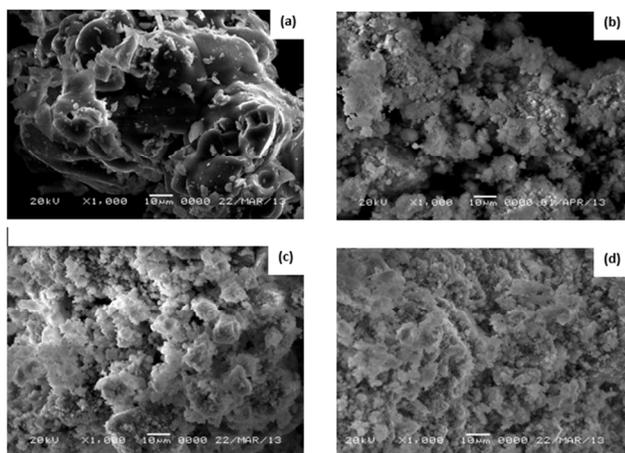


Fig. 1 SEM images of (a) Pristine KSi; (b) KSi – 5% TiO_2 ; (c) KSi – 5% TiCl_3 ; (d) KSi – 5% Nb_2O_5 .

remain unchanged with some additional peaks related to the additives. In case of TiCl_3 , TiCl_3 reacts with KSi and forms KCl , leading to a disproportionation of KSi. In case of Nb_2O_5 ,

some traces of NbO_2 were also found, which is obviously due to reduction of Nb_2O_5 phase to NbO_2 during milling.

Figure 1 shows the morphology of pristine KSi and KSi milled with additives. As seen from the figure 1(a), the particle size of as annealed sample is more than 10 μm . The morphology of pristine KSi used in this work is completely different from that reported in the earlier work, where the bubble shape on the surface indicate an oxidation [13]. In our case, we do not observe any bubbles and the surface is free from oxidation. This must be due to the employed experimental condition, as KSi is very sensitive to air and moisture. Milling of KSi with additives for 1h reduces the particle size of all the samples as shown in figure 1(b) – 1(d). The particles were agglomerated and shown as cloud type morphology. This probably will be helpful to provide several diffusion path and therefore to increase the ab/desorption kinetics.

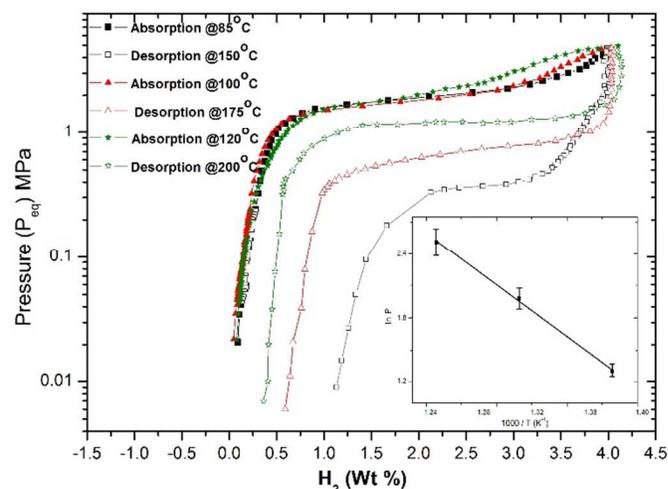


Fig. 2 Pressure-Composition Isotherms for KSi system. Inset shows van't Hoff plot for desorption reaction.

The ab/desorption kinetics is very slow for pristine KSi, thus 1h milled KSi sample is employed for PCI measurement and the isotherms are shown in figure 2. The rate of hydrogen absorption below 85 °C is extremely slow to measure PCI, while the plateau pressure is very high at higher temperature than 120 °C, which is at out limits of the instrument. Therefore, this slow kinetics limits us to measure the absorption isotherms at 85, 100, and 120 °C. The plateaus for all three temperatures are found overlapping each other as a quite unusual phenomenon. This has to be due to non-achievement of real equilibrium pressure under studied conditions. On the other hand, the desorption isotherms were made at 150 °C, 175 °C, and 200 °C with a reasonable difference in temperatures. The plateau pressures were observed as 0.37, 0.73, and 1.2 MPa at the above temperatures, respectively. These desorption isotherms were used to calculate the enthalpy change of desorbing reaction by using van't Hoff plot shown as inset of figure 2. The desorption enthalpy is found to be 40.1 \pm 1.5 kJ mol⁻¹ H_2 , while the entropy value is 106 \pm 3 JK⁻¹mol⁻¹ H_2 . These values are different from the values 28 kJ mol⁻¹ H_2 and 52 JK⁻¹mol⁻¹ H_2 reported by Chotard et al [9].

In order to confirm the ab/desorption temperatures obtained from PCIs and van't Hoff plot, DSC experiments were performed under 5 MPa H_2 for absorption reaction. Figure 3 shows the DSC curves of all the samples under 5 MPa H_2 with scanning rate of 1 °C/min. It is clearly evident that pristine KSi does not show any exothermic peak up to 200 °C, which is due

to slow kinetics of absorption and inactivation of KSi sample towards hydrogen absorption, and indicates the necessity of activation cycles. After 3 activation cycles an exothermic peak appears at 110 °C. On moving to 1h milled KSi sample, the exothermic peak is observed at slightly lower temperature than that of the activated pristine sample. Even more reduction in peak temperature in a range 110-100 °C is observed for the samples with different catalysts.

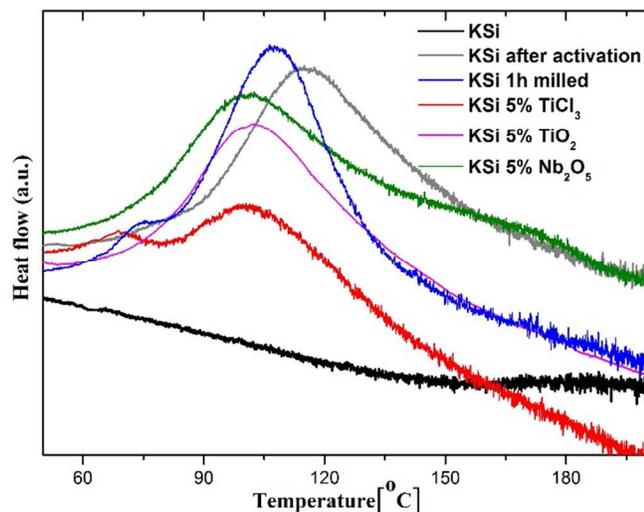


Fig. 3 DSC curve of pristine and milled (with / without) KSi samples under 5.0 MPa H₂ pressure; scan rate 1 °C/min.

KSi is converted to KSiH₃ phase in all the samples after DSC measurement under 5 MPa H₂ (supplementary figure 2). KSi with TiCl₃ additive shows some traces of KH & Si (does not influence the sorption process much) in addition to KSiH₃ as major phase. In case of Nb₂O₅ added KSi sample, the traces of Nb₂O₅ together with NbO₂ were found even after hydrogenation, although the peak intensities were found to be reduced.

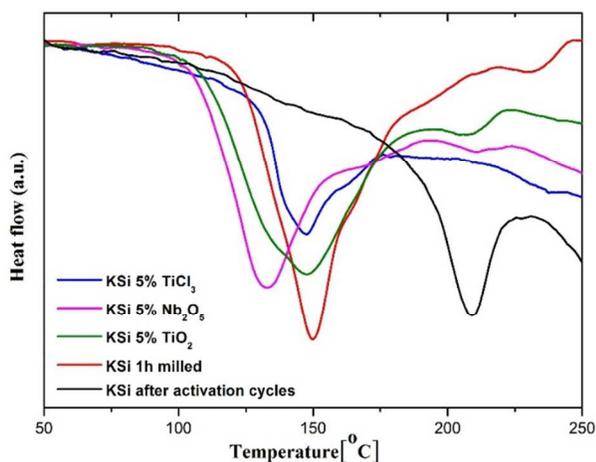


Fig. 4 DSC curve of all hydrogenated KSi samples under 0.1 MPa Ar atmosphere; scan rate 1 °C/min.

In order to observe desorption behaviour of all the samples, DSC measurement is performed under 0.1 MPa Ar atmosphere with heating rate of 1 °C/min. It can be seen from figure 4 that

KSiH₃, formed after several activation cycles on pristine KSi, could desorb hydrogen at 210 °C, which is in close agreement with the report by Chotard et al [9]. Milling treatment for 1 h under 0.1MPa Ar leads to the peak temperature reduction significantly down to 150 °C, probably due to the reduction of activation energy. A slight decrease in temperature is observed with the addition of catalyst. Nb₂O₅ is found to be the most effective catalyst with a peak temperature of 130 °C. Thus Nb₂O₅ is chosen to play further in order to understand its catalytic effect on ab/desorption behaviour. Four different samples were taken into account by varying the catalyst amount (1 and 5 mol%), particle size (normal and mesoporous), and milling time (1h and 20h). 1h milled KSi with 5 mol% normal Nb₂O₅ shows the existence of Nb₂O₅ and KSi phase independently (supplementary figure 3). Small amount of NbO₂ were also observed. While replacing normal Nb₂O₅ with mesoporous Nb₂O₅ (22Å), even a small quantity of 1 mol% reduces the peak intensities of all the phases; the peak intensity further reduces with increasing amount of mesoporous Nb₂O₅. A longer milling time i.e. 20 h vanishes all the peaks completely and turned the crystalline state of KSi to amorphous state (see also supplementary figure 3).

The above samples were then employed to DSC measurement under 5 MPa H₂ with a scan rate of 10 °C/min and results are summarized in figure 5. Single absorption peak is observed for 1h milled KSi-5 mol% normal Nb₂O₅ with peak temperature 140 °C. On using 1 mol% mesoporous Nb₂O₅ instead of normal Nb₂O₅ as a catalyst, a shoulder peak appeared at 100 °C, with a major peak remained at the same position as that for normal Nb₂O₅. This shoulder peak increases its height upon increasing the content of mesoporous Nb₂O₅ from 1 mol% to 5 mol%. The peak height corresponding to 140 °C is observed to be decreased at the same time. An increase in the milling time from 1h to 20h of KSi – 5 mol% mesoporous Nb₂O₅ sample vanishes the peak at 140 °C completely and the shoulder peak turned into a mature single peak of absorption with a peak temperature of 100 °C. The presence of two peaks can be explained as a presence of two different species of KSi: 1) highly activated part; 2) less activated part.

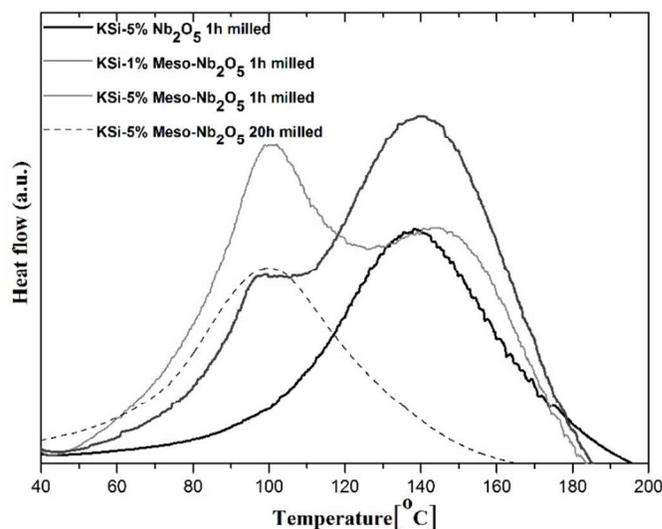


Fig. 5 DSC curve of KSi samples milled with Nb₂O₅ under 5.0 MPa H₂ pressure; scan rate 10 °C/min.

In order to confirm the presence of different species in the sample, XPS experiments were performed on KSi milled with a) 5 mol%

normal Nb₂O₅ for 1h, b) 5 mol% mesoporous Nb₂O₅ for 1h, c) 5 mol% mesoporous Nb₂O₅ for 20h. The spectra corresponding to Nb 3d band for the three samples are shown in fig. 6. The XPS spectra of KSi sample with 1 mol% mesoporous Nb₂O₅ is not shown here as it was not possible to trace Nb species due to the small amount of catalyst in the sample. The spectra corresponding to as received normal Nb₂O₅, NbO₂, NbO and mesoporous Nb₂O₅ are also shown as reference. It is clear from the spectra that as-received mesoporous Nb₂O₅ contains some traces of NbO phase. The spectra corresponding to NbO contains Nb₂O₅ as a major phase. Since XPS is surface analysing technique, this observation must be due to surface oxidation of NbO as XRD (not shown here) reveals the existence of NbO as a major phase. XPS spectra of Nb₂O₅ and NbO₂ show the binding energies corresponding to Nb 3d5/2 bands in line with the literature [17, 18]. On comparing the spectra of sample a and sample c in fig. 6, it is found that sample c contains only NbO phase instead of starting catalyst Nb₂O₅, which must have been transformed during milling procedure. Thus NbO is the responsible catalyst for improving the absorption behaviours of sample c as shown in figure 5. Sample b shows the presence of several overlapped peaks which could be indexed corresponding to NbO and NbO₂ phase, indicating the presence of two DSC peaks at 100 °C and 140 °C, respectively. From the linear variation of phase transformation, it can be assumed that the small shoulder at 100 °C in DSC curve for KSi – 1 mol% mesoporous Nb₂O₅ is also due to the small content of NbO phase presented in as received mesoporous Nb₂O₅.

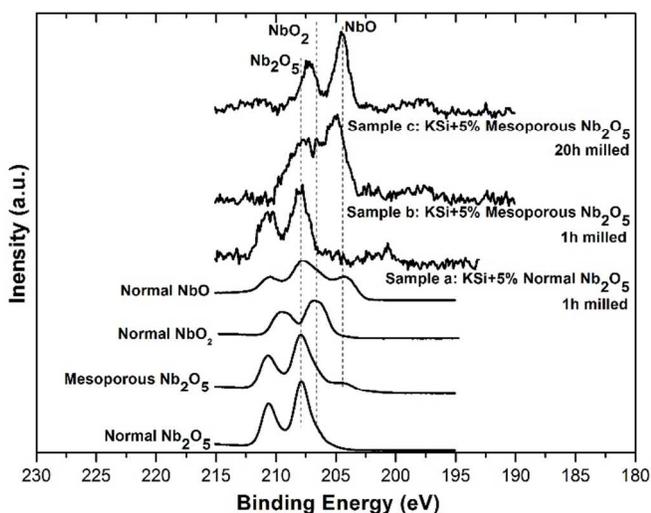


Fig. 6 XPS spectra for Nb3d bands of KSi samples milled with Nb₂O₅ under different conditions; the spectra of as received normal Nb₂O₅, mesoporous Nb₂O₅, normal NbO₂ and normal NbO is also shown at the lower part of figure for the comparison.

Hydrogenated state of all Nb₂O₅ added KSi samples shows no disproportionation observed in any samples in contrast to the case of carbon added KSi [13] (Supplementary figure 4). As discussed in ref. 13, the disproportionation occurs due to the extra local heat generated during hydrogenation process, we also agree to the fact. However we experienced from our experiment that this disproportionation due to the local heat generation also depends on the experimental procedure and can be avoided or lowered by controlling the reaction procedure and environment. In order to make clear the hydrogenating properties, two different condition for the same samples were compared. One sample was hydrogenated by introducing hydrogen to the sample at room temperature and then

increased temperature up to 100 °C by 10 °C/min and kept it for 30 min at the same temperature. On the other hand, another sample was hydrogenated by first heating up to 100 °C under vacuum and then exposing to the 5 MPa H₂ instantly. The later product disproportionate into KH and Si phases due to a drastic exothermic heat, while the product following first pathway maintains reversible characteristic of KSi to KSiH₃ transformation (Supplementary figure 5).

Figure 7 shows the TG spectra of all the samples in order to calculate total H₂ content corresponding to KSi → KSiH₃ conversion reaction. The hydrogen capacity shown here is normalized to the KSi counterpart. Except TiCl₃ doped KSi all other samples have shown the capacity in the range of 3.6 – 4.3 wt.%, which is very close to the theoretical capacity (4.3 wt.%) of KSi alloy. The formation of KCl during milling, as observed in XRD pattern explains the capacity of only 3.1 wt.% shown by this system.

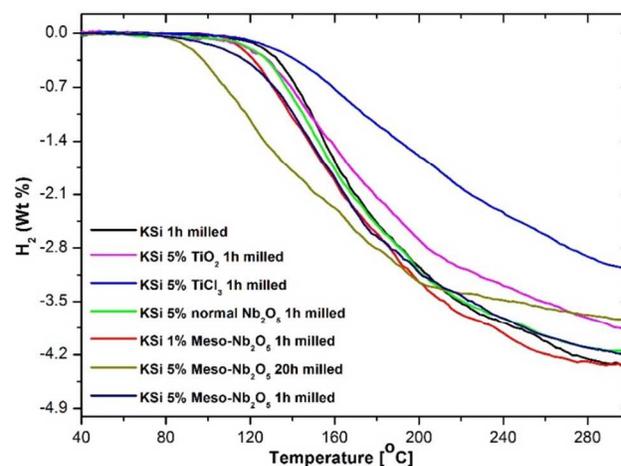


Fig. 7 TG spectra of all hydrogenated KSi samples. Y-axis is normalized to the hydrogen content of KSi phase.

Since the activation energy for desorption of KSiH₃ is high, the basic aim of this paper is to lower the activation energy which in turn improves the kinetics at lower temperature. For calculating the activation energy of desorption we use Kissinger's equation [19]. According to Kissinger's method, the peak positions in thermal analyses vary with heating rate if other conditions remains same and this can be used to calculate activation energy of reaction by plotting a curve between $\ln K$ and $1/RT_p$ using following equation,

$$\ln K = -\frac{E_{des}}{RT_p} + \ln \frac{Rk_0}{E_{des}} \quad (1)$$

where $K = \beta/T_p^2$; β is heating rate, T_p is peak temperature, R is gas constant and E_{des} is activation energy of desorption. Thus, DSC experiments for all the samples were performed under Ar atmosphere with different heating rates i.e. 1, 2, 5, and 10 °C/min (Supplementary figure 6 and Supplementary table 1). The calculated activation energy for pristine KSi was found to be 142 kJmol⁻¹H₂, which decreases to 130 kJmol⁻¹ H₂ upon milling for 1 h under Ar atmosphere. The effect of Nb₂O₅ as a catalyst is clearly evident because the lowest activation energy is found to be 63 kJmol⁻¹ H₂ for 20 h milled KSi-5 mol% mesoporous Nb₂O₅.

Conclusions

KSiH₃ system provides an alternative to BCC hydrogen storage alloy system owing to its thermodynamic parameters and almost double gravimetric hydrogen content compare to most of the BCC alloys. However, the high activation energy hindered its merits. In this work, we have shown that the reversibility at around 100 – 120 °C of KSi - KSiH₃ systems can be achieved by the addition of mesoporous Nb₂O₅ (22Å). 20h milled KSi – 5 mol% mesoporous Nb₂O₅ sample shows much lower desorbing activation energy i.e. 63 kJmol⁻¹ H₂ in comparison to 142 kJmol⁻¹ for the pristine KSi sample. The presence of NbO is found to be responsible for this improvement. We also suggested the suitable working condition for absorption reaction in order to maintain the reversibility of KSiH₃ system without disproportionation. Our results generate the possibility for making other light weight alkali – silicon systems i.e. Li-Si, Na-Si (even with a higher hydrogen content 7.9 and 5.6 wt.% respectively) reversible in future works.

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